



# Jana2006 Cookbook

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Solved examples on various topics covered by crystallographic computing system Jana2006. The cookbook cumulates examples from all Jana workshops. The program Jana2006, the latest cookbook and data for examples are available in [jana.fzu.cz](http://jana.fzu.cz).

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# Installation notes

For the workshop, following programs are necessary:

- Jana2006 for most tasks
- Diamond for plotting crystal structures
- Superflip (part of Jana2006 distribution) for solution of phase problem
- Vesta for visualization of electron density with isosurfaces and for magnetic structures
- PETS for data processing of electron diffraction patterns
- ImageJ for viewing graphical output from PETS

Diamond can be replaced by any other plotting software capable to read CIF in command line. For the workshop we recommend Diamond because the connection with Jana2006 is very well tested.

## Installation of Diamond

Install demo version of Diamond from the directory Setup\Diamond installation in the flash disk.

Copy the licence file “yourlicence.lic” to the same directory where Diamond.exe has been installed. Usually it will be c:\Program files\Diamond 4

*This time limited license has been kindly provided by Crystal Impact for this workshop.*

*Note: Diamond started from Jana2006 may behave differently than when started separately. For instance, it doesn't offer automatic wizards.*

## Installation of Vesta

Unpack the archive “Vesta\_2.1.2.zip” from the directory Setup\Vesta to a directory of your choice

## Installation of Jana2006

Execute janainst.msi from the directory Setup\Jana2006 and follow instructions.

*The installation creates shortcut to Jana2006 in the desktop and in Start → Programs*

Start Jana2006, go to “Tools → About Jana2006” and verify the version string.

*The version date should be close to the workshop date*

- Don't use your “old” preinstalled versions of Jana2006
- Don't use flash disk for calculation. Copy the example files to hard disk.
- Don't install Jana2006 to desktop or flash disk

## Configuration of Jana2006

Start Jana2006

Go to “Tools → Preferences”, **adjust size of the window** (for instance 60% of the screen height) and font height (about 11 points)

Go to “Tools → Programs”; focus with mouse the textbox “Graphic viewer”; press “Browse” and localize Diamond.exe (usually in Program Files x86)

Focus “3d visualization of maps”; press “Browse” and localize VESTA.exe

*(VESTA is needed for examples 9.x, 10.x, 12.x and 13.x)*

For using a different text editor than Notepad define its pathname in the textbox “Editor name”.

## Installation of ImageJ (only for electron diffraction)

Install ImageJ from the installer in the directory Setup\ImageJ to a directory of your choice. Use ij148-jdk6-64bit-setup.exe, if you have a 64-bit system. Use ij148-jdk6-setup.exe for a 32-bit system, or if you are not sure.

## Installation of PETS (only for electron diffraction)

Copy the file pets.exe from the directory Setup\PETS to a directory of your choice.

## Add ImageJ and PETS in the system variable PATH:

*Under Windows XP:*

Go to "Start → Settings → Control Panel"

Double click "System"

Go to "Advanced → Environment variables"

In the list "System variables" find and double click "Path"

In the small window that opens, add the full paths to the files ImageJ.exe and pets.exe (without the file names), separated by a semicolon

*Under Windows 7:*

Right click on the Computer icon on your Desktop and choose "Properties → Advanced system settings → Environment variables"

In the list "System variables" find and double click "Path"

In the small window that opens, add the full paths to the files ImageJ.exe and pets.exe (without the file names), separated by a semicolon

## Launching PETS:

*PETS must be called with the input file as a command-line argument. There are several ways of launching PETS:*

### **Method 1 – the most convenient:**

Locate the file .pts (input to PETS) on your system

Right-click to open context menu

"Open → Select program from a list → Browse..."

Locate the file pets.exe on your system; Open

Make sure the checkbox next to "Always use the selected program to open this kind of file" is checked  
OK

*PETS starts. Next time you want to run PETS, it is sufficient to double click the icon of the pts file you want to run. Unfortunately, this method fails on some systems, notably if the extension pts is already associated with another software.*

### **Method 2:**

*Place the shortcut to PETS on Desktop:*

Locate the file pets.exe on your system

Select it and copy it to clipboard (Ctrl+C)

Place cursor on the place on the desktop where you want to place the icon of PETS

Right-click → Paste shortcut

*Now you can run PETS by drag-and-dropping the file .pts on the icon on the desktop. Unfortunately, even this method does not work on all systems.*

### **Method 3 – works always:**

Open DOS terminal (Start → All programs → Accessories → Command Prompt)

Move to the directory with the file .pts you want to use (use command cd)

Run PETS by typing "pets filename.pts", where filename.pts is the file you want to use.

## Upgrade of Jana2006 installed from janainst.msi (new way of installation)

Execute janainst.msi and follow instructions. Make sure the installation directory is the same like for the previous version.

*The installation wizard will reinstall Jana2006. For the same version it will offer "Modify – Repair – Remove".*

## Upgrade of Jana2006 installed from janainst.exe (old way of installation)

Previously Jana2006 was installed from the self extracting archive janainst.exe. The user had to define "by hand" the system environment variable JANA2006DIR. The installation from janainst.msi in some cases cannot reinstall Jana2006 installed from janainst.exe.

Start Jana2006 (old installation)

Go to "Tools → About Jana2006" and note the version string.

Start janainst.msi and follow instructions. Make sure the installation directory is the same like for the old version.

Start Jana2006 (new installation)

Go to "Tools → About Jana2006" and verify the version string is new.

## Troubleshooting (for upgrade of Jana2006 installed from janainst.exe)

### 1. Installation from janainst.msi was running without warnings but the version string of Jana2006 remains old

Start janainst.msi again. It will offer "Modify – Repair – Remove". Used "Remove" and uninstall old version of Jana2006.

Start janainst.msi (the third time) and follow instructions. Make sure the installation directory is the same like for the old version.

Start Jana2006 (new installation)

Go to "Tools → About Jana2006" and verify the version string is new.

### 2. Another issues or when method 1 fails

Localize installation directory of Jana2006 and make backup copy of jana2006.ini and jana2006.hst

Delete installation directory of Jana2006

Go to "Start → Settings → Control Panel → System"

Go to page "Advanced"

Press "Environment variables"

Delete all instances of JANA2006DIR in User variables as well as in System variables

Start janainst.msi and follow instructions.

Return files jana2006.hst and jana2006.ini to the installation directory (where jana2006.exe is located)

Start Jana2006 (new installation)

Go to "Tools → About Jana2006" and verify the version string is new.



# Example 1.1: Zn

Revised: 4 March 2019

Data	Topic	Level
X-ray single crystal data	Solution of a simple crystal structure from single crystal data	Basic

## Tasks

---

Solving a simple structure from single crystal X-ray data

- creating new jobname
- reading input files
- determination of symmetry
- solving a structure with charge flipping
- editing of atomic parameters
- refinement
- hydrogen assignment

## Initial data

---

### Data

Single crystal data measured with Oxford Diffraction four-circle diffractometer

### Input files:

Zn.hkl, Zn\_red.sum

### Additional information:

Chemical formula:  $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{ZnCl}_6$

Frame scaling, absorption correction: done by the diffractometer software

## Contents

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# Instructions

## I. Data import

### 1. Creating new jobname

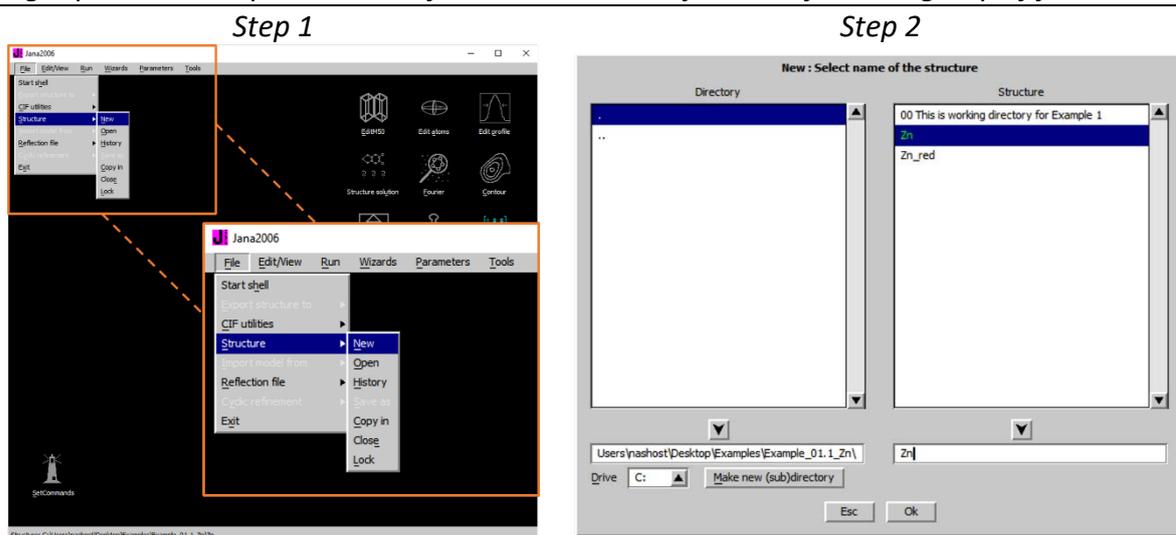
Start Jana2006

“File → Structure → New” opens a file manager (*Step1*)

Left pane: locate directory with input files; Right pane: double-click Zn (*Step2*)

#### Notes

Right pane detects possible Jana files and shows the jobname for each group of files

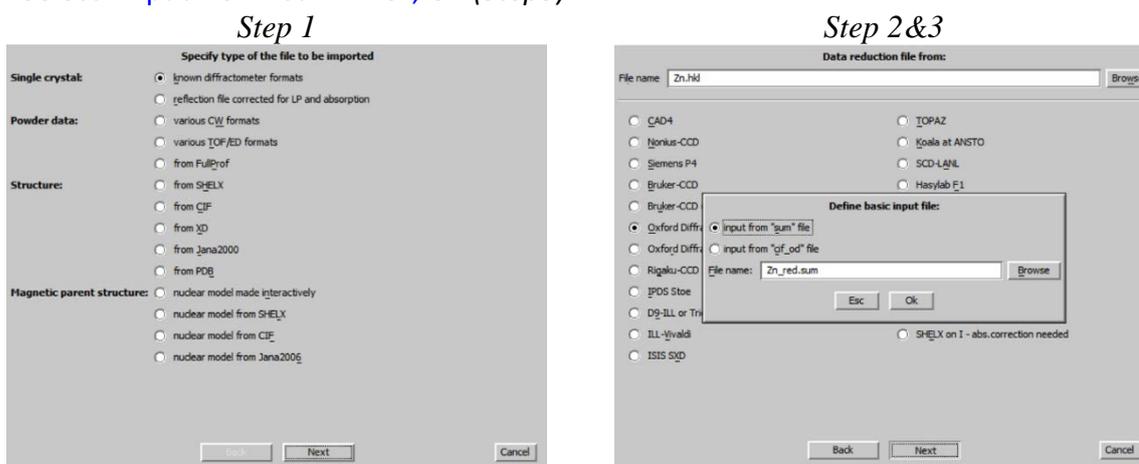


### 2. Import wizard

Select “Known diffractometer formats”; NEXT (*Step1*)

Select “Oxford Diffraction → CCD”; NEXT (*Step2*)

Select “Input from “sum” file”; OK (*Step3*)



Leave all settings unchanged; NEXT (*Step4*)

Leave all settings unchanged; NEXT; OK; (*Step5*)

The program reads 24240 reflections from the hkl file

### Step 4

Complete/correct experimental parameters

Cell parameters: 6.18671 12.91538 19.25699 90.01214 90.01502 89.97031

Number of input indices: 3 Info about metrics parameters

1st modulation vector:

2nd modulation vector:

3rd modulation vector:

X-ray tube

Wave length: 0.71073

Temperature: 293

Polarization correction:

- Circular polarization
- Perpendicular setting Info
- Parallel setting Info
- Guinier camera
- Linearly polarized beam

Monochromator parameters:

Perfectionness: 0.5

Glancing angle: 6.082144 Set glancing angle

Back Next Cancel

### Step 5

Define the reference cell/split by twinning

Cell parameters: 6.1867 12.9154 19.2570 90.012 90.015 89.970

Target dimension: 3 Twinning

1st modulation vector:

2nd modulation vector:

3rd modulation vector:

Max. satellite index:

Accuracy:

Number of domains:

Data related to domain #:

Multiply input  $F(hkl)/I(hkl)$  by: 1

Define transformation matrix

**INFORMATION**

All 24240 input reflections were properly handled

Ok

Back Next Cancel

For the absorption correction select "None or done before importing"; NEXT (Step6)  
FINISH (Step7)

### Step 6

Define parameters for absorption and scaling procedure

- None or done before importing
- Correction for spherical sample  radius of the sphere [mm]
- Gaussian integration method  integration grid
- Empirical correction and/or frame scaling

Define absorption coefficient =>

Define formula =>

Number of formula units:

Back Next Cancel

### Step 7

**INFORMATION**

The import wizard is complete. As a next step you can import another file or modify the previously imported ones.

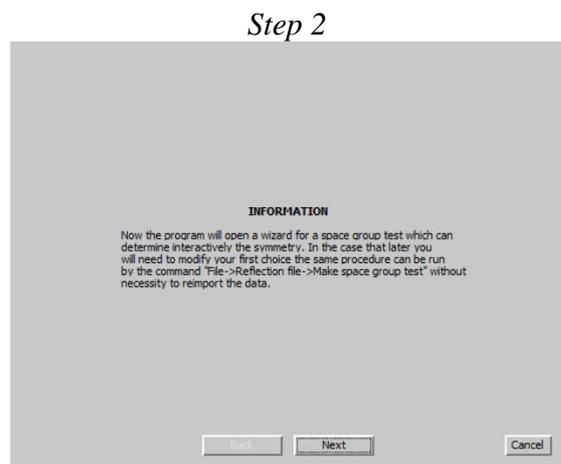
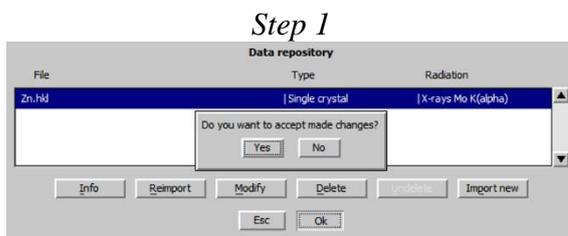
Back Finish Cancel

## 3. Data Repository

### Notes

Each line in the data repository window corresponds to one data set converted to Jana format. In this case, we use only one data set. Data repository is saved in the file Zn.m95.

OK; YES to accept the data set (Step1)  
Next; (Step2)



## II. Symmetry and data merging

### 1. Symmetry wizard

[On the screen: "Tolerances for crystal system recognition".]

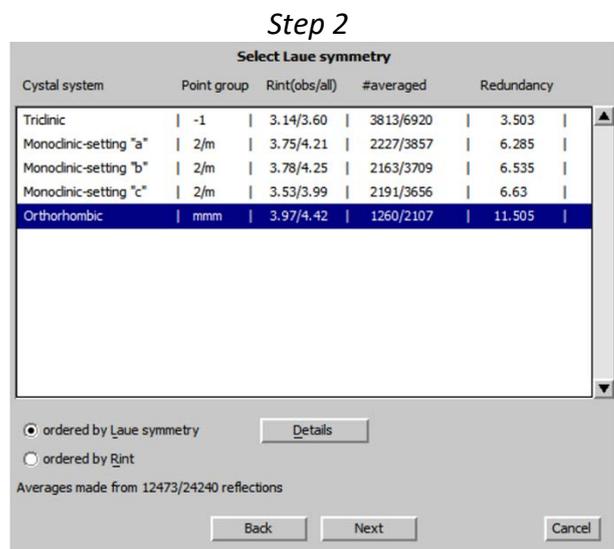
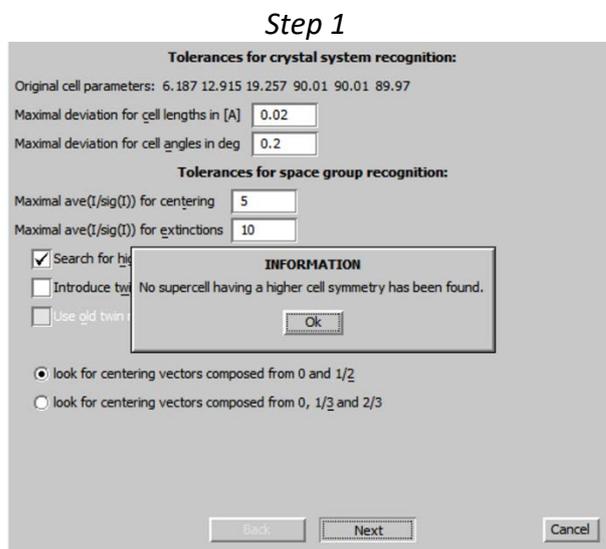
#### Notes

Symmetry Wizard can be started separately by "File → Reflection file → Make space group test".

Leave all settings default; NEXT; OK (Step1)

[On the screen: Select Laue symmetry]

Select Orthorhombic Laue symmetry; NEXT (Step2)



Select primitive unit cell; NEXT (Step3)

[On the screen: Select space group]

## Notes

The window shows possible space groups.

“Obs/all” column shows, for each space group, the number of reflections, which should be systematically extinct. For instance, Pbnm has “Obs/all”=2/1677, which means that 1677 reflections in the reflection file should be systematically absent, i.e. with intensity below the  $3\sigma$  limit. Nevertheless, two of them have intensity above the  $3\sigma$  limit and, therefore, violate the rules for systematic absences.

“Ave(I/sig(I))” lists average ratio  $I/\sigma(I)$  for columns “Obs/all”. For Pbnm this means that the 1677 theoretically absent reflections have the average  $I/\sigma(I) = 0.153$ , and the two of them violating the systematic absences have the average  $I/\sigma(I) = 4.783$ .

The limits for the average ratio  $I/\sigma(I)$  were defined previously in “Tolerances” window. Space groups exceeding the limits are not offered.

For selecting the proper space group, we are looking for the cases with high number of unobserved systematically absent reflections and having reasonably low average  $I/\sigma(I)$  for reflections violating the extinction rules. In our example, Pbnm is more likely than Pbnm because the number of experimentally confirmed absent reflections is much larger.

The list of the strongest reflections contradicting the selected space group can be displayed by “Details” button.

Jana2006 does not test data for center of symmetry. At this point, a centrosymmetric space group should be preferred unless we have already a strong reason to select a non-centrosymmetric space group. Thus, we select Pbnm and not Pbn21. Centrosymmetry is usually confirmed or denied in following steps by the symmetry analysis by Superflip (see Step 6).

Select Pbnm; NEXT (Step4)

### Step 3

**Select cell centering**

Centering	obs/all	ave(I/sig(I))
<input checked="" type="radio"/> P	0/0	0.000/0.000
<input type="radio"/> A	6342/12135	20.774/11.261
<input type="radio"/> B	5977/12142	22.134/11.307
<input type="radio"/> C	5869/12119	22.296/11.225
<input type="radio"/> I	6105/12123	21.308/11.132
n.a. R-obverse	8375/16163	21.222/11.399
n.a. R-reverse	8359/16162	21.222/11.381
<input type="radio"/> F	9094/18198	21.712/11.264

Warning: The cell centering need not be one you expect from collection as the program first transform the cell to the reduced form.  
Moreover after your selection the program makes another transformation whenever the centring is not the standard one.

### Step 4

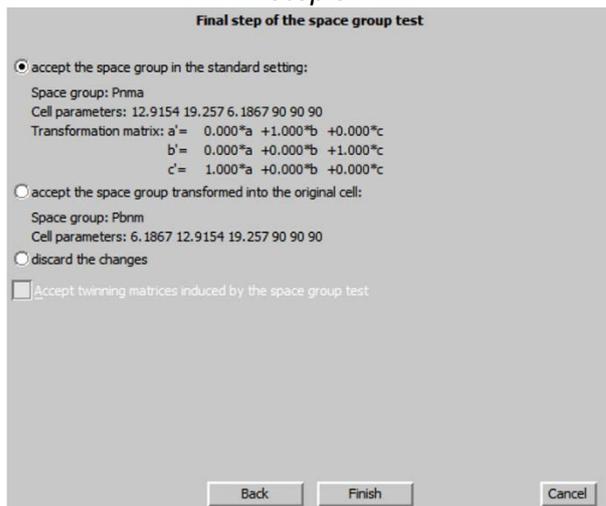
**Select space group**

Space group	obs/all	ave(I/sig(I))	FOM
Pbnm	2/1677	4.783/0.153	0.00060
Pbn21	2/1677	4.783/0.153	0.00060
Pbnm	0/1069	0.000/0.146	0.00094
Pbm2	0/1069	0.000/0.146	0.00094
Pb21m	0/1069	0.000/0.146	0.00094
Pnmm	2/608	4.783/0.165	0.00165
P21nm	2/608	4.783/0.165	0.00165
Pmn21	2/608	4.783/0.165	0.00165
P212121	1/84	5.545/0.275	0.01201
P22121	0/70	0.000/0.237	0.01428
P21221	1/54	5.545/0.332	0.01886
P21212	1/44	5.545/0.264	0.02264
P2221	0/40	0.000/0.287	0.02498
P2212	0/30	0.000/0.172	0.03243
P2122	1/14	5.545/0.462	0.07367

Accept the space group in the standard setting, i.e. like Pnma; FINISH (Step5)

Symmetry is saved in file Zn.m50.

## Step 5



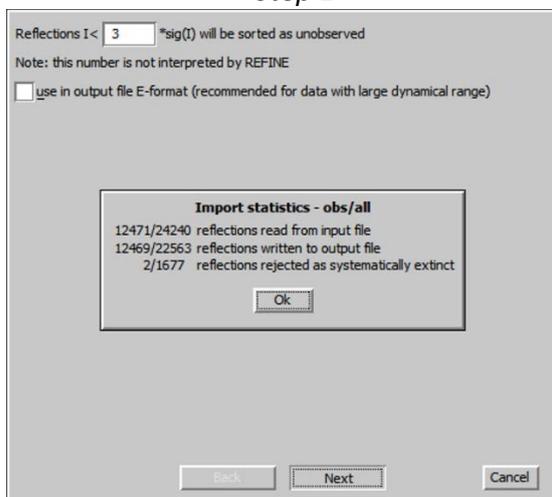
## 2. Creating refinement reflection file

### Notes

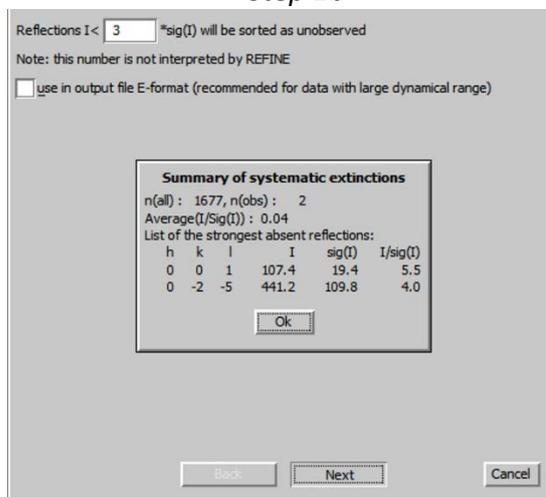
*In this step, the program creates file Zn.m90 containing the data set merged by symmetry and discarded forbidden reflections. M90 will be used for refinement.*

NEXT to confirm threshold 3sigma; OK; OK (to confirm Information windows) (Step1)

### Step 1



### Step 1b



[On the screen: settings for merging the reflections]

Check "Display graph sig(Icount)/sig(Istat)"; NEXT (Step2)

[On the screen: graphs of sigma]

### Notes

*The vertical axis shows the sigma of reflections calculated from merging statistics.*

*The horizontal axis for black circles (white on the screen): sigma as obtained from the diffractometer file*

*The horizontal axis for blue circles (green on the screen): sigma obtained from the diffractometer file and corrected by the "instability factor" calculated such that the values from the diffractometer file are fitted to the values from merging statistics.*

For highly redundant data sets with reliable merging statistics, it is recommended to use such "instability factor" for the weighting scheme during refinement (done at the end of this example).

QUIT

Step 2

graphs of sigma

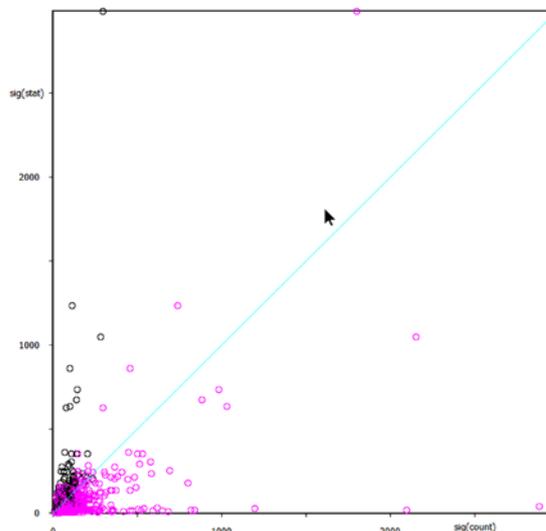
Perform averaging  
 Use non-averaged data

h k l  
 The slowest varying index     
 The fastest varying index

Full print  Apply culling  Add center of symmetry   
 Apply 1/sig(I) weights in averaging   
 Reflections  $|I-I(ave)| > 5 * sig(I(ave))$  will be printed  
 Reflections  $|I-I(ave)| >$   
 Display graph sig(I(count))/sig(I(stat))

Sigma(I(ave)) from:  
 Poisson   
 Equivalents   
 Maximum

Back Next Cancel



The program reports Rint 3.97% for 1259 observed reflections merged from 12466 observed reflections.

Select "Accept the new DatBlock and calculate coverage"; FINISH (Step3)

Step 2b

Step 3

Perform averaging  
 Use non-averaged data

h k l  
 The slowest varying index     
 The fastest varying index

Full print  Apply culling  Add center of symmetry   
 Apply 1/sig(I) weights in averaging   
 Reflections  $|I-I(ave)| > 5 * sig(I(ave))$  will be printed  
 Reflections  $|I-I(ave)| >$   
 Display graph sig(I(count))/sig(I(stat))

Sigma(I(ave)) from:  
 Poisson   
 Equivalents   
 Maximum

**Summary after averaging**

Rint(obs/all) = 3.97/4.35 for 1259/1858 reflections averaged from 12469/22563 reflections

Redundancy = 12.144

h(min) = 0, h(max) = 16  
 k(min) = 0, k(max) = 25  
 l(min) = 0, l(max) = 8

R(obs/all) from e.s.d. of I: 1.69/ 3.58

Information from culling: no reflection was culled

Ok

Back Next Cancel

Accept the new DatBlock and calculate coverage  
 Accept the new DatBlock  
 Discard the new DatBlock

Back Finish Cancel

### III. Structure solution

#### 1. Structure solution wizard

[On the screen: Structure solution]

Notes

Structure solution wizard can be executed separately through “Run → Structure solution” or by double clicking the icon “Structure solution” in the main window. Jana2006 does not contain solution procedures, it calls external programs. The program used in most our examples is Superflip (using the charge flipping algorithm) because it is distributed together with Jana2006. For standard structures, a good alternative is SHELXT but it cannot be distributed without registration so (users should connect it individually).

In “Formula” textbox type list of chemical elements: Zn Cl C N H (Step1)

Notes

Superflip as well as SHELXT does not need exact information about chemical elements because it is required only for analysis of the resulting electron density. Other solution methods like SIR may need the correct formula and number of formula units.

Select “Use Superflip”; leave other settings default; press “Run solution”

[On the screen: window of Superflip replaced after reaching the convergence with listing of Superflip]

Notes

Superflip converges (after noise suppression) with R value ~15%. For charge flipping, this is a very good result. The space group suggested from the symmetry search in the electron density map is Pnma, i.e. the same obtained previously in Jana2006. The low agreement factors at the bottom of the listing indicate good fit of the user-defined symmetry elements (here Pnma) with the resulting electron density map.

**Step 1**

**Structure solution**

use SIR: 2014      Formula: Zn Cl C N H

use Superflip      Formula units: 4      Calculate density

use Shelxt      Actual space group: Pnma      Change the space group

allow manual editing of the command file before start

use previously prepared input file for Superflip

use old solution and reinterpret it      Basis: 0

Repeat Superflip: Until the convergence detected      Maxcycles: 300000

Repeat Superflip: Number of runs

Use local normalization

Use a specific random seed

Define explicitly delta value

Iteration scheme:  CF      For peak search use:  EDMA - fixed composition

LDE       EDMA - fixed number of atoms

AAR       EDMA - peak interpretation by Jana2006

Starting model:  Random phases       Peaks from Jana2006

Patterson superposition map       Peaks from Jana2006 but first run Fourier

Run solution    Open the listing    Draw structure    Draw 3d map

Accept best solution    Quit

Press CLOSE to leave the listing

## 2. Verification of the structure solution from the structure solution wizard

[On the screen: Structure solution]

Press "Draw structure" (Step1)

Press "Draw + continue"

### Step 1

**Structure solution**

use SJR 2014  use Superflip  use Shelxt

Formula: Zn Cl C N H  
Formula units: 8  
Actual space group: Pnma

Buttons: Calculate density, Change the space group

Options:  
 allow manual editing of the command file before start  
 use previously prepared input file for Superflip  
 use old solution and reinterpret it  
 Repeat Superflip: Until the convergence detected  
 Repeat Superflip: Number of runs  
 Use local normalization  
 Use a specific random seed  
 Define explicitly delta value

Iteration scheme:  CF  LDE  AAR  
For peak search use:  EDMA - fixed composition  EDMA - fixed number of atoms  EDMA - peak interpretation by Jana2006  Peaks from Jana2006  Peaks from Jana2006 but first run Fourier

Starting model:  Random phases  Patterson superposition map

Buttons: Run solution, Open the listing, Draw structure, Draw 3d map, Accept last solution, Quit

[On the screen: window of Diamond]

Start "Build  $\square$  Get molecules" or use  on the bottom toolbar

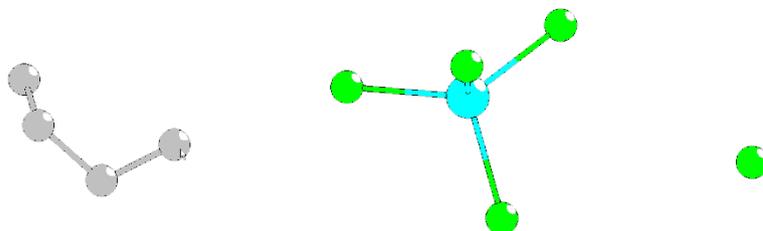
Rotate the molecule ( and  on the bottom toolbar) to get an optimal view.

Move the mouse pointer over the terminal carbon atoms. Diamond will show the labels of the atoms. Note the labels (probably C1,C2) of the terminal carbons.

#### Notes

*By comparison with the chemical diagram, it is clear that the terminal carbon atoms are in fact nitrogen atoms. We have to note their labels in order to change them later to nitrogen.*

[On the screen: plot of the structure in Diamond]



Quit Diamond (without saving changes)

[On the screen: Structure solution]

Press "Draw 3d map" (Step1b)

Step 1b

**Structure solution**

use SJR 2014  
 use Superflip  
 use Shelxt

Formula: Zn Cl C N H  
 Formula units: 8  
 Actual space group: Pnma

allow manual editing of the command file before start  
 use previously prepared input file for Superflip  
 use old solution and reinterpret it  
 Repeat Superflip: Until the convergence detected  
 Repeat Superflip: Number of runs  
 Use local normalization  
 Use a specific random seed  
 Define explicitly delta value

Bisot: 0  
 Maxcycles: 300000

Iteration scheme:  CF  
 LDE  
 AAR

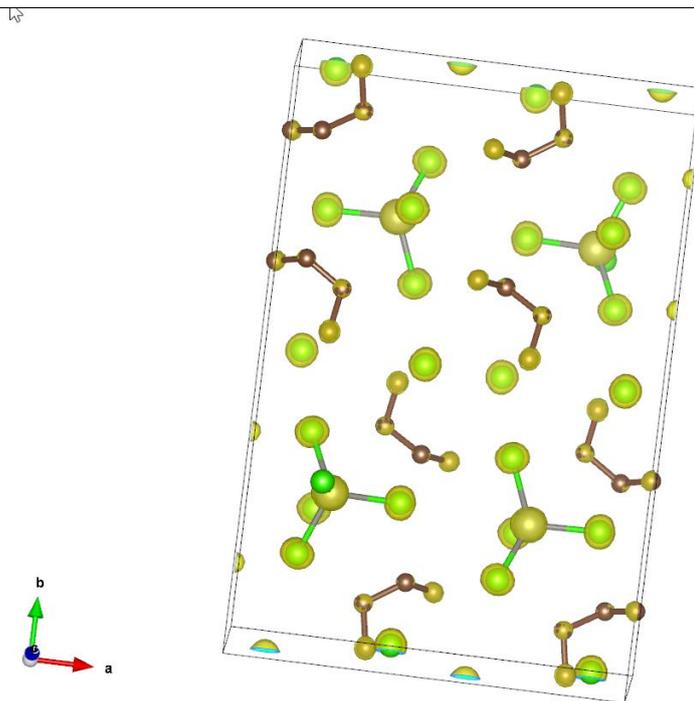
For peak search use:  EDMA - fixed composition  
 EDMA - fixed number of atoms  
 EDMA - peak interpretation by Jana2006  
 Peaks from Jana2006  
 Peaks from Jana2006 but first run Fourier

Starting model:  Random phases  
 Patterson superposition map

[On the screen: window of VESTA]

#### Notes

This button starts Vesta (requires path to Vesta set in Tools → Programs), which plots the electron density produced by Superflip together with atomic positions found by Jana2006.



Quit VESTA without saving the plot

Press “Accept last solution”. This action will also close the structure solution wizard

### 3. Assignment of correct chemical types

[On the screen: basic Jana window]

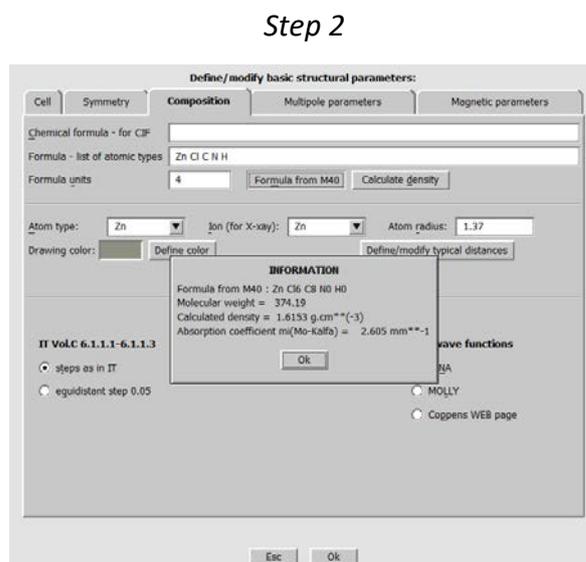
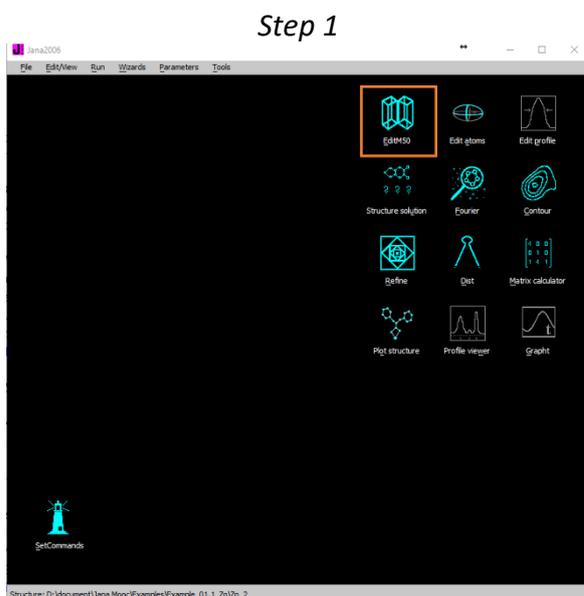
Start EditM50; (Step1)

Go to page Composition; enter 4 for "Formula units", press "Formula from M40" (Step2)

#### Notes

*It displays the formula Zn Cl6 C8 (for Z=4). However, the expected composition (without hydrogens) is Zn Cl6 C4 N4. This means that some nitrogens have been falsely assigned as carbons. The expected chemical formula also suggests that nitrogens should be at the terminal positions of the organic part.*

[On the screen: Information about formula]



OK; YES for updating the formula.

#### Notes

*Number of elements in the formula are not important for refinement. This information is useful only for interpretation of difference Fourier maps and for creating the final CIF. The chemical types in m40 are defined by their sequence numbers in the chemical formula. Nevertheless, the order of atoms in the formula can be arbitrarily changed if it is done through EditM50. Also new chemical elements can be included at an arbitrary position of the formula.*

OK; YES to rewrite M50

Start "Edit atoms" (Step3)

[On the screen: list of atoms]

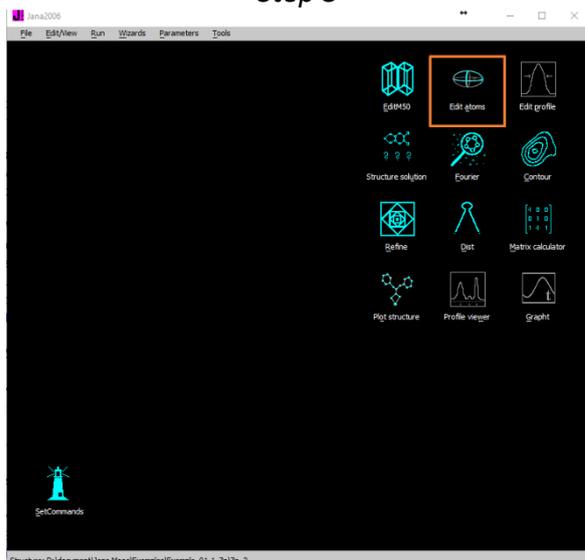
Select (with Ctrl-left mouse button) the previously noted terminal carbon atoms

#### Notes

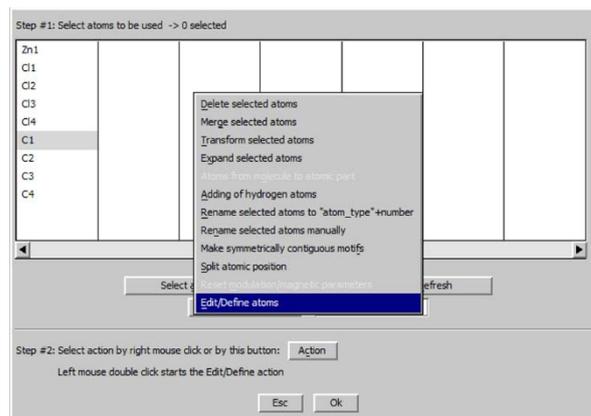
*Plotting of the structure can be repeated by "Plot structure" icon*

Start "Action → Edit/define" (Step4)

### Step 3



### Step 4



Choose "Type" nitrogen; OK (Step5)

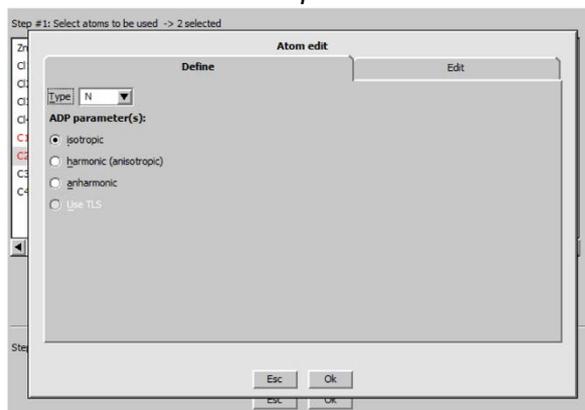
[On the screen: list of atoms. The labels are still the original ones but the chemical type of two selected atoms is nitrogen]

Press "Select All"

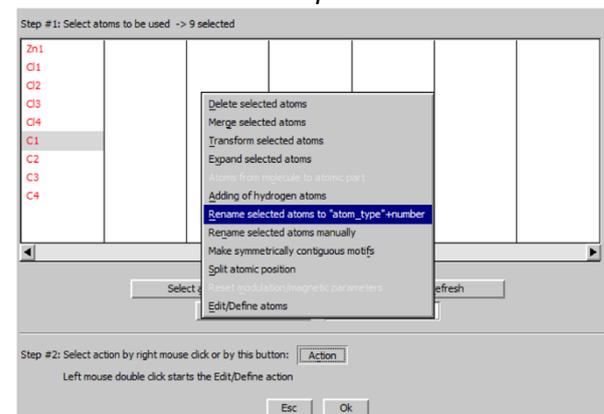
Press "Action" or right-click on one of the selected atoms

Choose "Rename selected atoms to atom\_type + number" (Step6)

### Step 5



### Step 6



[On the screen: list of atoms with labels corresponding to chemical types]

You should see one zinc, four chlorines, two nitrogens and two carbons.

Press "Select All"

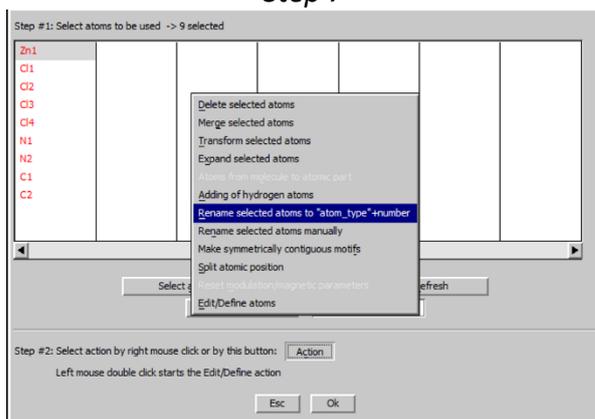
Press "Action" or right-click on one of the selected atoms

Choose "Make symmetrically contiguous motifs" (Step7)

### Notes

This makes editors of Acta E happy and it is necessary for using some special tools like rigid body (later in this Cookbook). The symmetrically contiguous motif means that the atoms are at bonding distances without applying symmetry operations.

## Step 7



OK; YES to save the changes

## IV. Refinement and model improvement

### 1. Refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine. (Step1)

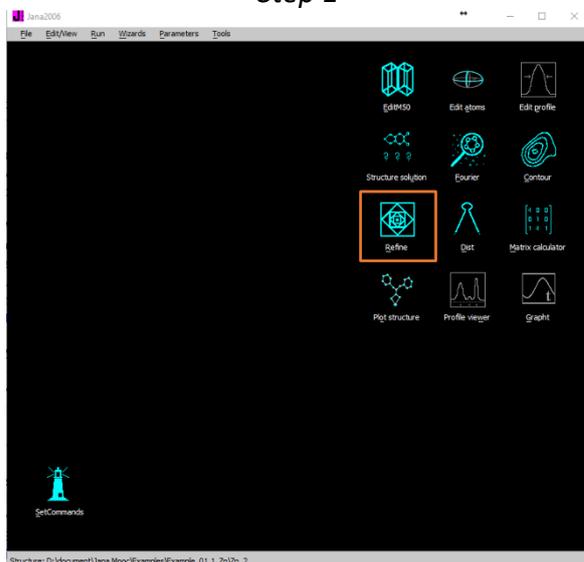
[On the screen: refinement options]

Define 100 of cycles; OK (Step2)

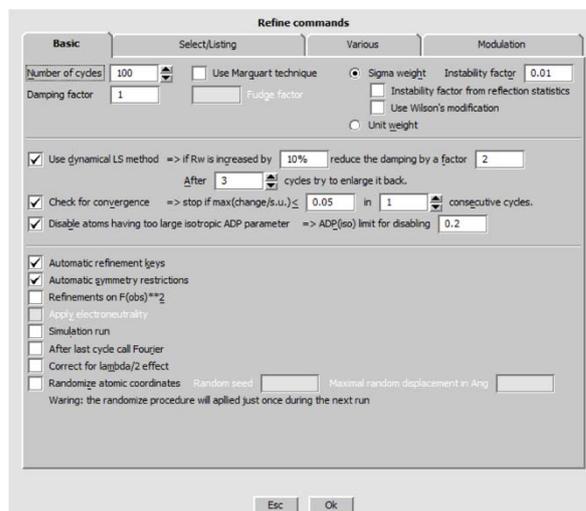
Choose “YES+START”

Refinement converges with  $R_{obs}$  value about 6%

### Step 1



### Step 2



Start “Edit atoms” (Step3)

[On the screen: list of atoms]

Press “Select all” and “Action → Edit/define”

Choose “harmonic” for ADP parameters. (Step4)

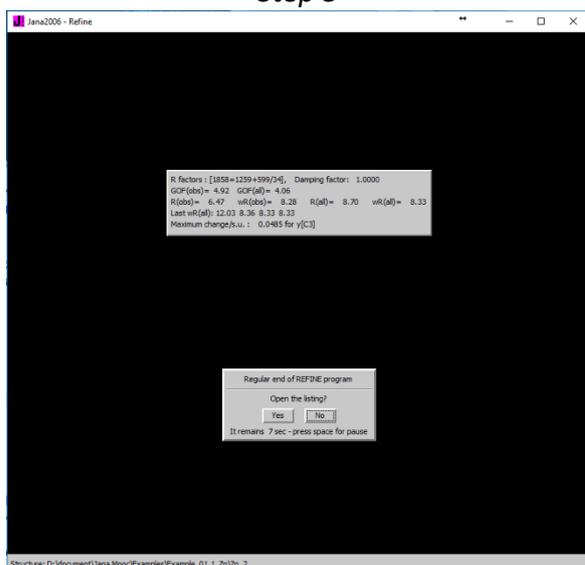
### Notes

*This defines anisotropic temperature parameters for all atoms.*

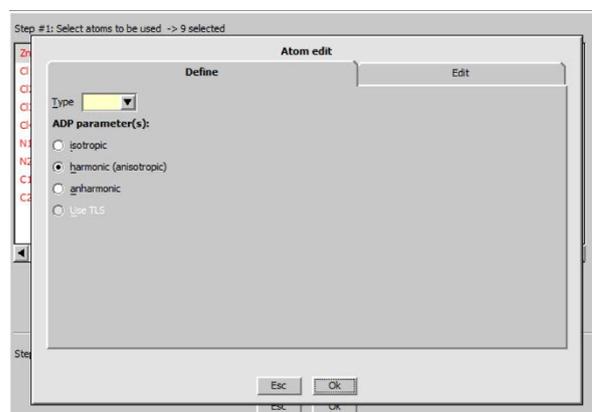
OK, OK, Yes to save changes

Refinement converges with  $R_{obs}$  value about 4 % for 73 refined parameters.

Step 3



Step 4



Double-click the icon Refine.

## 2. Adding of hydrogen atoms

[On the screen: basic window of Jana]

Start "Edit atoms"

Select carbons and nitrogens

Start "Action → Adding of hydrogen atoms" (Step1)

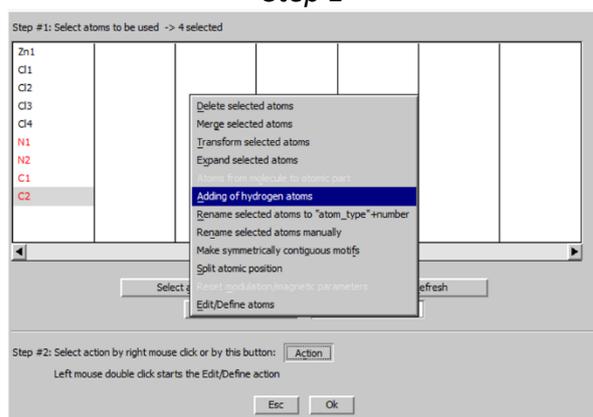
[On the screen: Adding of hydrogen atoms dialogue]

Leave all settings default; OK (Step2)

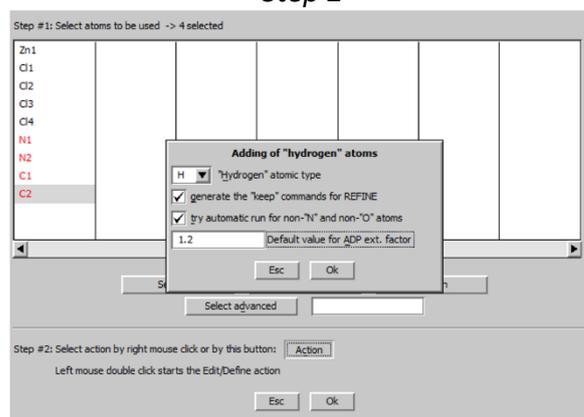
The procedure adds automatically C-H hydrogen atoms, while for adding hydrogens to the terminal  $NH_3$  groups it goes to the manual mode.

[On the screen: Adding of hydrogen atoms for N1]

Step 1



Step 2



For the type of coordination select "Tetrahedral", change number of neighbors to 1

## Notes

Using tetrahedral geometry instead of trigonal around nitrogen follows from the chemistry. The terminal groups must be protonated to reach the charge balance. The only neighbor of N1 is C1 (or C2 depending on how the maxima were assigned after running Superflip). You can verify this by focusing the textbox with C1 (or C2) and pressing "Select neighbors".

Define names of hydrogens, for instance H1N1, H2N1 and H3N1 (Step3)

Start "Locate position in the map"

[On the screen: difference Fourier map showing the hydrogen maxima]

Press "Optimal" and "Apply" (Step4)

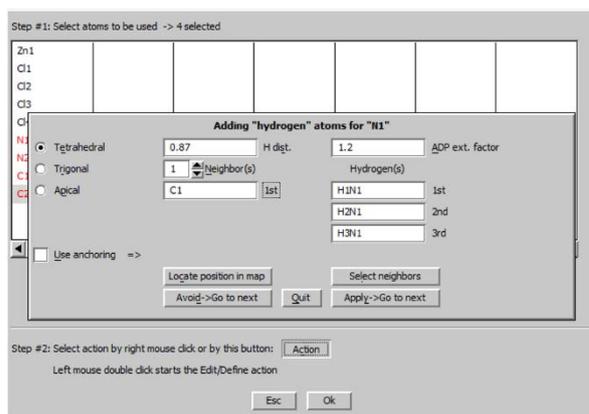
## Notes

Locating position in the map is not necessary. In most cases, the proper rotation of NH<sub>3</sub> or CH<sub>3</sub> group is correctly refined from the initial positions. However, in this case the map helps us to confirm the NH<sub>3</sub> groups.

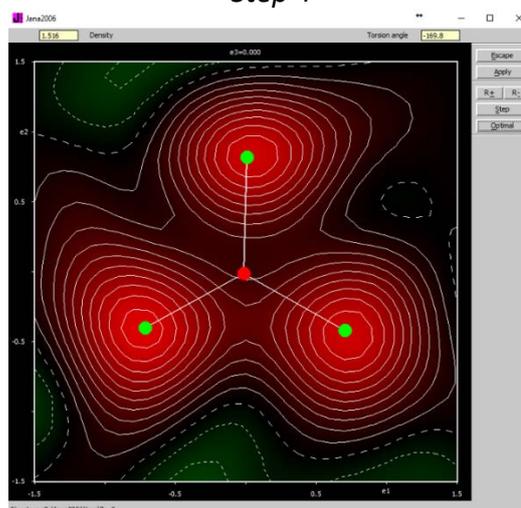
[On the screen: Adding of hydrogen atoms to N1]

"Apply → Go to next"

Step 3



Step 4



Repeat the procedure for N2

[On the screen: list of atoms]

## Notes

Total number of atoms should be 19 (can be verified with Select All).

The ideal geometry of hydrogen atoms is kept by commands, which can be viewed or edited in "Refinement commands → Various → Keep commands".

OK to close Atoms-Edit; Yes to save changes

"Plot structure" to check results of hydrogen assignment

[On the screen: window of Diamond]

Start "Build → Connectivity" or press button 

[On the screen: Connectivity dialogue]

Press "Evaluate" to see which bonds will be used by Diamond. Bonds between Cl and H should be disabled.

Plot the structure with 

Use  at the bottom toolbar of Diamond to see ADP ellipsoids.  
Quit Diamond

[On the screen: basic window of Jana2006]

Double-click Refine and refine the final structure

#### Notes

Refinement converges with R factor 2.5%, goodness of fit 1.9. Number of refined parameters is still 73 because the positions of hydrogen atoms are defined geometrically.

### 3. Extinction correction

[On the screen: basic window of Jana2006]

Open listing of Refine (by "Edit/View → View of Refine")

Press "Go to" and select "Statistics Fo, sin(th)/lambda after refinement" (Step1)

#### Notes

R value should decrease with increasing intensity or with lowering the diffraction angle. Here the R value for the strongest reflections, as well as for the lowest angle reflections, is higher than in the neighboring shell. This suggests that extinction correction is required.

#### Step 1

Statistics as a function of sin(th)/lambda and structure factors

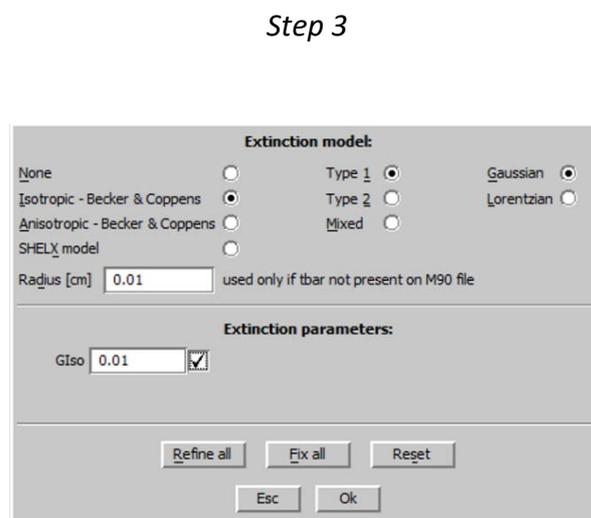
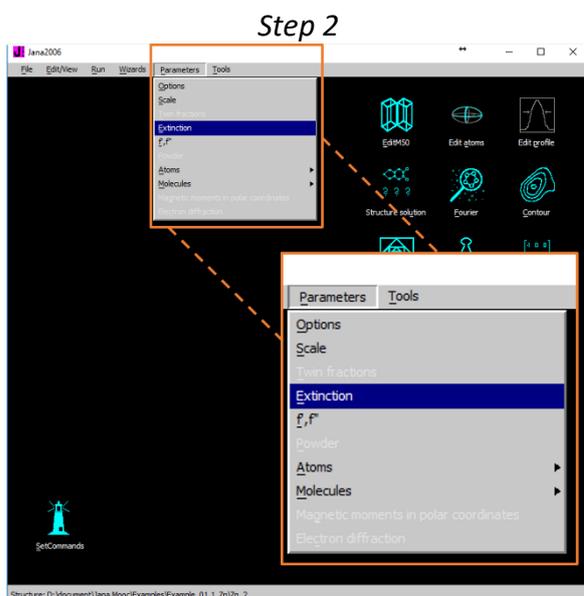
sin(th)/lambda	0.291439	0.368932	0.427538	0.475982	0.512727	0.554318	0.594972	0.658297		
limits	70	86	76	73	69	52	56	44		
number +	87	72	81	85	88	105	102	113		
-	157	158	157	158	157	157	158	157		
together	7.7660	3.0174	4.6645	5.6186	2.6114	1.1699	0.6461	0.4025		
av. wd F	87.1	79.4	92.4	143.3	84.4	42.7	36.7	35.8		
numerator +	-244.4	-51.0	-65.5	-61.8	-75.0	-92.0	-87.4	-121.4		
-	331.4	130.4	157.9	205.1	159.4	134.8	124.1	157.2		
together	13350.7	8800.7	7243.2	6315.5	5740.3	5419.9	4603.0	4596.6		
denominator	2.48	1.48	2.18	3.25	2.78	2.49	2.70	3.42		
R factor										
struct. factors	limits	16.9	21.8	26.6	32.8	41.0	54.5	79.4	395.3	unobs
number +	-	48	55	47	40	61	73	108	94	228
-	109	103	110	118	96	84	50	63	371	
together	157	158	157	158	157	157	158	157	599	
av. wd F	3.8859	4.3382	3.1198	1.7533	3.6924	1.9339	2.0287	5.2277	0.2141	
numerator +	90.7	88.7	84.3	30.7	55.1	53.9	95.9	132.6	418.6	
-	-96.6	-96.9	-111.3	-102.1	-66.8	-65.0	-31.4	-228.4	-620.7	
together	187.3	185.6	165.6	132.8	121.9	118.9	127.3	361.1	1039.4	
denominator	2172.3	3040.4	3798.0	4720.9	5770.0	7441.1	10376.3	18759.3	4634.5	
R factor	8.62	6.10	4.36	2.81	2.11	1.60	1.23	1.92	22.48	
final check										
number +				526				526		
-				733				733		
together				1259				1259		
numerator +				601.9				601.9		
-				-798.6				-798.6		
together				1400.5				1400.5		
denominator				56080.8				56080.8		
R-factor				2.50				2.50		

Close the refinement listing

"Parameters → Extinction" (Step2)

Select "Isotropic-Becker&Coppens" "Type 1" "Gaussian"; OK (Step3)

Refinement of the extinction coefficient is enabled by default



[On the screen: basic window of Jana2006]

Double-click Refine and refine the final structure

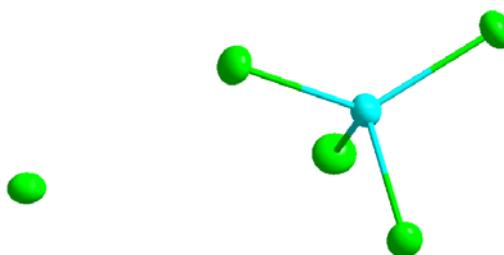
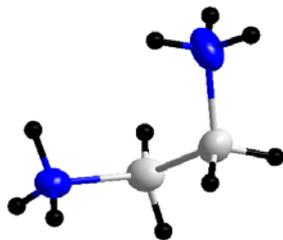
Refinement converges with R factor 2.24%, goodness of fit 1.77, 74 parameters.

Check the extinction coefficient through “Parameters → Extinction”

View listing of Refine; Go to “Statistics”; check improved R value for strongest reflections.

#### Notes

The resulting structure



Right-click the icon of Refine.

[On the screen: refinement options]

Check “Refinements on  $F(\text{obs})^{**2}$ ”; OK; YES to start the program

#### Notes

Standard refinement calculates with  $F^2$  while Jana2006 is still using  $F$  by default. In order to get a standard result, we will re-refine the structure on  $F^2$ .

Refinement converges with R factor 2.19%, goodness of fit 1.61, 74 parameters.

For good data, refinement on  $F$  and  $F^2$  usually gives very similar results.

Jana2006 does not refine the weighting scheme. The goodness of fit therefore corresponds to the experimental sigma of reflections corrected by the instability factor. For the moment, we are using the default instability factor 0.01. In the next step, we will use the instability factor calculated during merging of reflections (see above):

Right-click the icon of Refine.

[On the screen: refinement options]

Check “Instability factor from reflection statistics”; OK; YES to start the program

#### Notes

*There are almost no changes in the refinement results because the calculated instability factor is close to the default one. Its value can be seen in Edit/View → View of Reflection report (search for the string “instability”).*

## References

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# Example 2.1.1: PbSO<sub>4</sub>

Revised: 8 March 2019

Data	Topic	Level
X-ray powder data	Simple structure from powder	Basic

## Tasks

---

Profile refinement

Ab-initio structure solution

Structure solution using Histogram matching

## Initial data

---

### **Data**

Powder data measured with laboratory diffractometer

X-ray Cu Kalpha1/Kalpha2

### **Input files:**

PbSO4.mac (powder profile data)

PbSO4.txt (additional information)

### **Additional information:**

Chemical formula: Pb S O4

Unit cell: 8.48 5.4 6.96 90 90 90

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# Instructions

## I. Data import

### 1. Creating new jobname

Start Jana2006

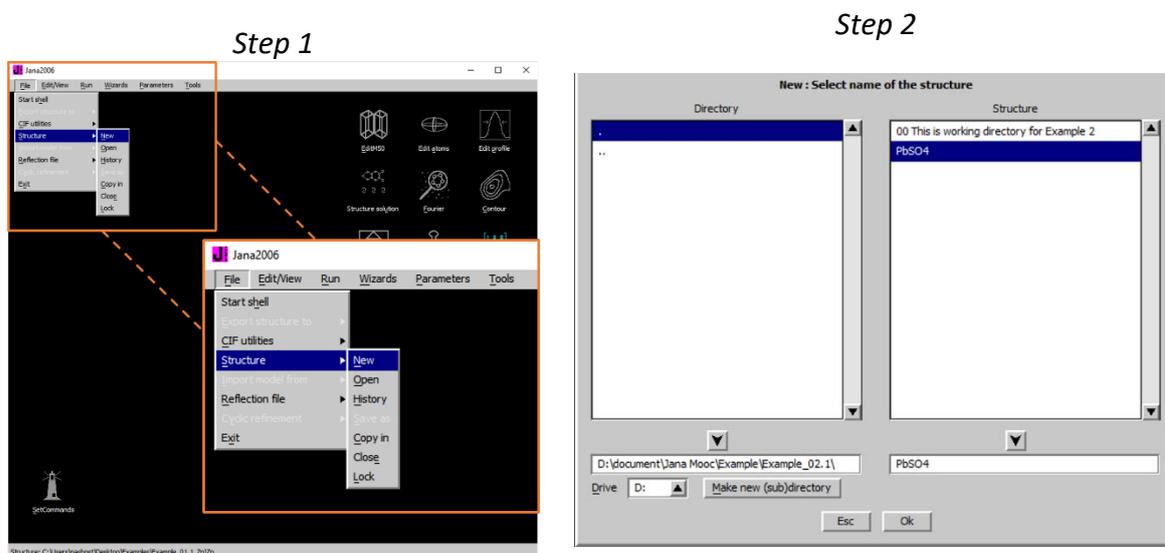
“File → Structure → New” opens a file manager (*Step 1*)

Left pane: locate directory with input files;

Right pane: double-click **PbSO4** (*Step 2*)

#### Notes

*Right pane detects possible Jana files and shows the jobname for each group of files*

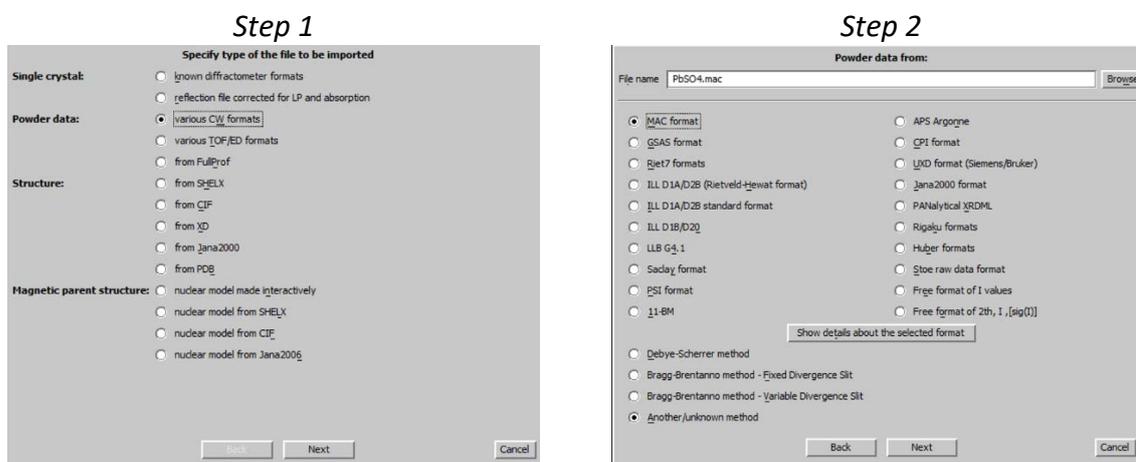


### 2. Import wizard

Select “**Various CW formats**”; NEXT (*Step 1*)

CW stands for constant wavelength

Select “**MAC format**” and “**Another/unknown method**”; NEXT (*Step 2*)



Enter cell parameters **8.48 5.4 6.96 90 90 90**;

For wavelength type first **select Kalpha1/Kalpha2 doublet** and then select **X-rays Cu**; NEXT

(Step 3)  
 FINISH (Step 4)



OK;YES (Step 5)  
 Select "Yes, I would like to continue with the wizard"; OK (Step 6)

**Notes**  
 At this point Jana2006 offers wizard for determining powder profile parameters, space group and structure. We shall use the wizard but all its tools could be also started separately.



## II. Le Bail refinement/pattern matching

[On the screen: Refinement of the powder profile by the le Bail algorithm] (Step 1)  
 "Show powder profile" (Step 2)

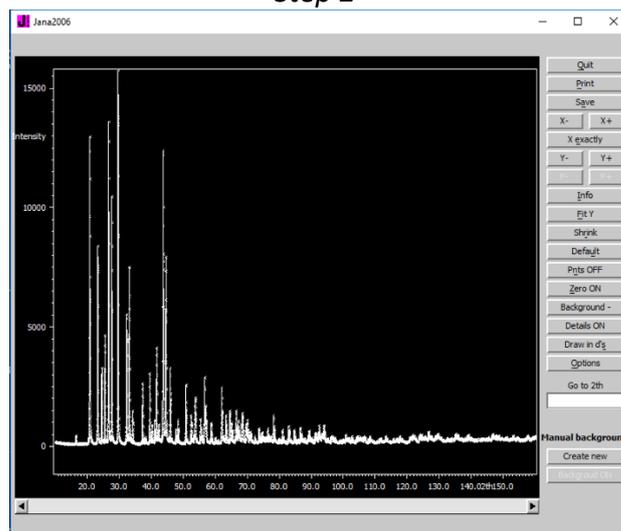
**Notes**  
 Profile viewer shows experimental powder profile

Quit; Leave profile viewer

### Step 1

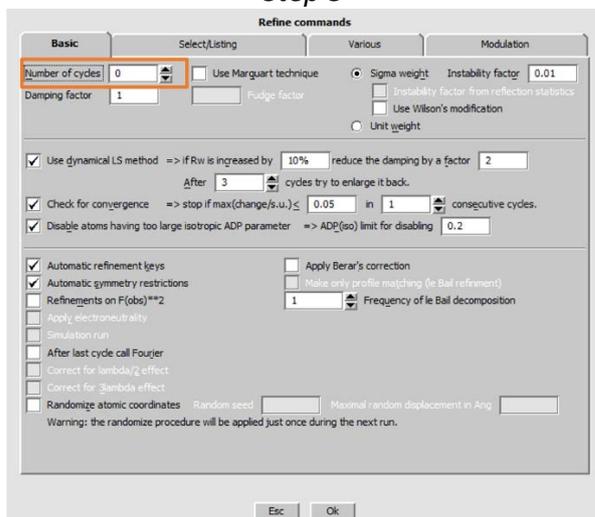


### Step 2

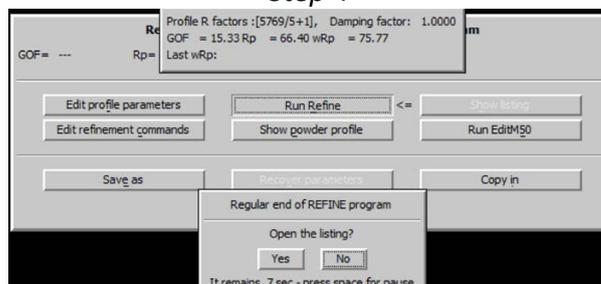


“Edit refinement commands”; set 0 cycles; leave other settings default; OK (Step 3)  
“Run Refine” (Step 4)

### Step 3



### Step 4



“Show powder profile” (Step5)

### Notes

Now the profile viewer shows both experimental and calculated powder profile, and the difference curve.  
The calculated profile is based on default profile parameters.  
The calculated profile is stored in PbSO4.prf

Leave profile viewer by QUIT

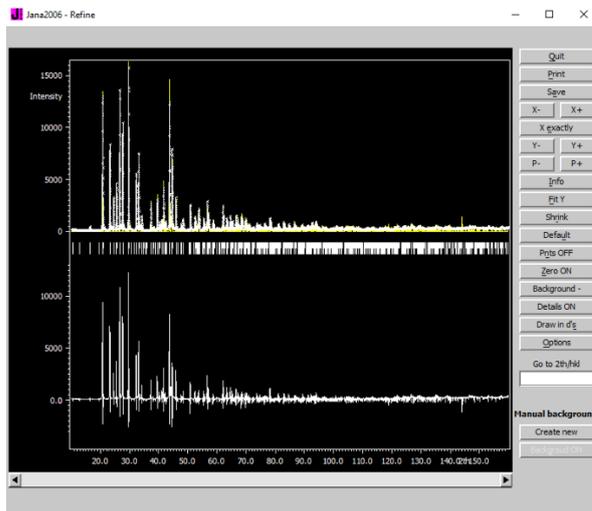
“Edit profile parameters”

[On the screen: Powder options]

In “Cell” page select refinement of a, b and c (Step 6)

### Step 5

### Step 6



In “Profile” page select Cutoff to 12\*FWHM; activate refinement of **GW**; (Step 7)  
 In “Corrections” page activate refinement of “shift”;  
 In “Corrections” page select “Legendre polynomials” with 5 terms for background calculation (Step 8)

### Notes

*Refinement of background terms is enabled by default*

### Step 7

### Step 8

Leave Powder options (OK), save changes (YES)  
 “Edit refinement commands”; set 10 refinement cycles; OK (Step 9)  
 “Run Refine”

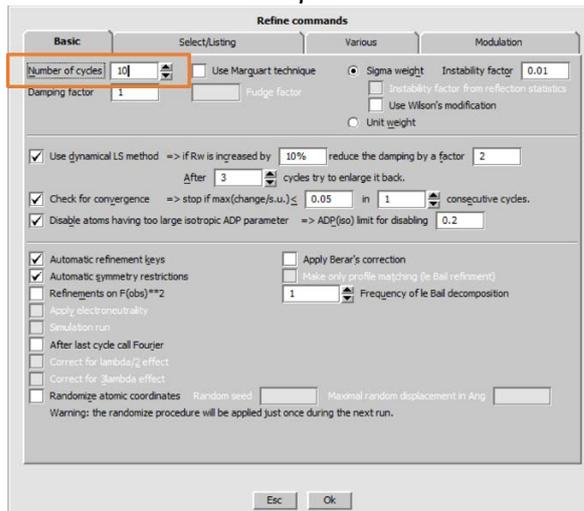
### Notes

*After 10 refinement cycles, refinement converges with profile parameters GOF ~ 3, Rp ~ 11.4, wRp ~ 16.4.*

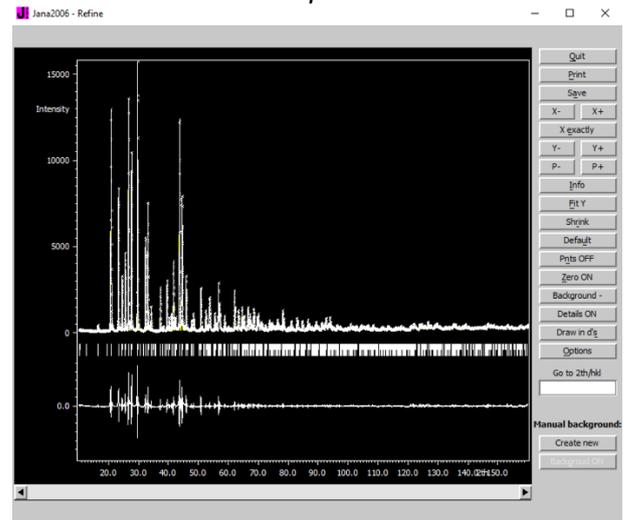
*The refinement may be slow because at this point we are using symmetry P1*

“Show powder profile” (Step 10)

### Step 9



### Step 10



In Powder profile viewer press “Default” and move close to theta 20° (Step 11)

### Notes

The observed peaks are systematically broader which may indicate that Lorentzian broadening is to be combined with the Gaussian profiles.

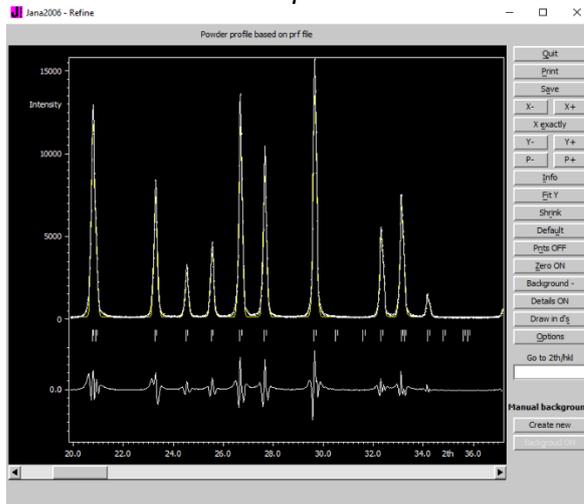
Leave profile viewer

“Edit profile parameters”

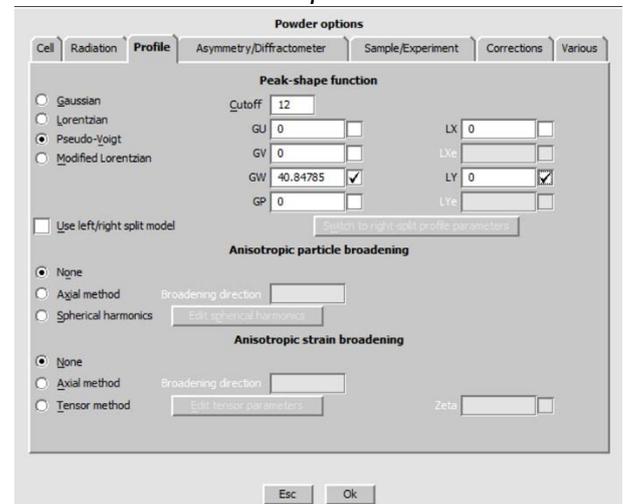
[On the screen: Powder options]

In page “Profile” select **Pseudo-Voigt** and activate refinement of **LY**; (Step 12)

### Step 11



### Step 12



OK; YES;  
“Run Refine”

### Notes

After 10 refinement cycles, refinement converges with profile parameters  $GOF \approx 2.3$   $Rp \approx 8.0$   $wRp \approx 11.39$ .

“Show powder profile” (Step 13)

“Quit”

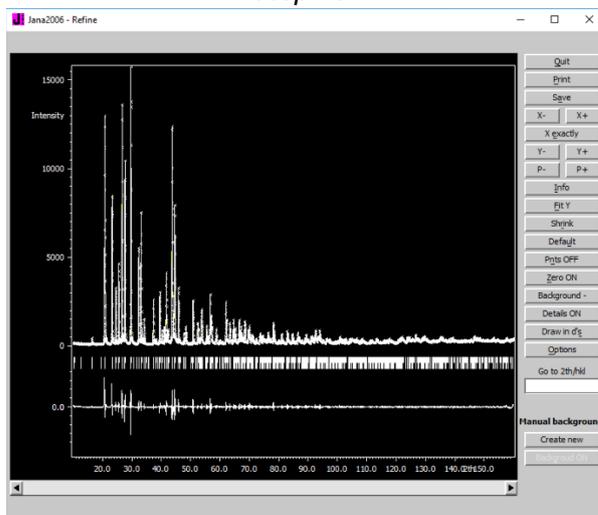
“Edit profile parameters”

[On the screen: Powder options]

In page "Profile" activate refinement of LX. (Step 14)

OK;YES;

### Step 13



### Step 14

"Run Refine"

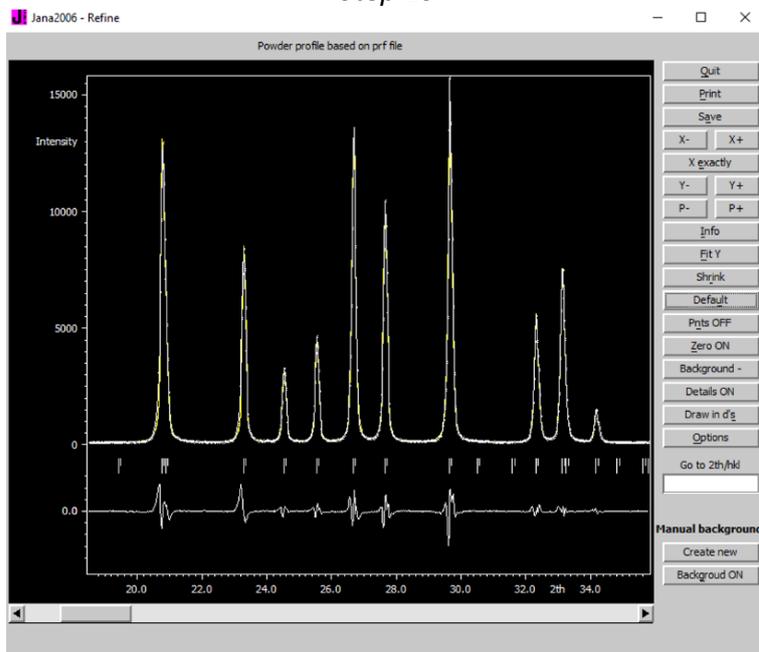
### Notes

After 10 refinement cycles, refinement converges with profile parameters  $GOF \sim 1.8$ ,  $R_p \sim 6.3$ ,  $wRp \sim 8.7$ .

"Show powder profile" (Step 15)

"Quit"

### Step 15



### Notes

The observed peaks at low angles still have some asymmetry. (Use "X+" and "X-" buttons to see it better)

“Edit profile parameters”

[On the screen: Powder options]

In page “Asymmetry” select the Berar-Baldinozzi correction and activate refinement of asym1, asym2, asym3, asym4; (Step 16)

OK; Yes;

The asymmetry can be described by several functions, see Example 2.2 For this case Berar-Baldinozzi function with four parameters sufficiently describes the asymmetry.

“Run Refine”

#### Notes

After 10 refinement cycles, refinement converges with profile parameters  $GOF \sim 1.5$ ,  $R_p \sim 5.5$ ,  $wR_p \sim 7.6$ .

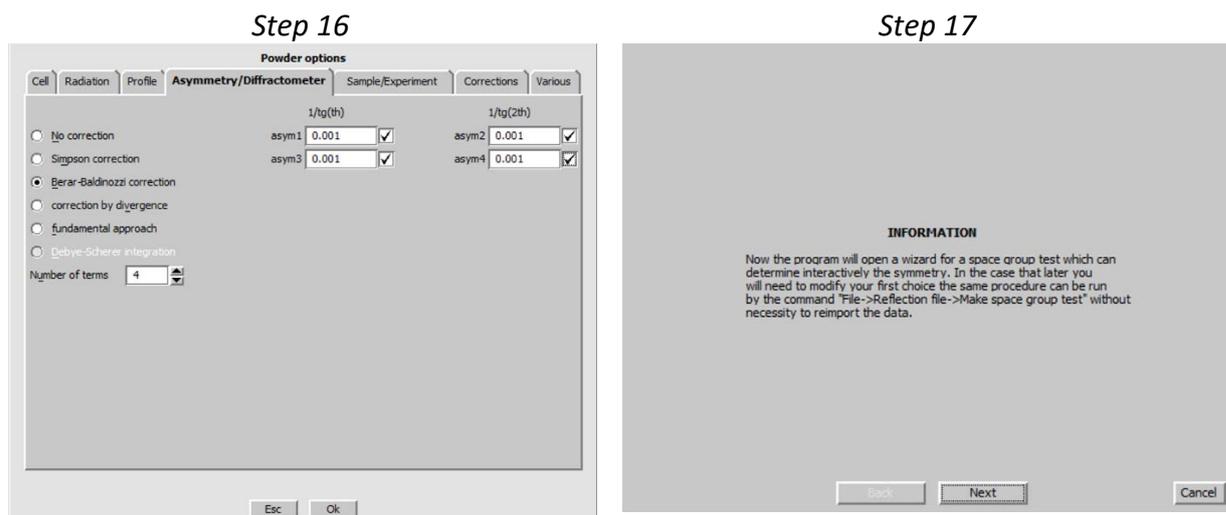
FINISH; YES to close the refinement tool;

CANCEL to skip the space group wizard; (Step 17)

#### Notes

In this example, we will use Superflip for the space group determination. You may also perform the space group test here and compare the results, which should be the same.

OK;



### III. Structure solution and Rietveld refinement

#### 3. Structure solution

[On the screen: Structure solution]

#### Notes

This part of wizard can be also started separately by “Run → Solution”

Type formula **Pb S O4**; Formula units **4**

Select “Use Superflip”

Check “allow manual editing of the command file before start”

Check “Repeat Superflip: number of runs”

Set “Maxcycles” to **2000** (Step 1)

## Step 1

Structure solution

use Expo 2014  
 use Superflip  
 use Shelx  
 use in le Bail decomposition structure information for already identified phases

Formula Pb S O4  
Formula units 4  
Actual space group: P1

allow manual editing of the command file before start  
 use previously prepared input file for Superflip  
 use old solution and reinterpret it  
 Repeat Superflip: Until the convergence detected  
 Repeat Superflip: Number of runs => 10  
 Use local normalization  
 Use a specific random seed  
 Define explicitly delta value

Iteration scheme:  CF  
 LDE  
 AAR

For peak search use:  EDMA - fixed composition  
 EDMA - fixed number of atoms  
 EDMA - peak interpretation by Jana2006  
 Peaks from Jana2006  
 Peaks from Jana2006 but first run Fourier

Starting model:  Random phases  
 Patterson superposition map

Buttons: Run solution, Open file history, Show parameters, Update parameters, Repeat last solution, Quit

Press “Run solution” to start Superflip

### Notes

*Jana makes le Bail decomposition and then it opens the text editor to see the prepared input file for Superflip.*

```
title PbSO4_Superflip
perform CF
outputfile "PbSO4_Superflip.m81" "PbSO4_Superflip.m80"
outputformat jana
dimension 3
cell 8.4810 5.3991 6.9606 90.00 90.00 90.00
spacegroup P1
centro no
centers
0.000000 0.000000 0.000000
endcenters
symmetry
x1 x2 x3
endsymmetry
composition Pb4 S4 O16

# Keywords for charge flipping
repeatmode 10
bestdensities 1 symmetry
polish yes
maxcycles 2000
delta AUTO
weakratio 0.000
Biso 0.000
randomseed AUTO
searchsymmetry average
derivesymmetry yes
# End of keywords for charge flipping

# EDMA-specific keywords
inputfile PbSO4_Superflip.m81
```

Using the text editor, replace the command “**bestdensities 1 symmetry**” for “**bestdensities 1 rvalue**”

### Notes

*The command Bestdensities defines the criterion for selecting the best density from the ten subsequent runs. “1” means that only one best result will be saved. “Symmetry” means that the best mach with the user-defined symmetry will be saved, but this is not applicable for P1 symmetry. “rvalue” means that the result with the best R value will be saved. Full description of the Superflip commands is available here:*

[http://superflip.fzu.cz/download/superflip\\_user\\_manual.pdf](http://superflip.fzu.cz/download/superflip_user_manual.pdf)

Save and close the file

Superflip will start automatically and create this output file:

```
PbSO4_Superflip.slog
906 #####
907 # Iteration #
908 #####
909
910 Estimated delta: 3.3434
911 Random seed: 134545312
912
913 Searching for a proper delta:
914 Current delta = 3.34337 (k_ed = 1.00000)
915 Total/flipped ratio = 0.956.
916 Criterion for delta fulfilled, continuing iteration.
917
918 20 R: 44.767 Charge: 310.57 Peaks: 1.21 Score: ---
919 30 R: 43.081 Charge: 277.63 Peaks: 1.46 Score: ---
920 40 R: 39.737 Charge: 193.40 Peaks: 3.32 Score: ---
921 50 R: 32.117 Charge: 134.58 Peaks: 4.00 Score: ---
922 60 R: 31.535 Charge: 136.00 Peaks: 3.93 Score: ---
923 70 R: 30.658 Charge: 127.04 Peaks: 3.74 Score: ---
924 80 R: 30.581 Charge: 136.06 Peaks: 3.76 Score: ---
925 90 R: 30.548 Charge: 133.70 Peaks: 3.78 Score: ---
926 100 R: 27.989 Charge: 130.27 Peaks: 3.79 Score: ---
927
928 Calculation successfully converged after 124 cycles.
929 Last iteration record:
930 124 R: 30.206 Charge: 135.79 Peaks: 3.75 Score: 11.50
931
932 5 cycles of noise suppression follow:
933 5 R: 27.123 Charge: 0.00 Peaks: 5.76
934 #####
935 # Checking the density for symmetry #
936 #####
937
938 Symmetry operations compatible with the lattice and centering:
939
940 Symmetry operation agreement factor
941 m(0,1,0): x1 -x2 x3 0.896
942 2_1(1,0,0): 1/2+x1 -x2 -x3 0.974
943 a(0,0,1): 1/2+x1 x2 -x3 1.842
944 2_1(0,0,1): -x1 -x2 1/2+x3 4.488
945 2_1(0,1,0): -x1 1/2+x2 -x3 4.950
946 n(1,0,0): -x1 1/2+x2 1/2+x3 5.343
947 -1: -x1 -x2 -x3 5.842
948 m(0,0,1): x1 x2 -x3 33.634
949 2(1,0,0): x1 -x2 -x3 34.153
950 m(1,0,0): -x1 x2 x3 38.652
951 2(0,0,1): -x1 -x2 x3 39.108
952 2(0,1,0): -x1 x2 -x3 39.536
953 b(1,0,0): -x1 1/2+x2 x3 75.950
954 c(1,0,0): -x1 x2 1/2+x3 78.798
955 b(0,0,1): x1 1/2+x2 -x3 107.801
956 a(0,1,0): 1/2+x1 -x2 x3 108.224
957 n(0,1,0): 1/2+x1 -x2 1/2+x3 113.345
958 n(0,0,1): 1/2+x1 1/2+x2 -x3 140.112
959 c(0,1,0): x1 -x2 1/2+x3 141.214
```

Delta estimation

Performing the algorithm

Symmetry reconstruction  
From the ELD

```
-----  
Space group derived from the symmetry operations:  
-----
```

```
HM symbol:      Pnma  
Hall symbol:    -p 2ac 2n  
Fingerprint:   3300320n{041Y53}22 (0,0,0)  
Symmetry operations:  
      1:          x1          x2          x3  
2_1(0,0,1):     1/2-x1      -x2      1/2+x3  
2_1(1,0,0):     1/2+x1      1/2-x2    1/2-x3  
      -1:         -x1         -x2         -x3  
2_1(0,1,0):     -x1      1/2+x2      -x3  
      a(0,0,1):   1/2+x1      x2      1/2-x3  
      n(1,0,0):   1/2-x1      1/2+x2    1/2+x3  
      m(0,1,0):   x1      1/2-x2      x3
```

Derived space group!

```
#####  
# Search for the origin of the space group #  
#####
```

Only trivial symmetry is present, no symmetry search can be performed.  
You can obtain more information about the reconstructed reflection phases by using 'expandedlog yes'.

Current FOM is worse than the best. Density will not be saved.

Properties of the saved density:

Run	Rvalue	Peaks	Symm.	Der.SG
1	26.67	5.40	100.00	Pnma

Last run from 10 completed.

In this case, the solution was not saved  
as the best solution

Summary of all runs:

Number of attempts	:	10
Maximum cycles	:	2000
Number of successes	:	10
Success rate [%]	:	100.0
Mean cycles per convergence(beta):		105
95% confidence interval for beta	:	61 - 218
95% confidence interval for SR	:	1.00 - 1.00

-----  
End of the calculation: 29.AUG 2018, 13:45:45  
-----

Superflip version: 05/17/16 12:53

## Notes

The output of Superflip contains 10 independent Superflip runs. At the end of each run we can see the space group derived from the electron density. In most cases, it is Pnma; therefore we will redefine space group and repeat the solution.

Close the Superflip output

[On the screen: "Structure solution" window]

Press "Change the space group" button and write Pnma instead of P1. OK; YES; (Step 2)

Press "Run solution";

## Notes

Check the input file again and see the difference. Now, the command "**bestdensities 1 symmetry**" can be used because we need the best match with the symmetry Pnma.

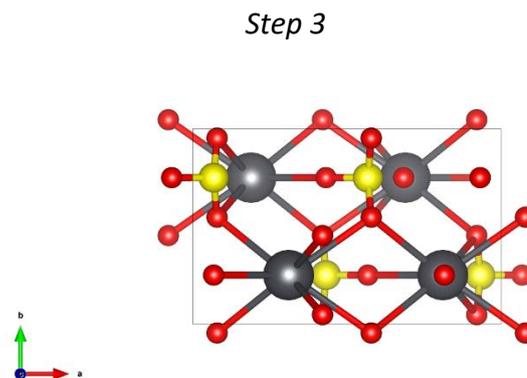
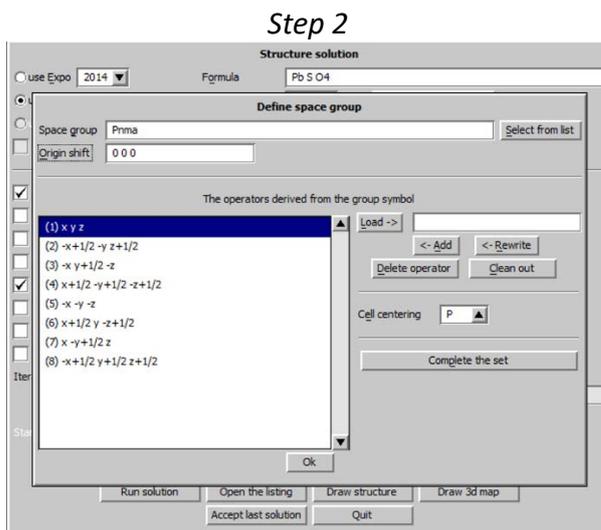
Close the file

Superflip will start automatically

Read the log file and close it;

[On the screen: "Structure solution"]

Press "Draw structure" to see the result in the external 3d viewer. (Step 3)



You may also press the “Draw 3D map” to see the resulted ELD map of Superflip.

## Notes

*The correct solution must show the SO<sub>4</sub> tetrahedron. If it is not present, you can run the ten trials again. Since Superflip starts from randomly generated phases, the result of the next run may be better. On the other hand, if you get more than 4 oxygen atoms for one Sulphur, the additional oxygen will be probably discarded during refinement by getting inacceptably large U<sub>iso</sub>.*

Press “Accept last solution”. This action will also close the structure solution wizard.

## 4. Refinement of the structure

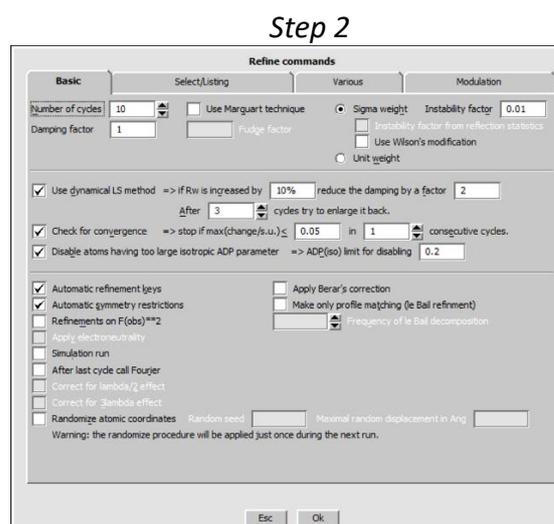
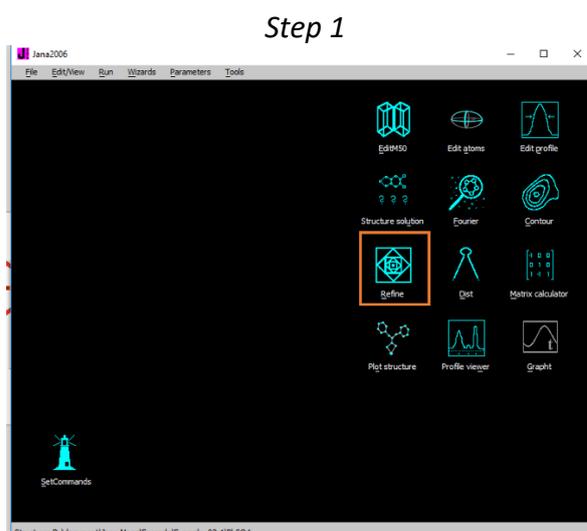
“File → Structure” → **Save As** to make **backup copy**

[On the screen: basic window of Jana]

Open **refinement options** (by the right-click on the icon of Refine). (Step 1)

[On the screen: refinement options]

Uncheck “**Make only profile matching**”, OK, Yes+start (Step 2)

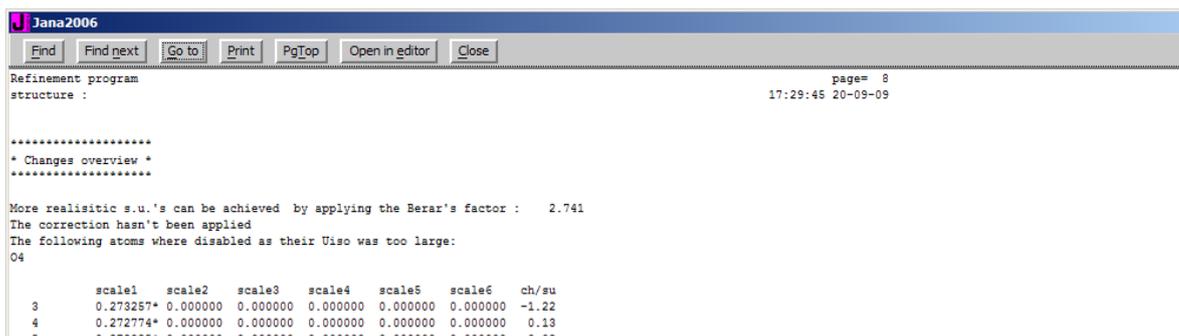


Wait for convergence and open the listing. (You can access the listing of Refine also by “Edit/View → View of Refine”)

## Notes

After 10 refinement cycles refinement converges with structure factors  $R(\text{obs}) \sim 3.5$ ,  $wR(\text{obs}) \sim 4$ ,  $R(\text{all}) \sim 3.6$ ,  $wR(\text{all}) \sim 4$ ; and profile factors  $GOF \sim 1.8$ ,  $R_p \sim 6.8$ ,  $wR_p \sim 9$ . It may happen that refinement fails due to wrong structure model. In such case, use "Tools -> Recover files" to get the original profile parameters and repeat Structure solution. Superflip starts from random phases and may return better result in the next attempt. The Recover files can only make one-step recovery. If you would run two subsequent refinements, the original files would be inaccessible. In such case, "File -> Structure" -> Copy In" can be used for recovery.

Press "Go to" and select "Changes overview":



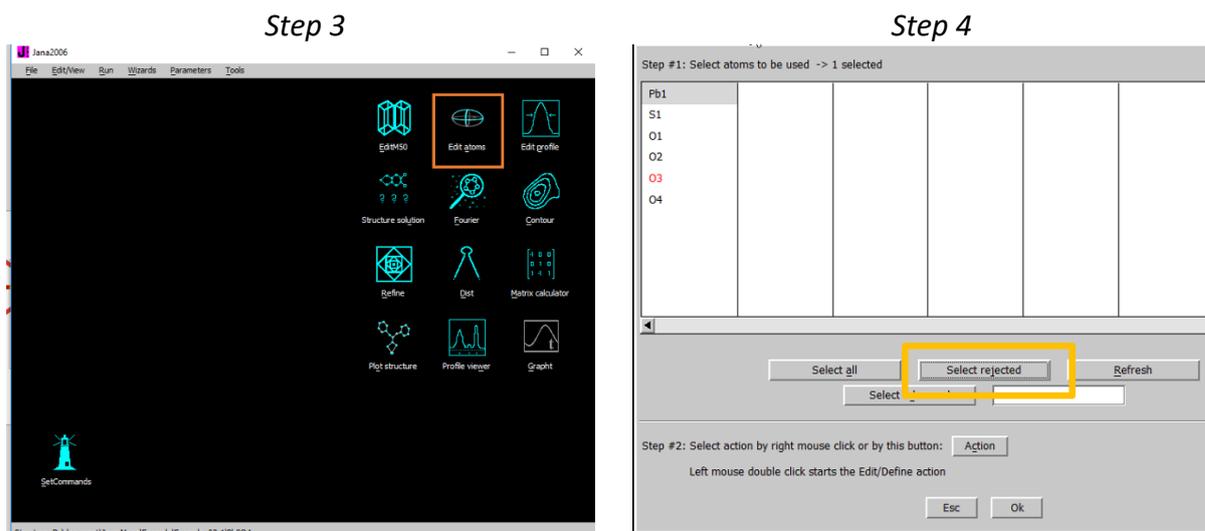
## Notes

At the beginning of "Changes overview" there might be list of disabled atoms automatically excluded from the refinement as their ADP is larger than the allowed limit. The excluded atoms are still present in M40 file with zero occupation. In order to delete them:

Run "Edit atoms", (Step 3)

press "Select rejected" (Step 4)

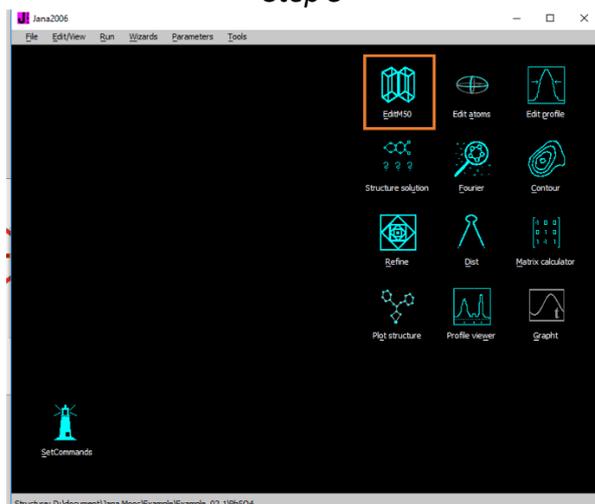
"Action -> Delete selected atoms"; Yes to all; OK



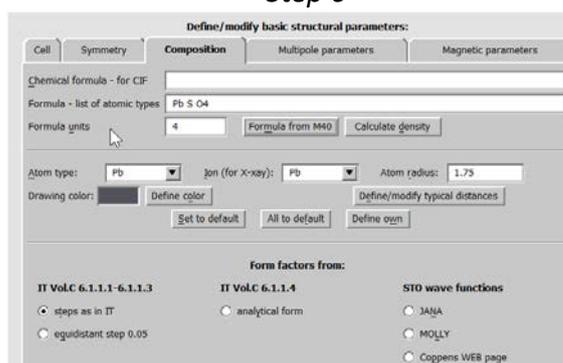
Start EditM50, (Step 5)

Select page "Composition" and press "Formula from M40". It should display "Pb S O4". (Step 6)

## Step 5



## Step 6



## 5. Using difference Fourier for completing structure model

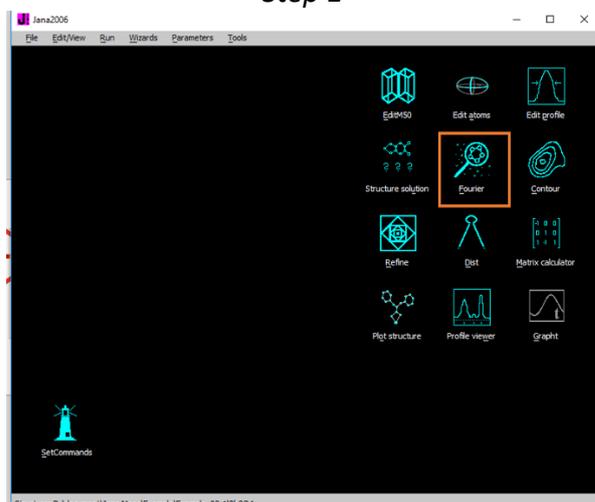
### Notes

*In the case that some of oxygen atoms are still missing they can be localized from the difference Fourier.*

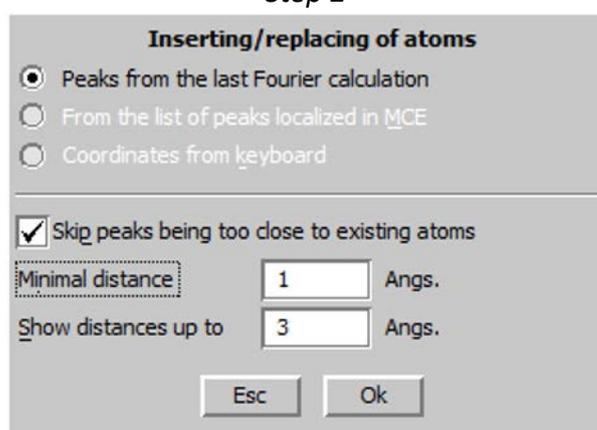
*If your structure is complete (EditM50 displays the correct formula) but you would like to try this part, please start "Edit Atoms" and delete some oxygen and refine the structure. The refinement step (possibly with zero cycles) is necessary because it prepares structure factors for Fourier calculation.*

Right-click on the Fourier icon opens the command editing procedure for Fourier. Select "**F(obs)-F(calc) – difference Fourier**"; OK; "Yes + Start"; (Step 1)  
"Do you want to start the procedure for including of new atoms ? Yes;

## Step 1



## Step 2



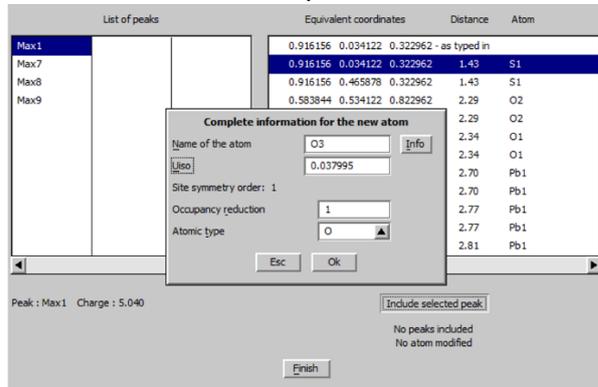
[On the screen: Inserting/replacing atoms]

### Notes

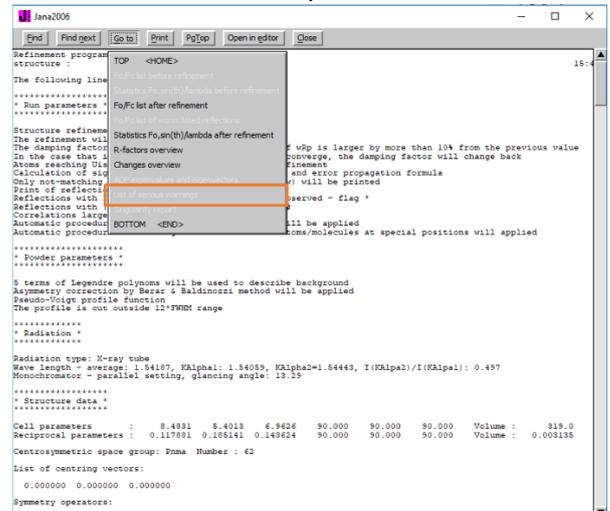
*The program transforms each found maximum to various symmetry equivalent positions where it is close to some already existing atoms. Only atoms at the user defined distance from the maximum (here between 1 and 3 Å) are considered. By selecting a particular line we select the maximum in the corresponding symmetry transformation.*

Include all missing atoms, i.e. the maxima with large enough charge and reasonable distance to some of already existing atoms; Use O\* for atom names (Step 3)  
OK; FINISH

### Step 3



### Step 4



Verify the formula with "Editm50 → Composition → Formula from M40"  
Repeat refinement (in case of changes)

**Notes**  
After 10 refinement cycles refinement converges with structure factor  $R(obs) \sim 3.5$ ,  $wR(obs) \sim 4$ ,  $R(all) \sim 3.6$ ,  $wR(all) \sim 4.0$ ; and profile factors  $GOF \sim 1.8$ ,  $R_p \sim 6. *$ ,  $wR_p \sim 9.0$ .

"Edit/View → View of Refine"

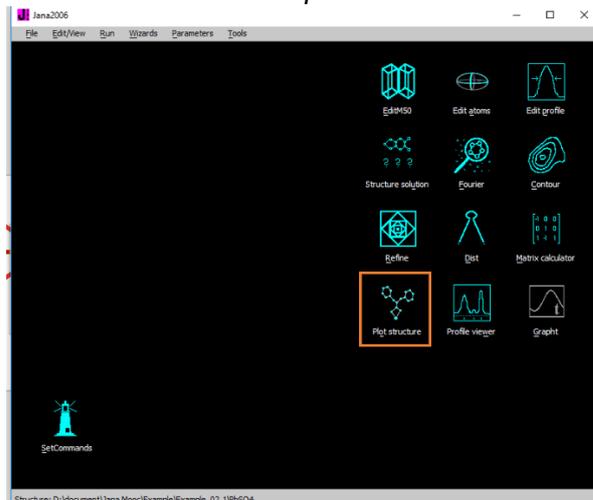
"GoTo → List of serious warnings" (Step 4)

This list should be empty, indicating no problems with ADP parameters

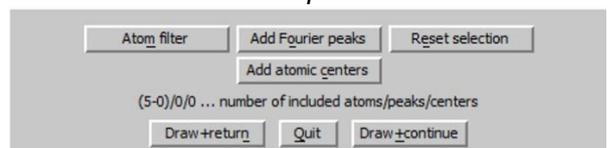
Plot structure (Step 5)

"Draw+continue" (Step 6)

### Step 5



### Step 6



[On the screen: window of Diamond]

Use button  at the bottom toolbar and plot only Pb and S (Step 7).

In Build → Connectivity adjust limits for S-O distances. Then complete coordination of Pb and S with .

**Step 8**

Add Atoms

Select one or more atoms from the atom site list:

No.	Symbol	Cx.	Wy.	X	Y	Z	S.O.F.
1	Pb1	4c	11/16	3/4	0.16761		
2	S1	4c	0.92644	1/4	0.18299		
3	O1	4c	1.09077	1/4	0.09414		
4	O2	4c	0.68633	3/4	0.54239		
5	O3	8d	0.92135	0.02765	0.31409		

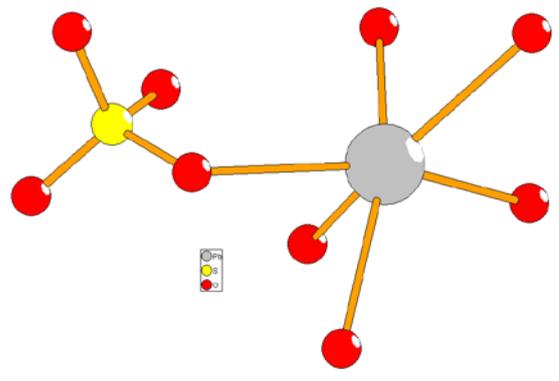
Symmetry operation(s):  
1: x, y, z  
2: 1/2-x, -y, 1/2+z  
3: 1/2+x, 1/2-y, 1/2-z  
4: -x, 1/2+yy, -z  
5: -x, -y, -z  
6: 1/2-x, y, 1/2-z

Bravais translation(s):  
1: +(0,0,0)

Integer cell translations:  
 0 <= X <= 0     0 <= Y <= 0     0 <= Z <= 0   

You may also specify one or more atom codes or code ranges,  
e.g. "15550-41 35550-11-65550-11"

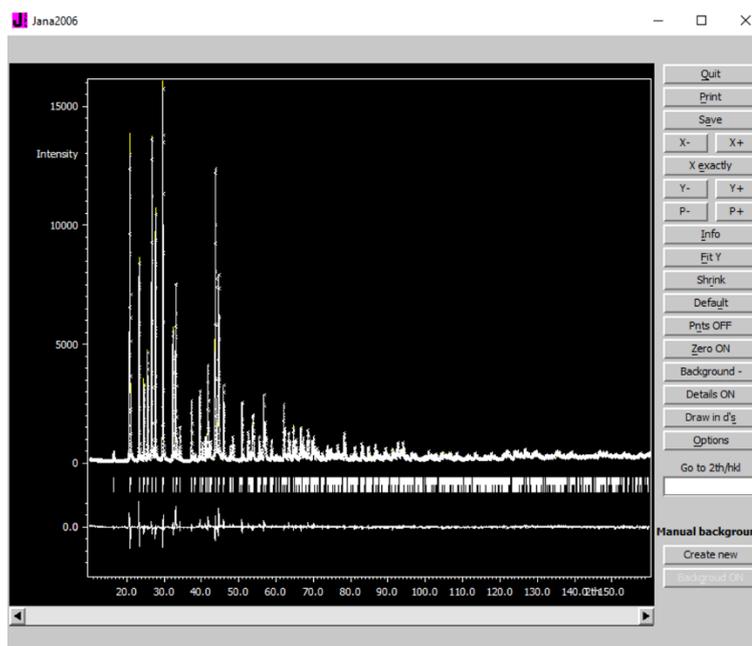
**My resulting structure**



### The final R values in Jana

```
R factors : [384=381+3/17]
R(obs)= 3.49  wR(obs)= 4.04  R(all)= 3.54  wR(all)= 4.05
=====
Profile R factors :[5769/16+17],  Damping factor: 1.0000
GOF = 1.79  Rp = 6.69  wRp = 8.83
Last wRp: 8.83
Maximum change/s.u. : -0.0070 for b
```

### The final powder pattern



## References

---

# Example 2.1.2: 17equ

Revised: 15 October 2018

Data	Topic	Level
X-ray Powder synchrotron data	Simple organic structure	Basic

## Tasks

Solving a simple organic structure from high quality synchrotron powder data using Jana2006 and Superflip

1. Import data to JANA2006
2. Perform Le Bail refinement (extraction of intensities)
3. Run Superflip to solve the crystal structure

## Initial data

### Data

synchrotron diffractometer  $\lambda = 0.41334 \text{ \AA}$ , capillary

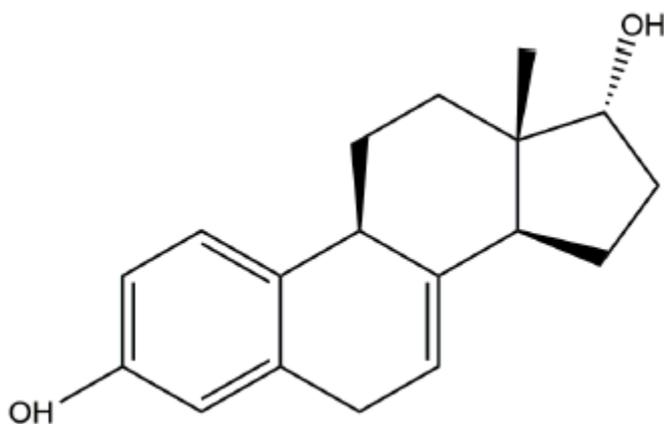
### Input files:

17equ.xy

### Additional information:

Chemical formula:  $C_{18}H_{22}O_2$  (17  $\alpha$ -Dihydroequilin)

Unit cell: 6.77 8.97 23.39 90 90 90



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# Instructions

## I. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click **17equ.xy**

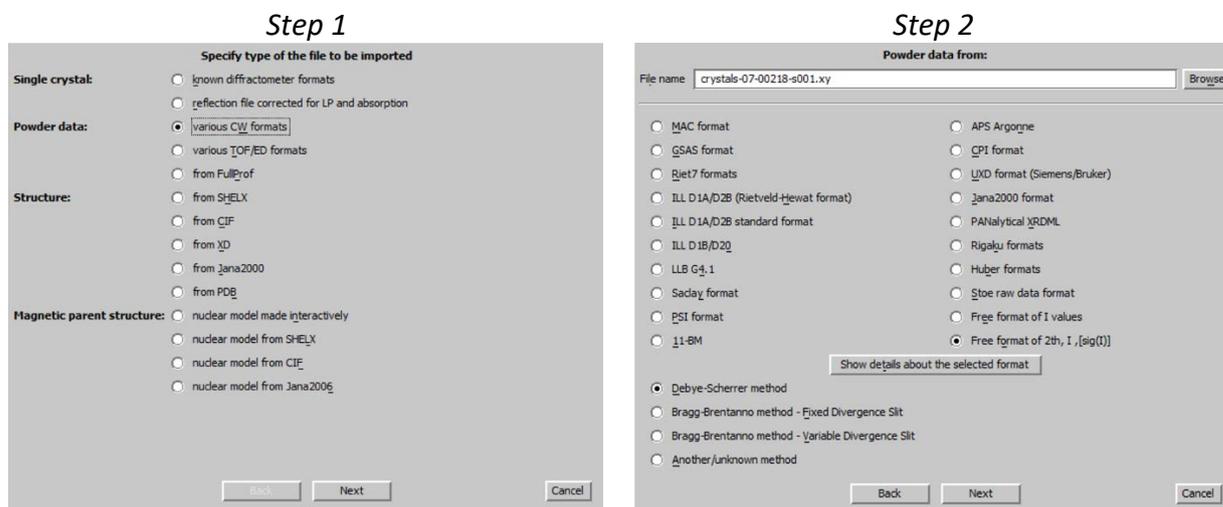
### 2. Import Wizard

Select “Powder data – various CW formats”; NEXT (Step 1)

[On the screen: Powder data form]

Select “Free format of 2th, I, [sig(I)]”

For method select “Debye-Scherrer”; NEXT (Step 2)



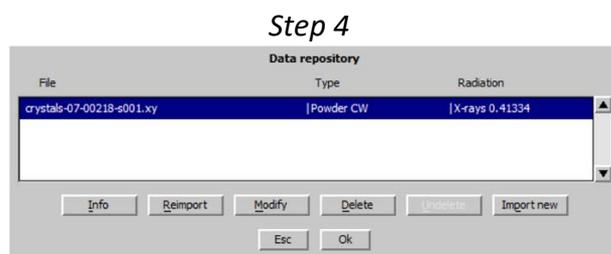
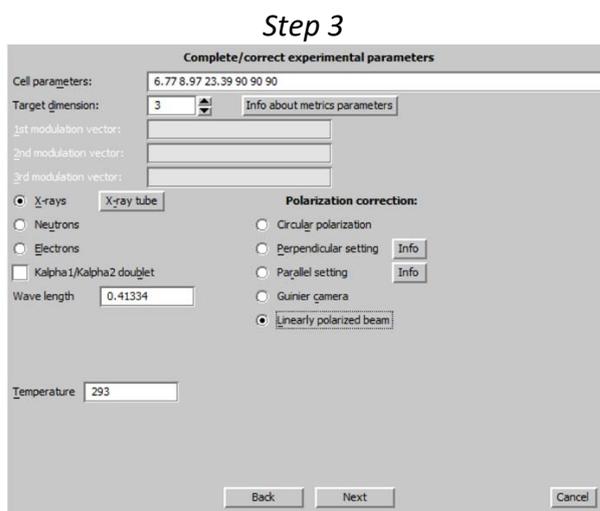
[On the screen: Complete/correct experimental parameters]

Fill unit cell parameters: **6.77 8.97 23.39 90 90 90**

Radiation: X-ray; wavelength is **0.41334**; **uncheck** Kalpha1/Kalpha2 doublet

For “Polarization correction” select “**Linearly polarized beam**” (Step 3)

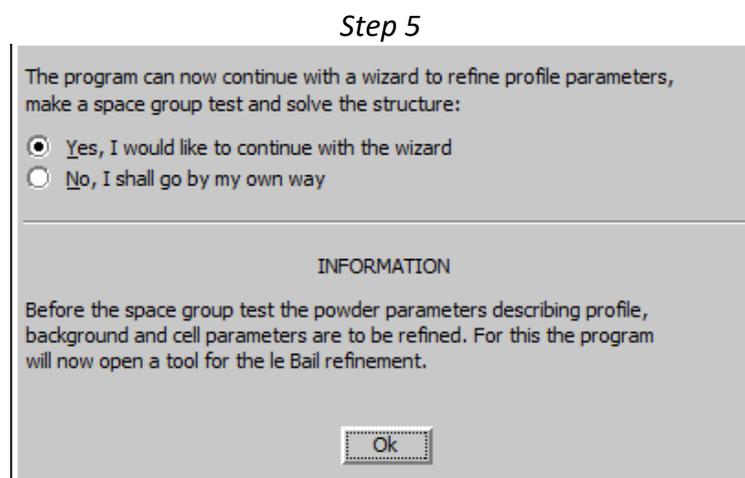
NEXT; FINISH; OK to close data repository; (Step 4)



YES to accept the data set

[On the screen: question how to continue]

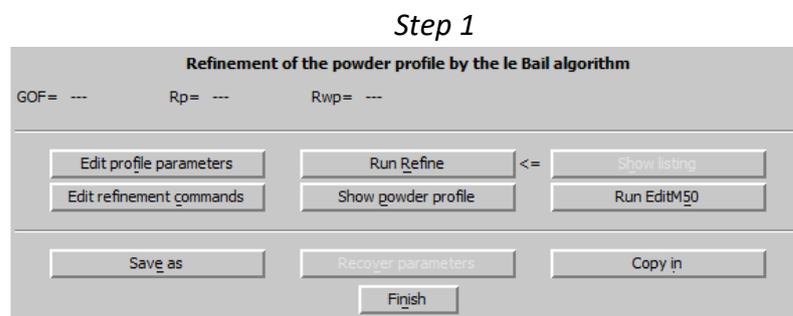
Select "Yes, I would like to continue with the wizard"; OK (Step 5)



## II. Le Bail refinement

### 1. Profil matching (extraction of intensities)

[On the screen: Refinement of the powder profile by the le Bail algorithm] (Step 1)

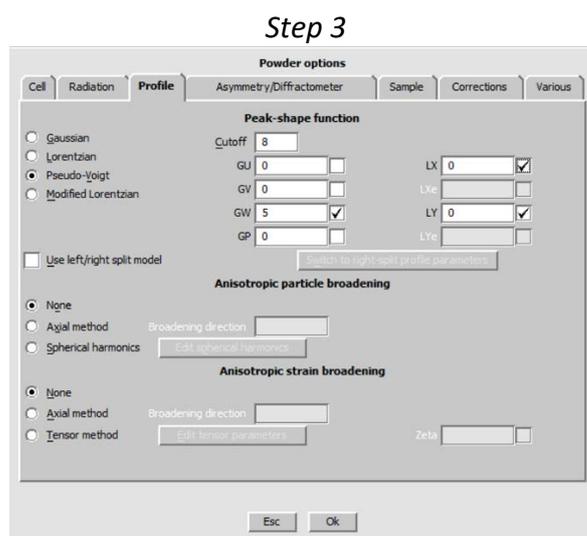
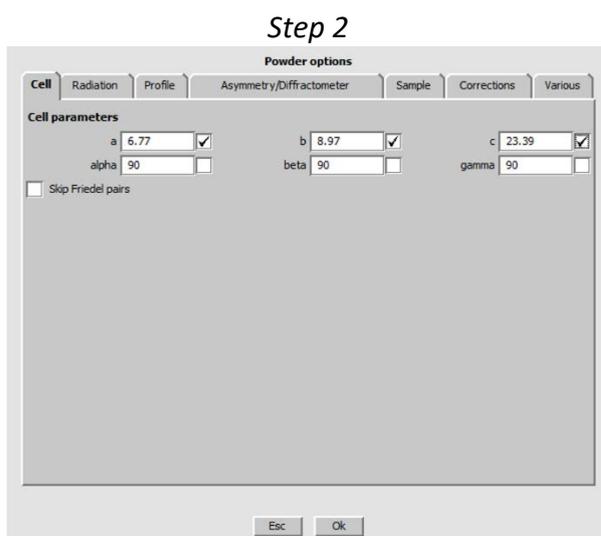


Press "Show powder profile" – just to see how it looks like

Press "Edit profile parameters"

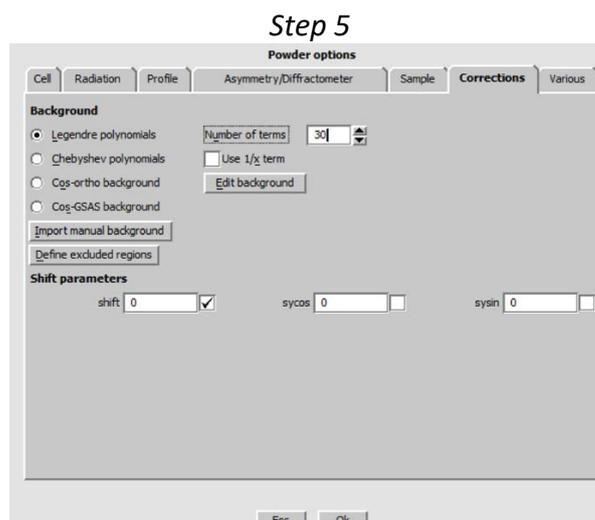
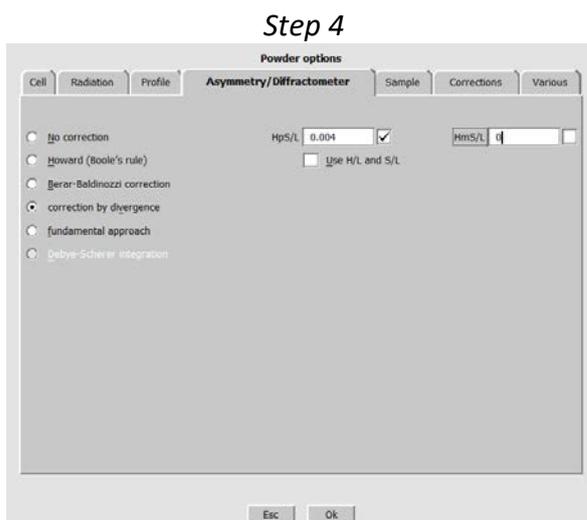
In page "Cell" activate refinement of **a, b, c** (Step 2)

In page "Profile" select Pseudo-Voigt function and activate refinement of **GW, LX and LY** (Step 3)



In page "Asymmetry/Diffractometer" select "correction by divergence", set **HpS/L to 0.004** and **HmS/L to 0**; enable refinement of **Hps/L** (Step 4)

In page Corrections: Activate refinement of "shift"; Change number of Legendre terms for **background to 30**; (Step 5)

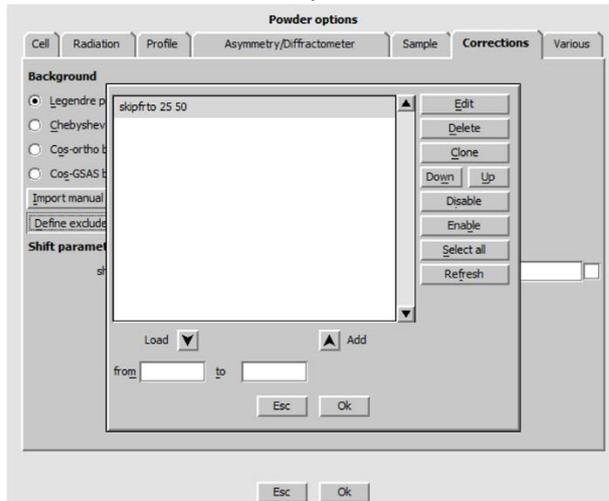


In page Corrections: click on "Define excluded regions" and set from 25 to 50 (Step 6) OK; Yes to rewrite

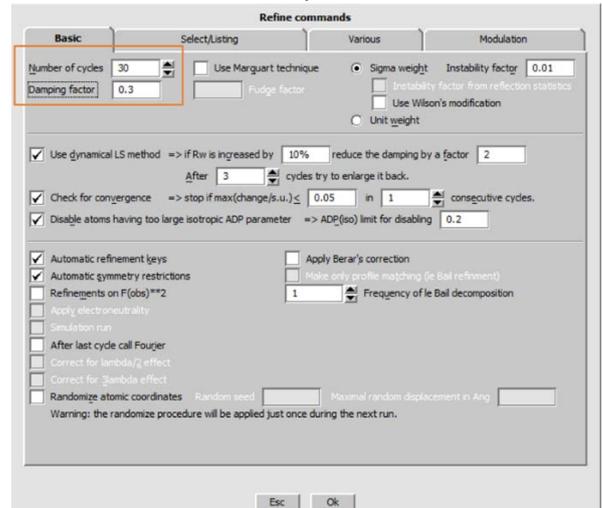
Press "Edit refinement commands"

Set **30 refinement cycles** and set **Damping factor to 0.3**; OK; (Step 7)

## Step 6



## Step 7



Press "Run Refine"

### Notes

*In many cases, refinement of all profile parameters from the scratch could not be done simultaneously. In such cases, we start refinement with a few most important profile parameters and allow the other parameters in next refinement runs. In this example, we can refine immediately all profile parameters but with damping factor of 0.3.*

*Refinement of 38 profile parameters slowly converges to the profile R value  $R_p \sim 5.5\%$  and  $GOF \sim 1.1$ . Waiting for the full convergence is not necessary. Refinement can be interrupted by End. Do not use Cancel – in such case the profile viewer would not display the latest difference curve..*

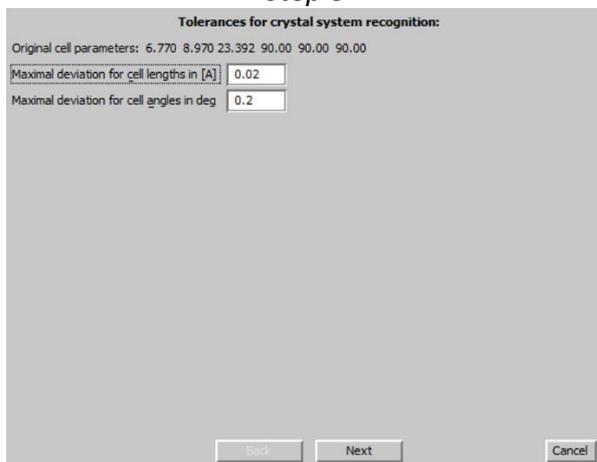
## 2. Space group determination

FINISH;YES;NEXT; NEXT (Step 8); NEXT (Step 9)

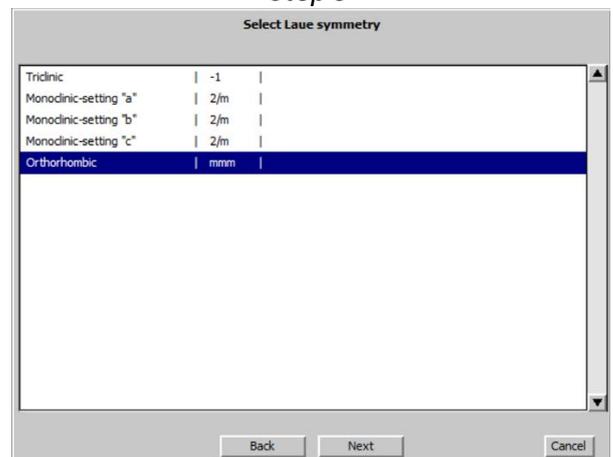
[On the screen: Select Laue symmetry]

Select **Orthorhombic mmm** Laue symmetry; NEXT

### Step 8



### Step 9



Select **P centering**; NEXT (Step 10)

### Notes

For testing of A centring (and similarly for other cases) the program removes Bragg positions absent due to A centering and calculates  $R_p$ . In case  $R_p$  is similar to that of the primitive unit cell, the removed reflections did not contribute to the measured profile – this means A centering is correct. On the other hands, increased  $R_p$  means the reflection absent for A centering were needed for the profile description – this means A centering does not occur.

Select **P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>** ; ( Step 11)

### Notes

Space group determination is based on the same logic like determination of centering, using systematically absent reflection due to space group.

### Step 10

**Select cell centering**

Centering	Rp(obs)/Rp(all)	N(Extinct)/N(Gener)
<input checked="" type="radio"/> P	5.259/6.148	0.0000
<input type="radio"/> A	26.922/20.171	0.5015
<input type="radio"/> B	30.668/22.422	0.4964
<input type="radio"/> C	31.317/22.822	0.5021
<input type="radio"/> I	42.053/29.461	0.5003
n.a. R-obverse	20.073/15.577	0.6674
n.a. R-reverse	20.073/15.577	0.6674
<input type="radio"/> F	43.623/30.926	0.7500

Warning: The cell centering need not be one you expect from collection as the program first transform the cell to the reduced form.  
Moreover after your selection the program makes another transformation whenever the centring is not the standard one.

Back Next Cancel

### Step 11

**Select space group**

Space group	Rp(obs)/Rp(all)	N(Extinct)/N(Gener)	FOM
P212121	5.264/6.163	0.0203	6.1003
P22121	5.264/6.162	0.0164	6.1109
P21221	5.264/6.161	0.0155	6.1130
P2221	5.264/6.159	0.0116	6.1236
P21212	5.260/6.152	0.0087	6.1251
P2212	5.260/6.151	0.0048	6.1357
P2122	5.259/6.150	0.0039	6.1378
Pmmm	5.259/6.148	0.0000	6.1483
Pm2m	5.259/6.148	0.0000	6.1483
P2mm	5.259/6.148	0.0000	6.1483
Pmm2	5.259/6.148	0.0000	6.1483
P222	5.259/6.148	0.0000	6.1483
Pmcm	7.130/7.429	0.0715	7.1630
P2cm	7.130/7.429	0.0715	7.1630
Pmc21	7.130/7.429	0.0715	7.1630
Pmmb	7.046/7.285	0.0271	7.1862

Back Next Cancel

NEXT; FINISH (Step 12)

YES to run le Bail refinement again (Step 13)

### Notes

Le Bail refinement is now repeated without reflections absent due to the selected space group

### Step 12

**Final step of the space group test**

accept the space group in the standard setting:  
Space group: P212121  
Cell parameters: 6.7697 8.9695 23.3917 90 90 90  
Transformation matrix: a' = 1.000\*a +0.000\*b +0.000\*c  
                                  b' = 0.000\*a +1.000\*b +0.000\*c  
                                  c' = 0.000\*a +0.000\*b +1.000\*c

accept the space group transformed into the original cell:  
Space group: P212121  
Cell parameters: 6.7697 8.9695 23.3917 90 90 90

discard the changes

Back Finish Cancel

### Step 13

The last le Bail refinement has used a lower space group.

Do you want refine profile parameters once more?

### III. Rietveld refinement

#### 1. Superflip solution

[On the screen: Structure solution] (Step 1)

**Step 1**

**Structure solution**

use Expo 2009  
 **Use Superflip**  
 use Shebt  
 use in le Bail decomposition structure information for already identified phases

Formula: C18 H22 O2  
Formula units: 4  
Actual space group: P212121

allow manual editing of the command file before start  
 use previously prepared input file for Superflip  
 use old solution and reinterpret it  
 Repeat Superflip: Until the convergence detected  
 Repeat Superflip: Number of runs => 20  
 Use local normalization  
 Use a specific random seed  
 Define explicitly delta value

Iteration scheme:  CF  
 LDE  
 AAR

Starting model:  Random phases  
 Patterson superposition map

For peak search use:  EDMA - fixed composition  
 EDMA - fixed number of atoms  
 EDMA - peak interpretation by Jana2006  
 Peaks from Jana2006  
 Peaks from Jana2006 but first run Fourier

Biso: 0  
Maxcycles: 2000

Buttons: Run solution, Open the listing, Draw structure, Draw 3d map, Accept last solution, Quit

Set formula to " **C18 H22 O2**"

(just to see the input file for this moment)

Check "**Repeat Superflip: Number of runs**" and set **20** (it will change max cycles to 2000)

Select Iteration scheme "**CF**"

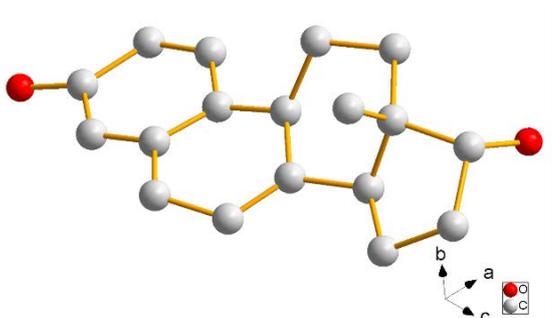
Start by "**Run solution**"

#### Notes

By default, Superflip recognizes the best solution like the electron density conforming with the user-defined symmetry. It might happen that no such good fit is found within the twenty trials – this can be seen either from the poor fit of symmetry elements in the Superflip output, or by plotting the resulting structure model. In case the solution is not found, repeat the 20 runs again with "**Use local normalization**" option. If troubles continue, try also AAR and LDE iteration schemes.

"**Draw Structure**" using diamond

"**Accept last solution**"



## 2. Refinement

If needed, **correct chemical types** in Edit Atoms.

“File → Structure → Save As” to make a **backup copy**

Start “Edit profile” and **fix all profile parameters except shift and background**

Right click; “Refine”

Uncheck **Make only profile matching (ie Bail refinement)**; Number of cycles **30**; Damping factor **0.3**

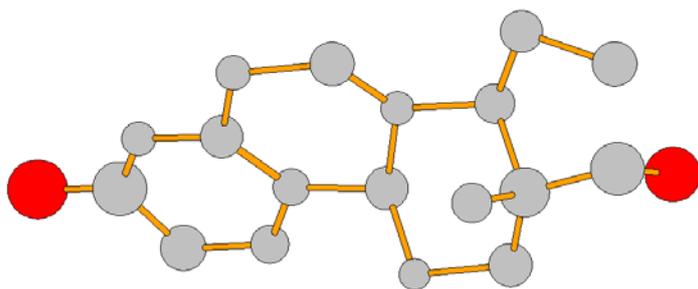
OK; **Yes+start**

$R_{obs} \approx 9.6$ ,  $wR_{(obs)} \approx 10.2$ ,  $GoF \approx 1.5$ ,  $R_p \approx 7.4$

Start **Profile viewer** and check the profile

“Plot structure” to see the structure model and size of isotropic ADP(Step 2)

Step 2



## 3. Add hydrogen atoms

Edit atoms -> **Select all carbon atoms**

Action -> **adding of hydrogen atoms**; OK (Step 4)

Apply-> Go to next (Step 5)

OK

*Hydrogen atoms of OH will remain undetermined. The structure refinement did not use any geometry restraints. With powder data, this means that even geometry of carbon atoms is inexact. The procedure for adding hydrogen atoms relies on proper geometry, therefore some hydrogen atoms will be added improperly.*

“Plot Structure” and **identify improperly added hydrogen atoms**

Start “Edit atoms”; delete improper hydrogen atoms; select their carbon atoms

Action -> **adding of hydrogen atoms**; **clear “try automatic run”**; OK

“Refine”

$R_{obs} \approx 7.4$ ,  $wR_{(obs)} \approx 8.0$ ,  $GoF \approx 1.4$ ,  $R_p \approx 6.5$

*Adding of hydrogen atoms improved the refinement factors as well as the geometry of carbon atoms*

Start “Edit profile” and **enable refinement of the previously fixed profile parameters**

“Refine”

$R_{obs} \approx 7.4$ ,  $wR_{(obs)} \approx 8.0$ ,  $GoF \approx 1.4$ ,  $R_p \approx 6.5$

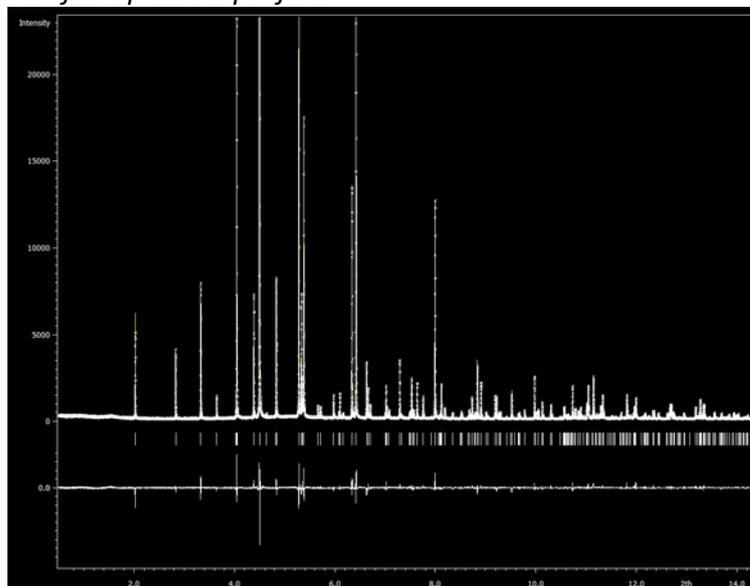
Edit atoms -> **Select all oxygen atoms**

Action -> **adding of hydrogen atoms**; OK  
Add hydrogen atoms of OH to apical positions  
“Refine”

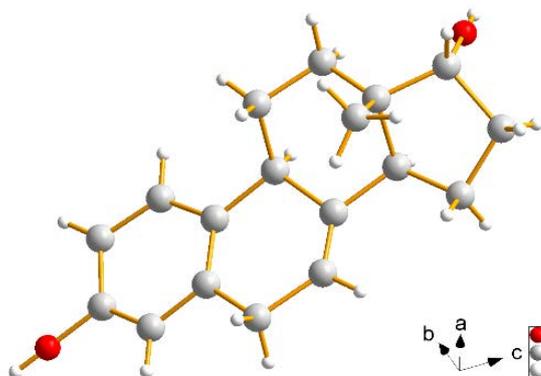
$R_{obs} \approx 6.8$ ,  $wR_{(obs)} \approx 7.1$ ,  $GoF \approx 1.3$ ,  $R_p \approx 6.4$

Although this is not correct OH geometry, adding of hydrogen atoms nevertheless improved considerably the fit.

The final powder profile:



The resulting structure model:



## References

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Kaduk et al. (*Crystals* **2017**, 7, 218; doi:10.3390/cryst7070218)

# Example 2.1.3: Ochlor

Revised: 16 October 2018

Data	Topic	Level
X-ray Powder data	Simple organic structure	Basic

## Tasks

Solving a simple organic structure from home-lab X-ray powder data using Jana2006 software and Superflip

1. Import data to JANA2006
2. Perform Le Bail refinement (extraction of intensities)
3. Run Superflip to solve the crystal structure
4. Use MCE to add atoms

Example 2.7, which shows the process of structure solution and refinement for high quality synchrotron data. This example focuses to troubles cause by lower data quality.

## Initial data

### Data

Laboratory diffractometer Epyrean of PANalytical, wavelength  $\text{CuK}\alpha_{1,2}$

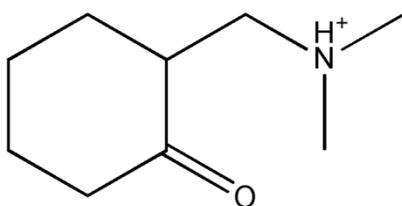
### Input files:

ochlor.xy

### Additional information:

Chemical formula:  $\text{C}_9\text{ONH}_{18}\text{Cl}$  (N,N-dimethyl(2-oxocyclohexyl)methanamine chloride)

Unit cell found: 8.26 18.85 6.71 90 92.58 90



Cl-

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# Instructions

---

## I. Data import

### 1. Creating new jobname

Start Jana2006  
"File → StructureNew" opens the file manager  
Left pane: locate directory with input files  
Right pane: double-click **ochlor.xy**

### 2. Import Wizard

Select "Powder data – various CW formats"; NEXT  
[On the screen: Powder data from]  
Select "Free format of 2th, I, [sig(I)]"  
For method select "Debye-Scherrer"; NEXT

[On the screen: Complete/correct experimental parameters]

Enter unit cell parameters: **8.26 18.85 6.71 90 92.58 90**  
Radiation: "X-rays"; "X-ray tube"; select **Cu**; check **Kalpha1/Kalpha2 doublet** (Step 1)  
NEXT; FINISH; OK to close data repository;

*Step 1*

Complete/correct experimental parameters

Cell parameters: 8.26 18.85 6.71 90 92.58 90

Target dimension: 3 Info about metrics parameters

1st modulation vector:

2nd modulation vector:

3rd modulation vector:

X-rays X-ray tube

Neutrons

Electrons

Kalpha1/Kalpha2 doublet

Wave length #1: 1.540593

Wave length #2: 1.544427

I(#2)/I(#1): 0.497

Temperature: 293

Polarization correction:

Circular polarization

Perpendicular setting Info

Parallel setting Info

Guinier camera

Linearly polarized beam

Monochromator parameters:

Perfectness: 0.5

Glancing angle: 13.28877 Set glancing angle

Back Next Cancel

YES to accept the data set  
[On the screen: question how to continue]  
Select "Yes, I would like to continue with the wizard"; OK

## II. Le Bail refinement

### 1. Profile matching (extraction of intensities)

[On the screen: Refinement of the powder profile by the le Bail algorithm]

Press "Show powder profile" – just to see how it looks like  
Press "Edit profile parameters"

In page "Cell" activate refinement of **a, b, c and beta**

In page "Profile" select Pseudo-Voigt function and activate refinement of **GW, LX and LY**

In page "Asymmetry/Diffractometer" select "correction by divergence", set **HpS/L to 0.01** and **HmS/L to 0**; **enable** only refinement of **HpS/L**

In page Corrections: Activate refinement of "**shift**"; Change number of **Legendre terms for background to 30**

OK; Yes to rewrite

Press "Edit refinement commands"

Set **30 refinement cycles** and set **Damping factor to 0.3**; OK

Press "Run Refine"

#### Notes

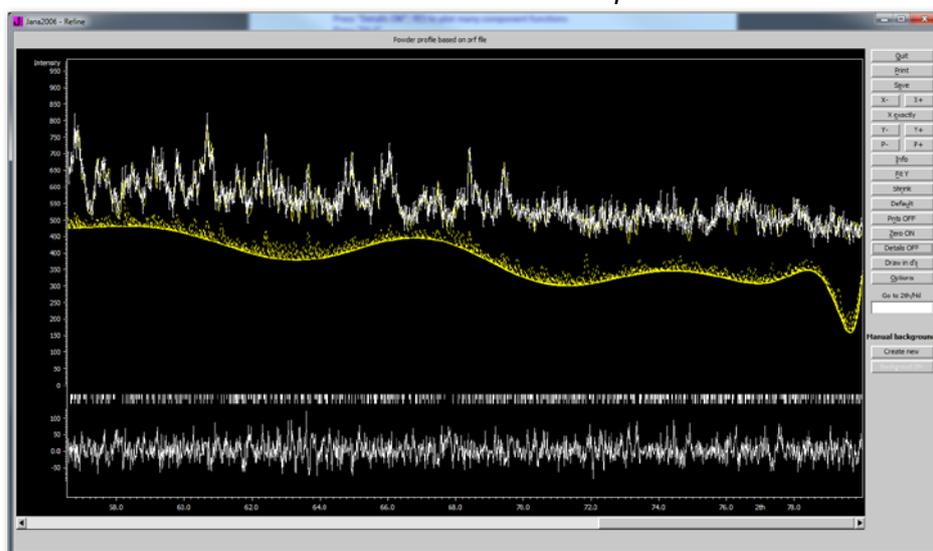
*In many cases, refinement of all profile parameters from the scratch could not be done simultaneously. In such cases, we start refinement with a few most important profile parameters and allow other parameters in next refinement runs. In this example, we can refine immediately all profile parameters but with damping factor of 0.3.*

*Refinement slowly converges to the profile R value  $R_p \sim 2.9\%$  and  $GOF \sim 1.2$ . Waiting for the full convergence is not necessary. Refinement can be interrupted by End. Do not use Cancel – in such case the profile viewer would not display the latest difference curve.*

"Show Powder profile"

Zoom at high angles; Press "Details ON"; YES to plot many component functions." (Step 1)

#### Step 1



#### Notes

*The calculated profile reveals problem with background. The too low background is compensated by too high calculated Bragg peaks, resulting in good fit achieved with incorrect parameters. We shall therefore use the manual background.*

Press "Details OFF"

Press "**Create new**" (lower right corner of the Powder profile viewer)

[On the screen: Options for generating background profile]

Use **60 background points** and significance intensity level 1; OK (Step 2)

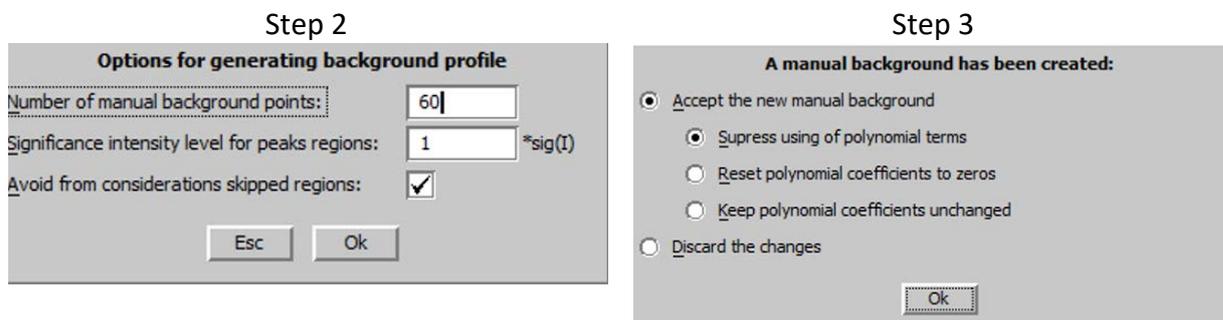
Check the manual background. It can be edited by **dragging the points by mouse**.

Press "Quit"

[On the screen: A manual background has been created]

Select "Accept the new manual background" and "Suppress using of polynomial terms"

OK (Step 3)



Now we are back in the le Bail wizard

Press "Run Refine"

The refinement swiftly converges with  $R_p \sim 2.9\%$ ,  $GOF \sim 1.2$ .

## 2. Space group determination

FINISH; YES; NEXT;

[On the screen: Refinement of the powder profile by the le Bail algorithm]

NEXT

Select **Monoclinic 2/m** Laue symmetry; NEXT

Select **P centering**; NEXT (Step 12)

Notes
For A centering (and similarly for other cases) the program removes Bragg positions absent due to A centering and calculates $R_p$ . In case $R_p$ is similar to that of the primitive unit cell, the removed reflections were not needed for profile description – this means A centering is correct. On the other hands, increased $R_p$ means the reflection absent for A centering were needed for the profile description – this means A centering does not occur.

Select  **$P2_1/n$**  space group (because it has low  $R_p$  factors and high extinction); (Step 13)

Notes
Space group determination uses the same logic like determination of centering, using systematically absent reflection due to space group.

NEXT; FINISH

YES to run le Bail refinement for the new symmetry

Profile is now refined without reflections absent due to symmetry OK;

### III. Rietveld refinement

#### 1. Superflip solution

[On the screen: Structure solution] (Step 1)

Step 1

The screenshot shows the 'Structure solution' dialog box. Key settings include: 'Use Expo' set to 2009, 'Formula' as C9 O N H18 Cl, 'Formula units' as 4, 'Actual space group' as P21/n, and 'Iteration scheme' set to CF. The 'Repeat Superflip: Number of runs' is set to 10. The 'Starting model' is 'Random phases'. Buttons at the bottom include 'Run solution', 'Open the listing', 'Draw structure', 'Draw 3d map', 'Accept last solution', and 'Quit'.

Set formula to "C9 O N H18 Cl"

Check "Repeat Superflip: Number of runs" and set 10 (it will change max cycles to 2000)

Select Iteration scheme "CF"

Press "Run solution"

#### Notes

We are looking for solution which confirms the space group P21/n. The screw axis has worse agreement factor and Superflip sometimes suggests (for the best selected run) the space group Pn. In such case, run solution again, possibly with increased number of cycles (3000) and/or with "Use local normalization". Sometimes using LDE or AAR iteration scheme instead of CF makes the job.

"Draw Structure" to see the resulting "best" structure model

"Draw 3D map" to see the resulting "best" density

Accept last solution

#### 2. Improve your model using MCE

The result of the automatic peak search will most probably be just a fragment of the molecule. Some missing atoms must be added manually.

Double-click "Contour" icon; "New plot"

Select Fourier map check 'Calculate new ones' and 'Draw maps as calculated' ; OK

In page Basic select the map type F(obs)-Fourier;

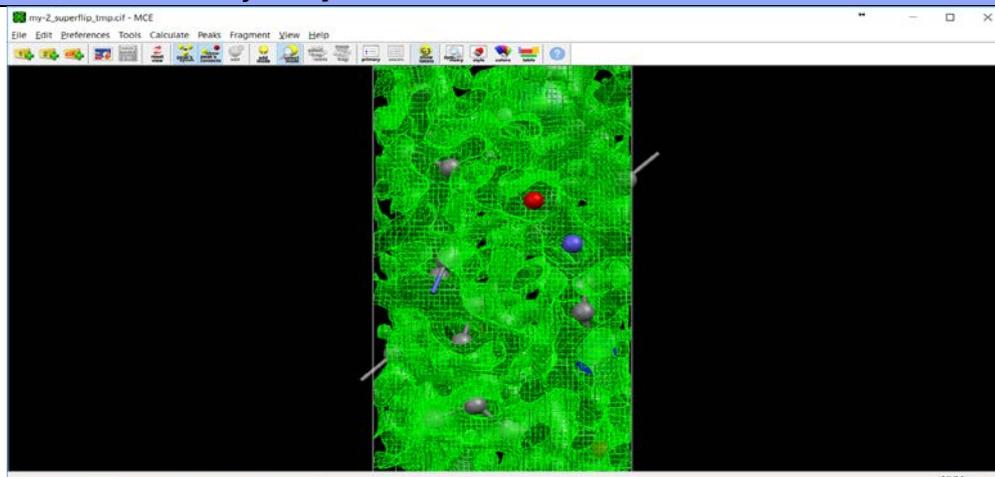
In page Scope Select the whole cell;

OK to calculate Fourier map

Usually, Fourier calculation uses structure factors (file M80) prepared by Refine. In this case, M80 has been prepared by Superflip.

Press **“Run MCE”**;

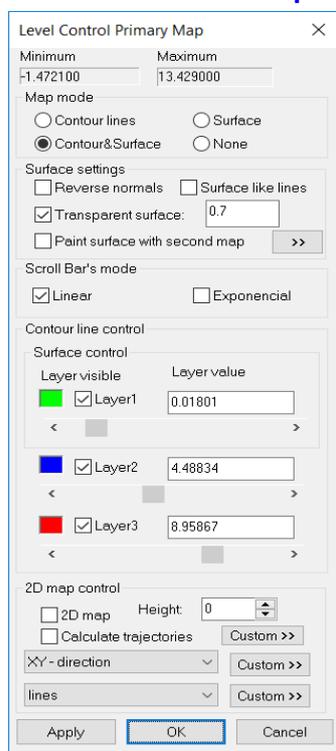
[On the screen: window of MCE]



Program MCE allows to interpret the ELD map manually. The procedure is as follow: (i) set the proper map iso levels, (ii) switch to the “adding mode”, (iii) place atoms, (iv) save atomic positions.

Rotate the model by dragging the left mouse button, zoom by the mouse-wheel (or by zooming on your touch-pad, if supported). Use keyboard arrows to move the scene.

View → **Level control primary map**



In the Map mode section, Select **“Contour lines”**.

**Change the layer value of the green layer to an appropriate level (e.g. 0.35)**

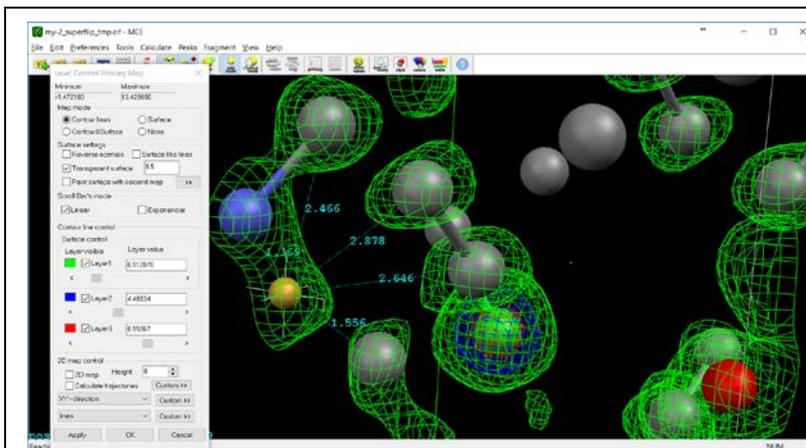
**Apply**

**OK to close the dialogue**

Preferences → **Add-atom mode**

**Right-click** at the place you want to add an atom.

Another **right-click** will **redefine the position**.



Peaks → **Add new peak**

Repeat the procedure for other missing atoms

Notes

peaks → *Clear peak list deletes all added peaks*

Preferences → *Selection mode enables deleting a selected atom by pressing “d” on the keyboard*

File → **Save peaks list**

for format select “General XYZ format”

**Exit MCE**

*[On the screen: Do you want to start the procedure for including of new atoms?]*

**YES**

*[On the screen: Inserting/Replacing of atoms]*

Select “From the list of peaks localized in MCE” (Step 2)

**OK**

Include peaks having reasonable distances to existing atoms (Step 3)

**Step 2**

**Inserting/replacing of atoms**

Peaks from the last Fourier calculation  
 From the list of peaks localized in **MCE**  
 Coordinates from keyboard

Skip peaks being too close to existing atoms

Minimal distance  Angs.

Show distances up to  Angs.

**Step 3**

List of peaks	Equivalent coordinates	Distance	Atom
Max1	0.799922 0.628699 0.280872 - as typed in		
Max2	0.700078 0.128699 0.219128	1.55	C6
	0.799922 0.628699 0.280872	1.55	C7
	0.299922 0.871301 -0.219128	2.22	N1
		2.37	C5
		2.41	C4
		2.69	N2
		2.76	C3

**Complete information for the new atom**

Name of the atom:

Uiso:

Site symmetry order: 1

Occupancy reduction:

Atomic type:

Peak: Max1 Charge: 2.000

No peaks included  
No atom modified

Finish; YES; QUIT (to leave Contour)

**“Plot structure”** to see the structure in Diamond

The structure model is very inaccurate at this moment and C-C distances may be too long. To see the molecule, adjust limit for C-C distances in Build - Connectivity

**Compare the displayed molecule with the chemical scheme**

In case of missing atoms return to Contour and MCE and try to complete the structure model

Start "Edit atoms"  
**correct chemical types**  
OK; YES;  
"Plot structure" to see the molecule in Diamond, compare again with the chemical scheme  
File → Structure → Save as → name "Backup"

### 3. Refinement

#### Notes

*For this structure, we can refine all parameters simultaneously with damping factor of 0.3.*

Right click on "Refine"

**Uncheck Make only profile matching (le Bail refinement); Number of cycles 30; Damping factor 0.3**

OK, Yes+start

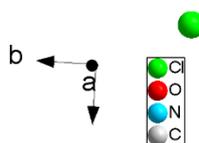
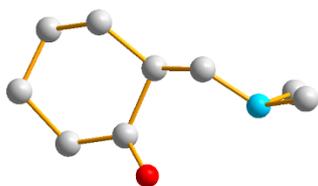
*Refinement converges with Robs ≈ 10, Rp ≈ 4, GoF ≈ 1.7*

"Profile viewer"

"Edit atoms"; Select all; Action; **Make symmetrically contiguous motifs;**

"Plot structure" (Step 1)

Step 1



### 4. Add hydrogen atoms

Edit atoms -> **Select all carbon atoms and N**

Action -> **adding of hydrogen atom;** OK

Apply-> Go to next

OK; YES to rewrite the files

"Plot Structure" to verify positions of hydrogen atoms

#### Notes

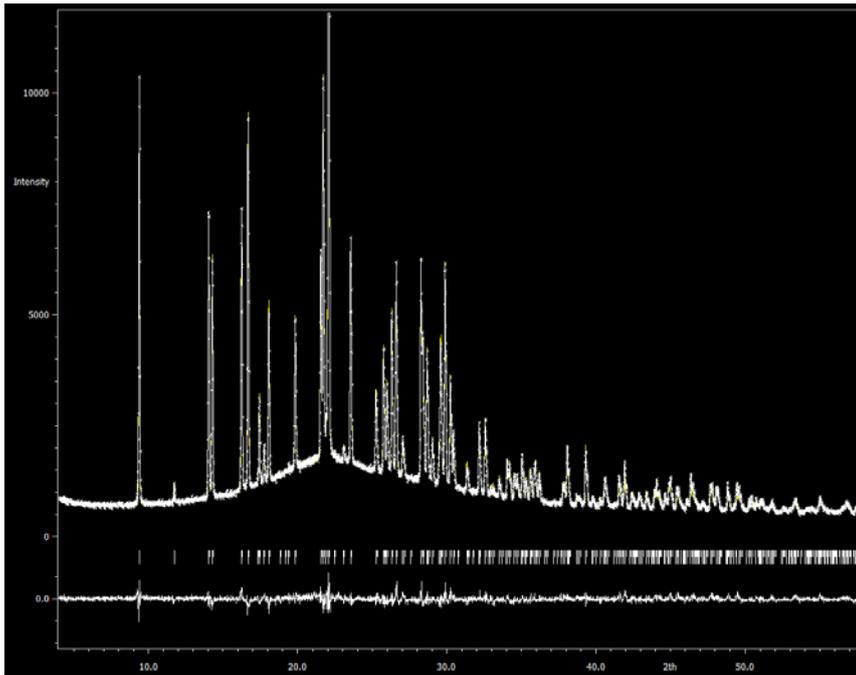
*The structure refinement did not use any geometry restraints. With powder data, this means that even geometry of carbon atoms is inexact. The procedure for adding hydrogen atoms relies on proper geometry, therefore some hydrogen atoms might be added improperly.*

"Refine"

*The final refinement converges with Robs ≈ 8, Rp ≈ 3.5, GoF ≈ 1.5, 9 profile parameters, 49 structure parameters*

"Profile viewer"

*The final profile:*



## References

---

# Example 2.2: Y<sub>2</sub>O<sub>3</sub>

Revised: 03 October 2018

Data	Topic	Level
X-ray powder crystal data	Powder data with strong asymmetry of peaks	Basic

## Tasks

---

Profile functions for an X-ray powder structure with strong asymmetry of peaks

## Initial data

---

### Data

Powder data measured with laboratory diffractometer experimental setup with Johansson-type monochromator and transmission mode in asymmetric Guinier type arrangement.

### Input files:

Y2O3-icsd.cif (crystal structure from data base)

Y2O3.dat (powder diffraction data)

### Additional information:

Chemical formula: Y<sub>2</sub>O<sub>3</sub>

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# Instructions

## I. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens the file manager

Left pane: locate directory with input files;

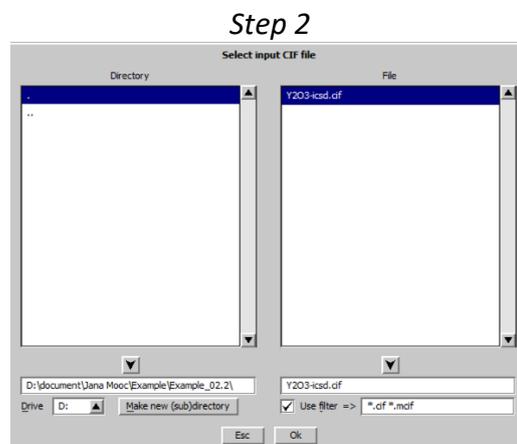
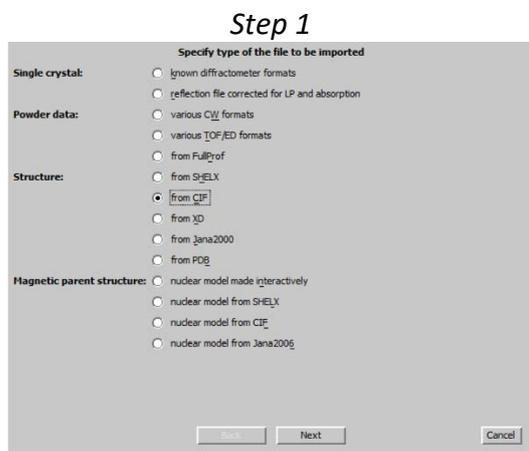
Right pane: double-click **Y2O3**

### 2. Import procedure

Select “Structure: **from CIF**”; NEXT (Step1)

[On the screen: Select input CIF file]

Select “**Y2O3-icsd.cif**”; OK (Step2)

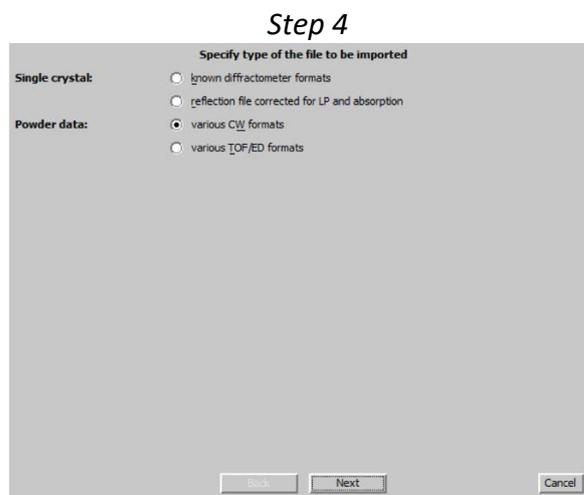
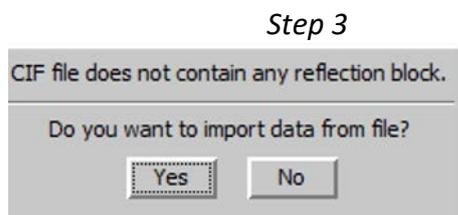


[On the screen: “CIF file does not contain any reflection block”]

Answer “**Yes**” (you want to import data from file) (Step 3)

[On the screen: Specify type of the file to be imported]

Select “Powder data: **various CW formats**” (CW = constant wavelength); NEXT (Step 4)



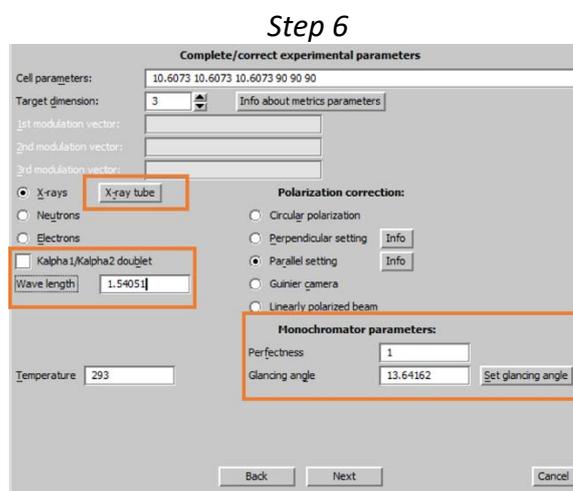
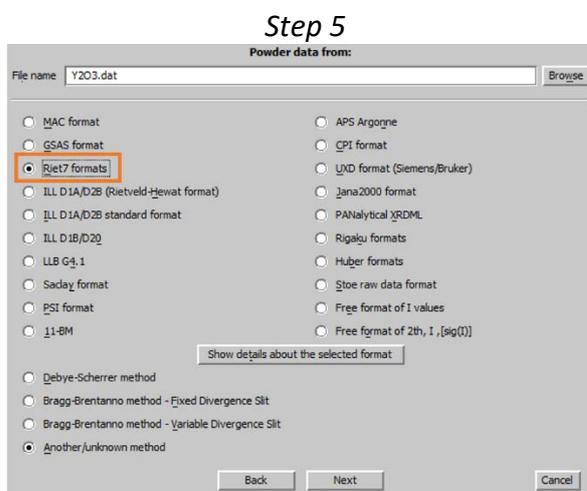
[On the screen: Powder data from:]

Select “**Riet7 formats**”; NEXT (Step 5)

[On the screen: Complete/correct experimental parameters]

For wavelength type use "X-ray tube" **Cu**, without Kalpha1/Kalpha2 doublet (wavelength **1.54051**)

Select "Parallel setting", "Glancing angle" **13.65232** (CuK $\alpha$ , Ge[111]) "Perfectness **1**"; NEXT; (Step 6)



FINISH

Accept the data in Data repository

## II. Le Bail refinement

### 1. Refinement of the powder profile

[On the screen: Basic Jana window]

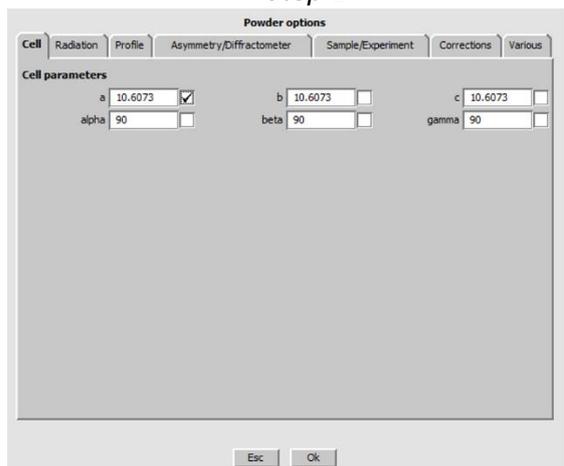
Start "Edit profile"

[On the screen: Powder options]

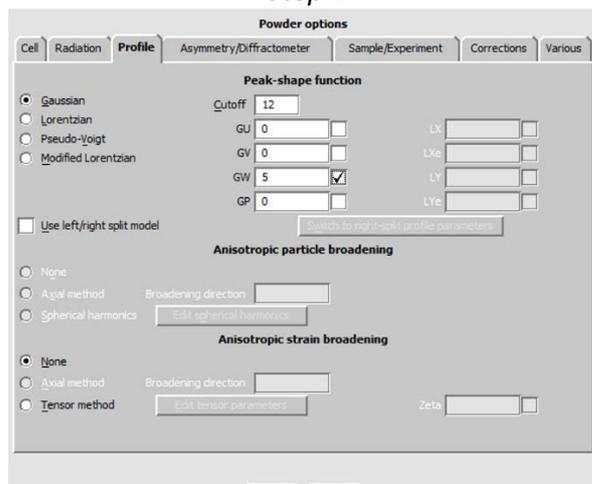
In "Cell" page select refinement of the parameter **a** (Step 1)

In "Profile" page select Cutoff to **12\*FWHM**; activate refinement of "**GW**" (Step 2)

### Step 1



### Step 2

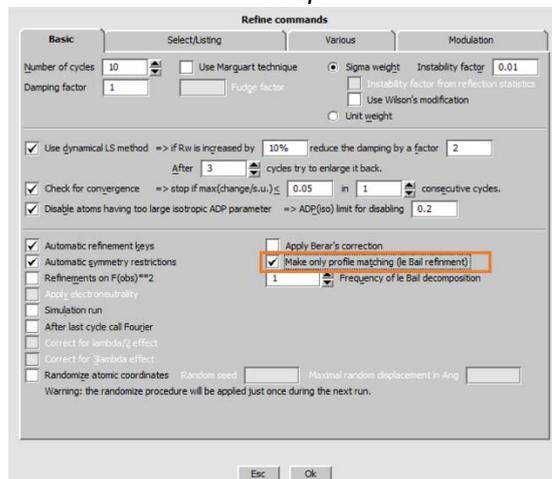


In "Corrections" page activate refinement of "shift"  
In "Corrections" page select "Legendre polynomials" with 5 terms for background calculation (Step 3)  
Refinement of background terms is enabled by default  
OK to leave Powder options, YES to save changes;  
[On the screen: Basic Jana window]  
Right click "Refine"  
Check "Make only profile matching"; (Step 4)  
Keep default values for other parameters; OK;  
[On the screen: Do you want to save new command?]  
Select "Yes+start"

### Step 3



### Step 4



### Notes

Refinement after 10 cycles finishes with  
GOF  $\approx 16.5$ ,  $R_p \approx 7.7$ ,  $wRP \approx 12.9$

Start "Profile viewer"  
[On the screen: Jana 2006 profile viewer]  
Press "X exactly" and select the  $2\theta$  interval from 19 to 35.(Step 5)

## Notes

The observed peaks are systematically broader which can indicate that Lorentzian broadening should be combined with the Gaussian profiles.

QUIT

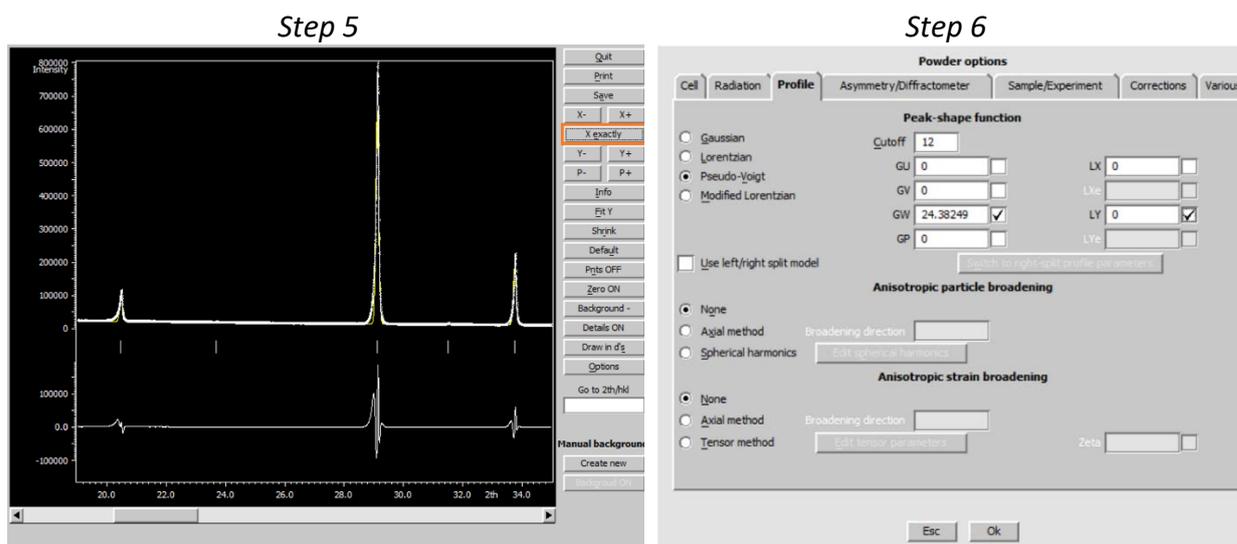
Start "Edit profile"

[On the screen: Powder options]

In page "Profile" select Pseudo-Voigt and activate refinement of **LY**; OK (Step 6)

Yes to rewrite changes

Run "Refine"



## Notes

Refinement after 10 cycles finishes with  
GOF  $\approx 15.6$ ,  $R_p \approx 7.1$ ,  $wRp \approx 12.2$

Start "Edit profile"

[On the screen: Powder options]

In page "Profile" activate refinement of **"GU"**; OK

Yes to rewrite changes

Run "Refine"

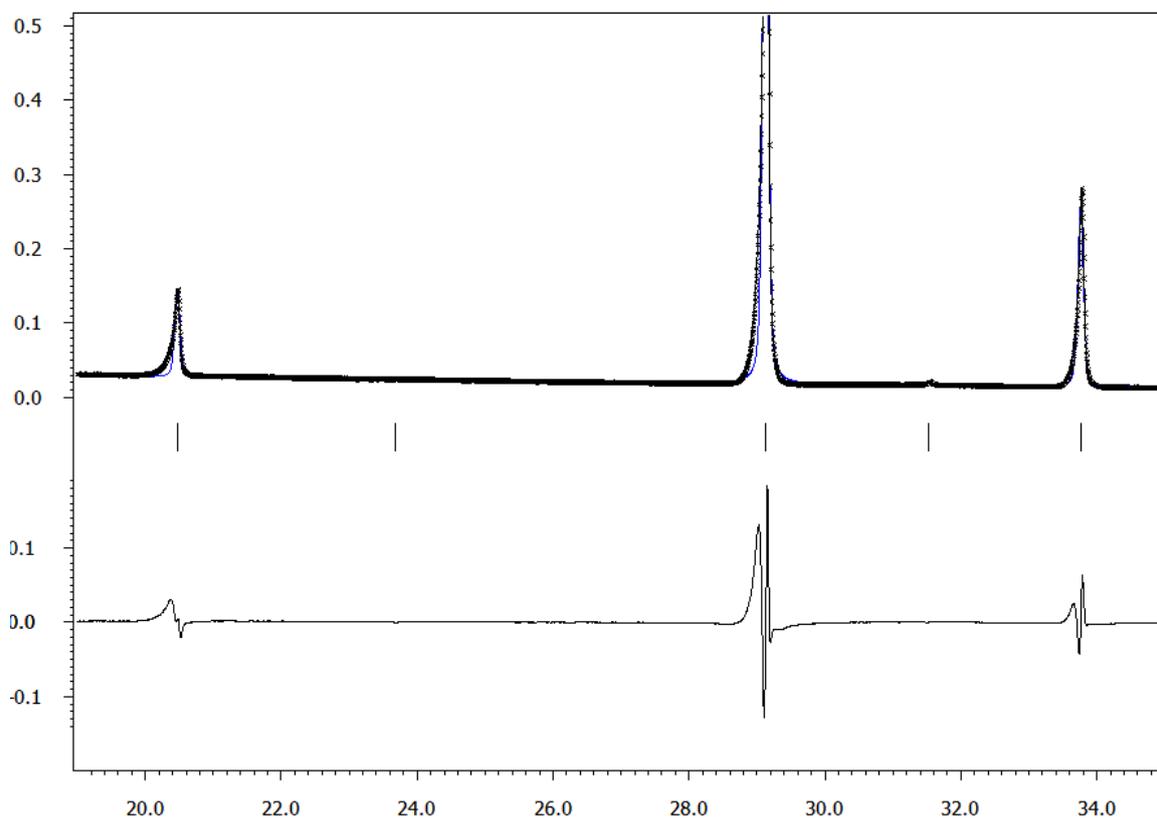
## Notes

Refinement after 10 cycles finishes with  
GOF  $\approx 14.6$ ,  $R_p \approx 7.0$ ,  $wRp \approx 1.5$

Start "Profile viewer"

[On the screen: Jana 2006 profile viewer]

Press "X exactly" and select the  $2\theta$  interval from **19 to 35**.



#### Notes

*The experimental peaks have still strong asymmetry, which is not explained by the current profile model.*

## 2. Asymmetry correction by the Howard's model

*[On the screen: Basic Jana window]*

#### Notes

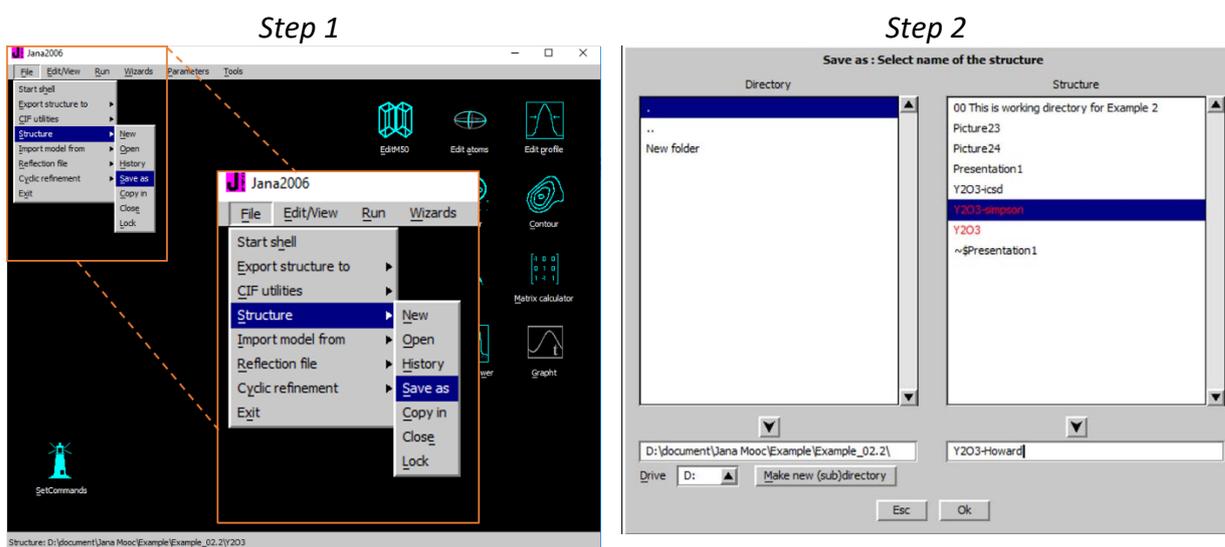
*In the following, we will test various asymmetry models, each of them with a different job name.*

Start "File → Structure → Save As" (Step 1)

*[On the screen: File manager for saving structure]*

In File manager focus the right-bottom textbox and define a name for testing the Howard's model, for instance "Y203-Howard"; OK (Step 2)

"Yes" (to continue with the new structure)



[On the screen: Basic Jana window]

Start “Edit profile”

[On the screen: Powder options]

In page “Asymmetry” select “Howard (Boole’s rule)”, use the default value and activate refinement of the “**asym1**” parameter; OK;  
Yes to rewrite changed files

[On the screen: Basic Jana window]

Run “Refine”.

#### Notes

Refinement after 10 cycles finishes with  
 $GOF \approx 11.8$ ,  $R_p \approx 6.1$ ,  $wRp \approx 9.2$

Start “Profile viewer”

[On the screen: Jana 2006 profile viewer]

Press “X exactly” and select the  $2\theta$  interval from **19 to 35**.

**QUIT**

#### Notes

The Howard's model improves considerably the profile fit. However, some discrepancies due to asymmetry are still visible.

### 3. Asymmetry by Berar-Baldinozzi<sup>1</sup>

[On the screen: Basic Jana window]

Start “File → Structure → History”

[On the screen: History]

Select the original structure **Y203**; OK

[On the screen: Basic Jana window]

Start “File → Structure → Save As

[On the screen: File manager for saving structure]

In File manager focus the right-bottom textbox and define a name for testing of the Berar-Baldinozzi model, e.g. “**Y203-BB**”; OK

“Yes” to continue with the new structure

[On the screen: Basic Jana window]

Start “**Edit profile**”

[On the screen: Powder options]

In page “Asymmetry” select “**Berar-Baldinozzi**”, use the default value and activate refinement of the “**asym1, asym2, asym3 and asym4**” parameters; OK  
“**Yes**” to rewrite changed files

[On the screen: Basic Jana window]

Start "Refine commands" (right-click on the icon "Refine")

In page "Basic" set **100** refinement cycles and Damping factor **0.3**

OK; YES+START to save commands and start refinement.

#### Notes

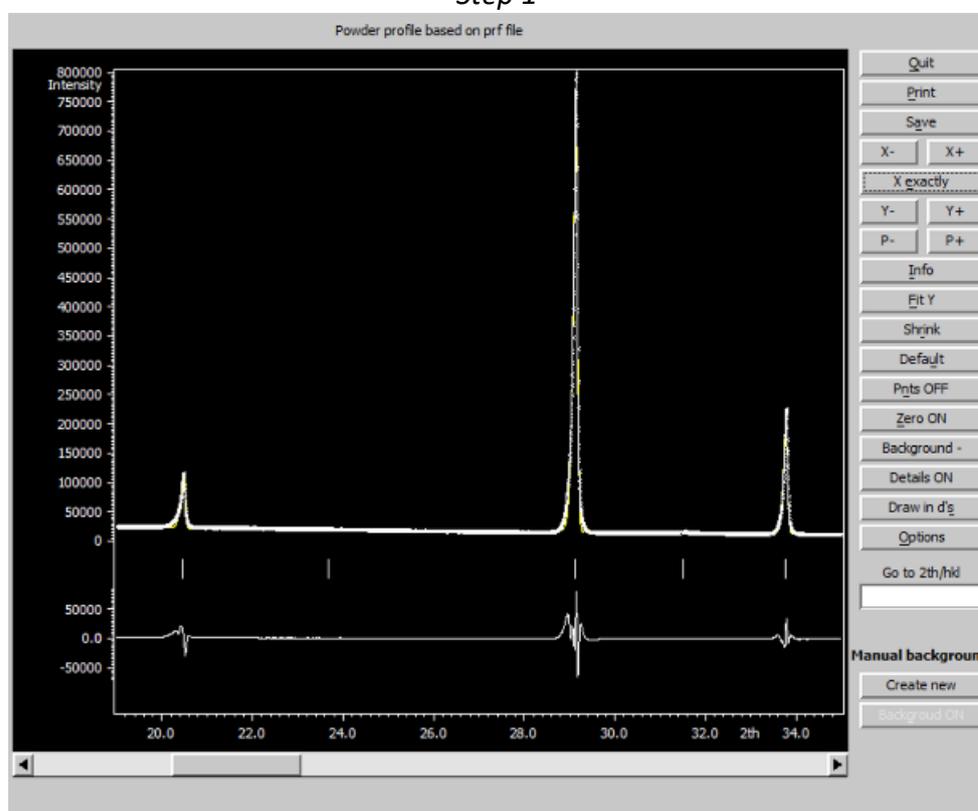
*Refinement after 100 cycles finishes with  
GOF  $\approx$  11.0, Rp  $\approx$  5.7, wRp  $\approx$  8.6*

Start “**Profile viewer**”

[On the screen: Jana 2006 profile viewer]

Press “X exactly” and select the 2 $\theta$  interval from **19 to 35**. (Step 1)

#### Step 1



#### Notes

*The fit is better than for the previous method but the number of asymmetry parameters is now four.*

#### 4. Asymmetry by axial divergence<sup>2</sup>

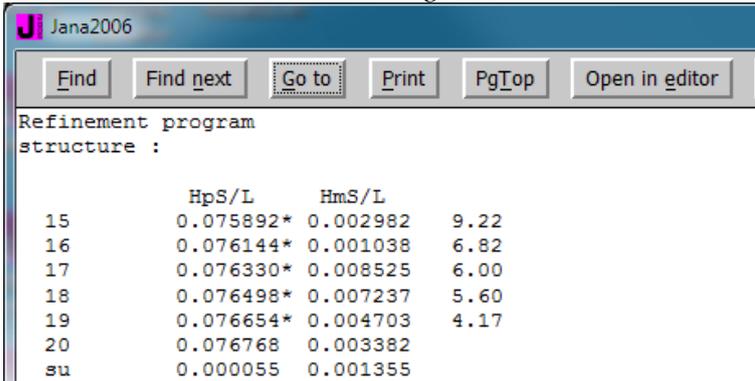
[On the screen: Basic Jana window]

Start “File → Structure → **History**”

Select the original structure **Y2O3**; OK  
 Start "File → Structure → Save As"  
 Save the structure like ,e.g. "**Y2O3-FCJ**"; OK  
 "Yes" to continue with the new structure  
 Start "**Edit profile**"  
 [On the screen: Powder options]  
 In page "Asymmetry" select "**correction by divergence**", use the default values and activate refinement of the "**HpS/L**" and "**HmS/L**" parameters; OK;  
**Yes** to rewrite changed files  
 [On the screen: Basic Jana window]  
 Right-click the icon Refine  
 [On the screen: Refine commands]  
 In page "Basic" set **30** refinement cycles and Damping factor **0.5**  
 OK; YES+START to save the changes and start refinement

Notes

Refinement after 30 cycles finishes with  
 $GOF \approx 8.2$ ,  $Rp \approx 4.7$ ,  $wRp \approx 6.4$   
 Open the refinement listing. (You can access the listing of Refine also by "Edit/View → View of Refine").  
 Press "Go to" and select "Changes overview":



	HpS/L	HmS/L	
15	0.075892*	0.002982	9.22
16	0.076144*	0.001038	6.82
17	0.076330*	0.008525	6.00
18	0.076498*	0.007237	5.60
19	0.076654*	0.004703	4.17
20	0.076768	0.003382	
su	0.000055	0.001355	

The parameter *HmS/L* oscillates, within three times the standard uncertainty is about zero which induces instability in the refinement. For this reason, we can change it to zero and keep it fixed.

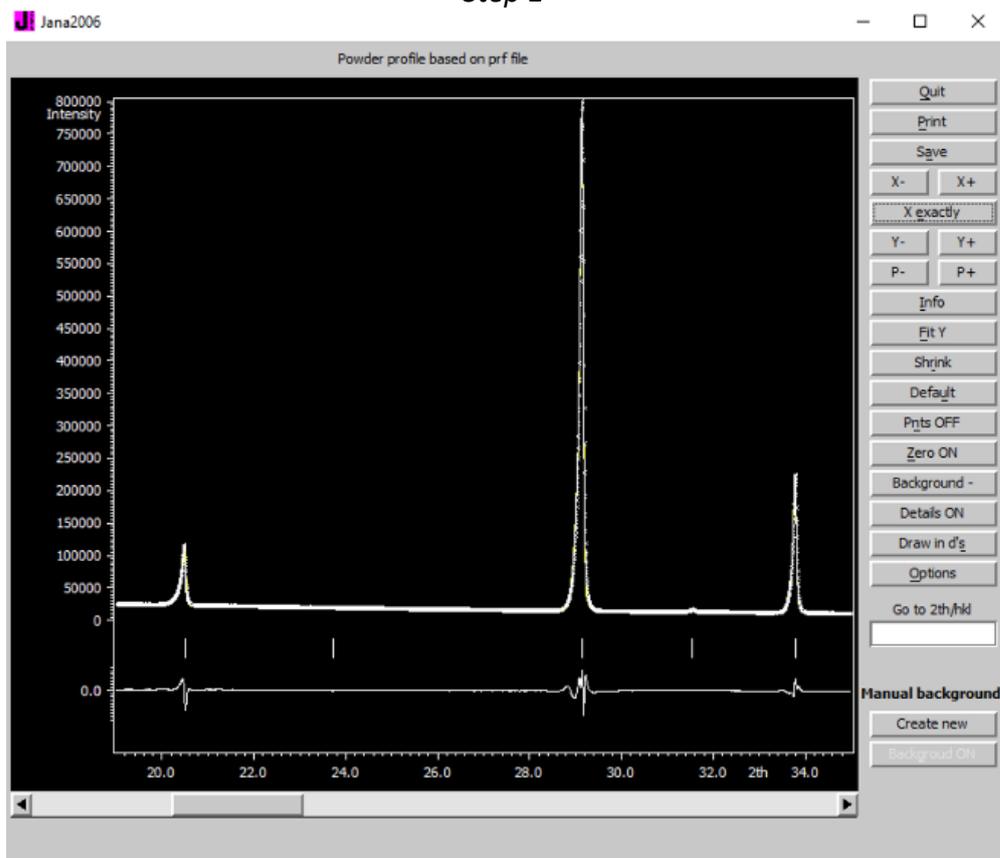
Start "Edit profile"  
 In page "Asymmetry" set **HmS/L** to **0** and **unselect** it; OK; "Refine"

Notes

Resulting factors are almost the same like before

Start "Profile viewer"  
 Press "X exactly" and select the  $2\theta$  interval from **19** to **35**.

## Step 1



### Notes

*With only one additional free parameter, the fit is significantly better than for the previous methods.*

*In Jana2006 there is also implemented the fundamental approach following closely the approach described by Cheary and Coelho (Example 2.8). This method was not applied in our example because it was developed for Bragg-Brentano geometry.*

### References

- [1] J.-F. BERAR and G. BALDINOZZI J. Appl. Cryst. (1993). 26, 128-129
- [2] Finger, Cox, Jephcoat, J.Appl.Cryst.(1994). 24, 892-900



# Example 2.3.1: MagCag

## Solution of simple organometallic structure from powder data

Revised: 4 October 2015

Powder data measured with diffractometer Empyrean (PANalytical) using CuK $\alpha$  radiation, focusing mirror and Debye-Scherrer geometry (sample in capillary), at ambient temperature.

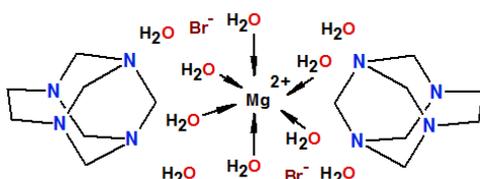
Input files: magcag.xrdml with powder profile

Additional information:

unit cell 9.19 21.38 8.12 90 113.78 90

composition Mg<sub>2</sub> O<sub>20</sub> H<sub>80</sub> Br<sub>4</sub> N<sub>16</sub> C<sub>28</sub>

Expected chemical scheme:



### 1. Creating new jobname

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click magcag

### 2. Import procedure

Select "Powder data – various CW formats"; NEXT

[On the screen: Powder data form]

Select "PANalytical XRDML"

For method select "Debye-Scherrer"

[On the screen: Complete/correct experimental parameters]

Fill cell parameters 9.19 21.38 8.12 90 113.78 90

Check the radiation (should be interpreted from the xrdml file as Copper with doublet):

<input checked="" type="radio"/> X-rays	X-ray tube	<b>Polarization correction:</b>	
<input type="radio"/> Neutrons		<input type="radio"/> Circular polarization	
<input type="radio"/> Electrons		<input type="radio"/> Perpendicular setting	Info
<input checked="" type="checkbox"/> Kalpha1/Kalpha2 doublet		<input checked="" type="radio"/> Parallel setting	Info
Wave length #1	1.540598	<input type="radio"/> Guinier camera	
Wave length #2	1.544426	<input type="radio"/> Linearly polarized beam	
I(#2)/I(#1)	0.5	<b>Monochromator parameters:</b>	
Temperature	293	Perfectness	0.5
		Glancing angle	13.2776
			Set glancing angle

NEXT; FINISH; OK to close data repository; YES to accept the data set

[On the screen: question how to continue]

Select "Yes, I would like to continue with the wizard"; OK

The typical steps for refinement of powder profile will be offered in the wizard. However, all steps can be also done separately from the basic window of Jana2006.

### 3. Refinement of the powder profile

[On the screen: refinement of the powder profile by the Le Bail algorithm]

Press "Show powder profile" – just to see how it looks like

Press "Default" to see more details

Quit powder viewer

Press "Edit profile parameters"

Unlike for structure parameters, refinement keys of profile parameters are not set automatically

In page "Cell" activate refinement of a,b,c,beta

In page "Profile" activate refinement of GW

In page "Corrections" activate refinement of "shift";

Change number of Legendre terms for background to 30;

OK; Yes to rewrite

Press "Edit refinement commands"

Set 100 refinement cycles and Damping factor

OK

Press "Run Refine"

Refinement of profile slowly converges to the profile R value  $R_p \sim 3.4\%$  and GOF  $\sim 7.5$ .

Waiting for the full convergence is not necessary. Refinement can be interrupted by End or Cancel - in this case End should be used in order to see the latest difference curve in the powder profile viewer.

In page "Profile" activate refinement of GV

OK, YES to save changes

Run several cycles of Refine

Refinement of profile slowly converges to the profile R value  $R_p \sim 3.0\%$  and GOF  $\sim 7.0$

For Gaussian parameters an important rule is that they cannot be refined all together because they are linearly dependent. Usually we refine GW, then GV and finally GU. In our case GU would not improve the fit.

"Show Powder profile"

The calculated profile fits quite well with the experimental one but some profiles are too narrow, especially for low angles

Quit profile viewer

"Edit profile parameters"

In page "Profile" change the type of the peak-shape function to "Pseudo-Voigt", activate refinement of LX and LY

OK, YES to save changes

"Run Refine"

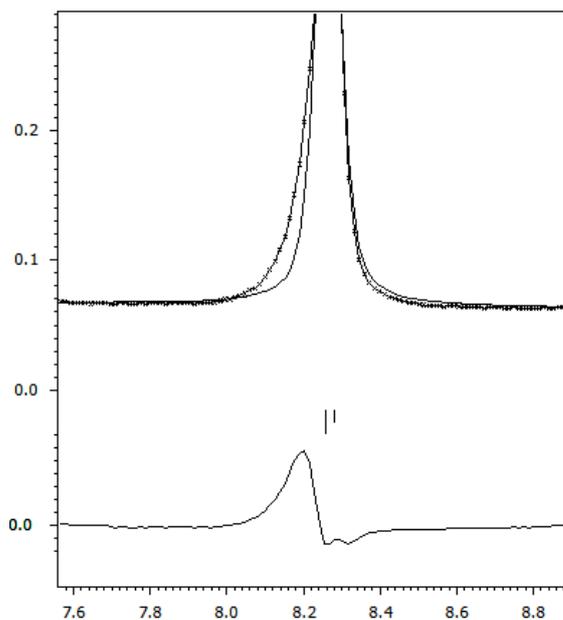
Refinement of profile slowly converges to the profile R value  $R_p \sim 1.6\%$  and GOF  $\sim 4.2$ .

"Show Powder profile"

Enlarge the profile and investigate details of the fit between the calculated and experimental profile.

We are especially interesting whether asymmetry of peaks has been correctly described. Not

correctly described asymmetry can be found for low angle reflections:



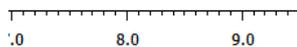
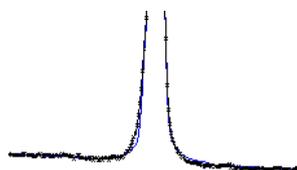
“Edit profile parameters”

In page “Asymmetry/Diffractometer” select “correction by divergence”  
Activate refinement of “HpS/L”, set HmS/L to zero and do not refine it  
OK; YES to save changes

“Run Refine”

Refinement of profile slowly converges to the profile R value  $R_p=1.4$  and  $GOF \sim 3.0$ .

“Show Powder profile”



Description of asymmetry seems to be better than before

Quit the profile viewer

Press "Save As" and **make a backup copy** of the structure

FINISH to close the Powder wizard

#### 4. Space group determination

[On the screen: Tolerances for crystal system recognition]

Use default; NEXT

[On the screen: Select Laue symmetry]

Select the highest one – monoclinic; NEXT

[On the screen: Select cell centering]

Select P centering as it gives the best profile fit; NEXT

[On the screen: Select space group]

Select space group  $P21/a$ ; NEXT

[On the screen: Final step of the space group test];

Accept the space group transformed into the original cell; FINISH

YES to refine profile parameters once more.

This new profile refinement uses only independent Bragg reflections compatible with  $P21/a$ .

The results are almost the same like for  $P-1$  but calculation taking into the account the symmetry is faster.

#### 5. Structure solution

[On the screen: information that the solution wizard will start]

OK

Type formula Mg O10 H40 Br2 N8 C14; Formula units 2

Select "Use Superflip"

Check "Repeat Superflip: Number of runs" and choose 10 runs

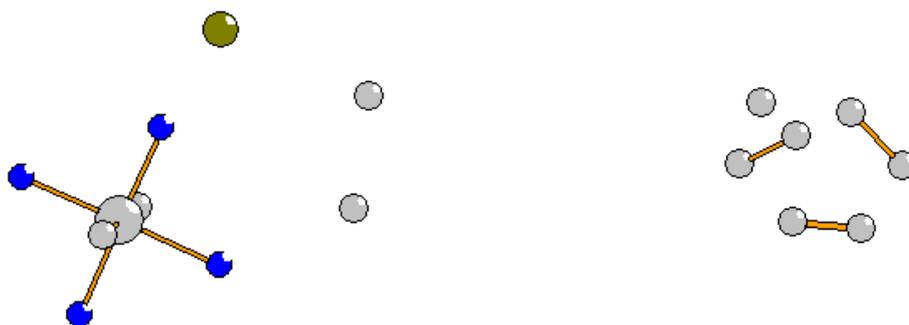
With this setting Superflip will run ten times and a solution with the best fit will be used

OK

The agreement factors of the symmetry printed at the bottom of the Superflip listing will be between 10-20, indicating rather worse fit for the screw axis.

Press the button "Draw structure"

The initial structure model should display octahedrally coordinated Mg located in one of inversion centers, isolated Br, two oxygens of the water molecules, a fragment of the  $N_4C_7$  cage and probably some false maxima. For instance:



Press button "Accept last solution"

Start File → Structure → Save as and make a backup copy

#### 6. Completing structure without hydrogen atoms

*In this part the task is to finalize the N<sub>4</sub>C<sub>7</sub> cage from the difference Fourier.*

*Rietveld refinement with initial structure model could destroy profile parameters:*

Start Parameters → Powder

Clear refinement keys for all refined powder parameters in page "Cell", "Profile", "Asymmetry/Diffractometer" and "Corrections"

*The stability of the structure model refined with powder data requires binding together ADP parameters of some atoms and keeping them isotropic. For instance, carbon and nitrogen atoms will all have the same isotropic ADP.*

Plot the structure and note atoms around Mg

Start "Edit atoms";

change the atoms around Mg to oxygen O1, O2, O3;

change all other atoms except Br and Mg to carbon.

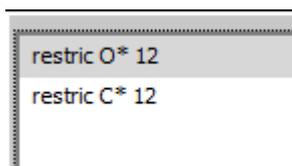
Start Refinement options, page "Various"

Start "Restrictions" and define:

The same ADP for O\*

The same ADP for C\*

*Be careful not to make by mistake identical their coordinates*



OK;

In page Basic change number of refinement cycles to 100 and damping factor to 0.5

Clear "Disable atoms having too large isotropic ADP parameter"

Clear "Make only profile matching"

OK; Yes+Start

*Rietveld refinement slowly converges with R<sub>obs</sub>=9%, R<sub>p</sub>=6%, and GOF=13.*

***The numbers are only indicative!***

*In case of oscillations, note the label of the oscillating atom. Plot the structure and try to identify and delete false maxima. In case of troubles, repeat charge flipping.*

Change ADP of Br to anisotropic and repeat refinement

*Br is slightly disordered and it can be described with an ellipsoid even from powder data*

For isolated carbon atoms out of the fragment of the cage change their chemical type to oxygen

Repeat refinement

*Two of the isolated positions will be oxygens of water. The others will probably move to the cage during the refinement.*

Start Fourier option

In the page "Basic" define "F(obs)-F(calc) – difference Fourier)

OK; YES+START

OK to start procedure for including new atoms

*The charge of difference maxima will be extremely low comparing with single crystal*

diffraction, however some of them will be carbon or nitrogen atoms. It is advisable to plot the maxima before refinement and to delete any strange position as false maxima.

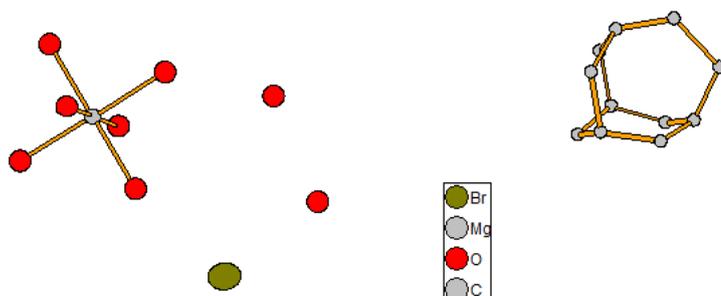
Repeat refinement

Repeat plotting and deleting false maxima

Repeat difference Fourier

Repeat adding of atoms

Finally, the structure will be completed like this:



Rietveld refinement converges with  $R_{obs} \sim 3.6\%$ ,  $R_p \sim 2.8\%$ , and  $GOF \sim 6.3$ .

ADP of carbon atoms of the cage may be negative at this stage

In the cage the atoms with three bonds are nitrogens.

Start "Edit atoms" and correct chemical types of the cage

Start Refinement options and add a restriction nitrogen atoms to have the same ADP:

```
restric O* 12
restric C* 12
restric N* 12
```

Run refinement

Rietveld refinement converges with  $R_{obs} \sim 3.2\%$ ,  $R_p \sim 2.4\%$ , and  $GOF \sim 5.2$ .

At this point ADP of nitrogens should be positive while ADP of carbons may still be close to zero

Start "Edit atoms"

Add hydrogen atoms to carbons of the cage (automatic mode)

Run refinement

Rietveld refinement converges with  $R_{obs} \sim 3.2\%$ ,  $R_p \sim 2.5\%$ , and  $GOF \sim 5.4$ . These values are slightly worse than in the previous step but ADP of carbon atoms become positive

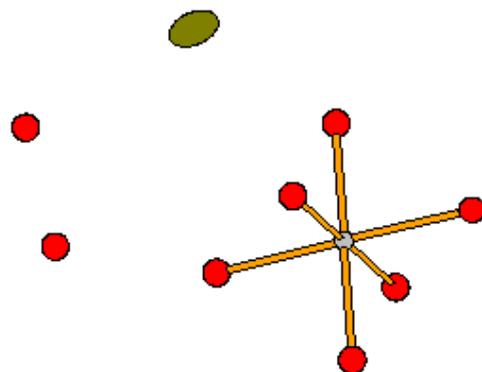
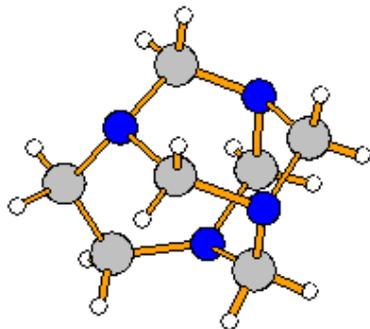
Start File → Structure → Save As and make a **backup copy**

Start Parameters → Powder

Activate refinement of all powder parameters which were fixed before starting with the Rietveld refinement

Run refinement

Rietveld refinement converges with almost the same  $R_{obs}$ ,  $R_p$  and  $GOF$ .



All oxygen atoms belong to water. In order to include scattering power of hydrogen atoms without adding them explicitly, their occupancy must be refined.

Activate refinement of occupancy of O1

Start refinement options, page "Various"

Start "Equations" and define the following equations:

equation : ai[o2]=ai[o1]

equation : ai[o3]=ai[o1]

equation : ai[o4]=ai[o1]

equation : ai[o5]=ai[o1]

Run refinement

Rietveld refinement converges with  $R_{obs} \sim 2.5\%$ ,  $R_p \sim 2.0\%$ , and  $GOF \sim 4.0$ . These values are significantly better.

Oxygen atoms of water, which is not coordinated to Mg, may have different ADP

Start refinement options, page Various

Start "Restrictions"

Delete the restriction for O\*

Define separately the same ADP for O1, O2, O3 and for O4, O5:

restric O1 12 O2 O3

restric O4 12 O5

Run refinement

The results are almost the same. Visual inspection of the powder profile shows good fit between the calculated and observed lines.



# Example 2.3.2: MagCag

## Preparation of the rigid body template in M45

Revised: 4 March 2015

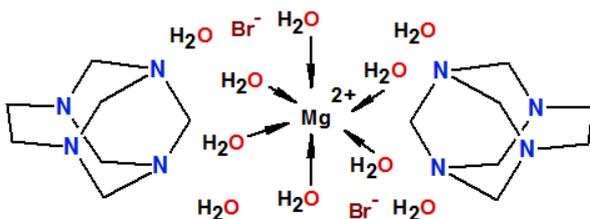
The purpose of this example is to prepare a template of the cage  $C_7N_4H_{14}$ , which will be used for the solution of the example 2.3.3 as a rigid body. The template will be defined in the file M45 and used in solution of the example 2.3.3.

The preparation of M45 has no special support in the current version of Jana2006. Part of the job must be done with a text editor.

In the following steps we shall use the CSD structure HICTOD and we shall prepare two versions of the cage: with C1 symmetry and Cs symmetry.

Input files: HICTOD.cif from the CSD database

Expected chemical scheme:



### 1. Reading structure from CIF

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory the input file

Right pane: double-click HICTOD

[On the screen: Specify type of the file to be imported]

Select : Structure → From CIF; NEXT

Select: HICTOD.CIF

NO to import data

### 2. Deleting symmetry equivalent atoms

It happens with some CSD CIF files that symmetry equivalent atoms are also present, which leads to their multiple occurrences when symmetry is applied. In the next step, we shall delete these atoms

Start "Edit Atoms"

Select atoms ending with "g" and "d"

Start "Action → Delete selected atoms"

OK; YES to save changes

### 3. Getting the cage from HICTOD

Start "Plot structure"; "Draw + continue"

Use ,  and  to plot atoms from M40

Use Picture → Viewing direction → c

Use  to display the unit cell

Use  to complete the fragments

Now the cage is clearly visible

The atoms of the cage are symmetry related by a mirror plane at  $y=0.25$

Press Undo, to see again only the symmetry independent atoms

Select atoms (symmetry independent) not belonging the cage

Using the right mouse button activate plotting of their labels; note the labels

Quit Diamond and return to Jana

Start "Edit Atoms"

Delete the atoms not belonging to the cage; OK; YES to rewrite changes

Start "Plot structure" and verify that only atoms of the cage are present

Return to Jana

### 4. Transformations

*M45 templates contain information about the point group symmetry. The axis c is used as the unique axis of the point group. For this reason the unit cell taken from CSD must be transformed in order to get the mirror plane of the cage perpendicular to c and located at  $z=0$ . Moreover, all atoms of the cage (not only symmetry independent atoms) must be present in the template.*

Start "Tools → Transformations → Origin shift"

Move the origin to point 0, 0.25, 0

*Now the mirror plane of the cage is located at  $y=0$  (can be verified in M40)*

Start "Edit Atoms"

Press "Select all"

Start "Action → Expand selected atoms"

Press "Next matrix"; "Fill by a symmetry operation"

Select "x, -y, z"; OK;

OK; OK; YES to rewrite changes

Start "EditM50"

Change symmetry to P1; OK; YES to rewrite M50

Start "Edit Atoms"

Press "Select all"

Start "Action → Merge selected atoms"; use default merging distance;

*The program merges 7 atoms, resulting in 25 atoms of the cage*

Start "Tools → Transformations → Cell transformation"

Press "by a matrix"

Define transformation matrix  $-1\ 0\ 0 / 0\ 0\ 1 / 0\ 1\ 0$

OK; OK; select "rewrite the old structure"; OK

Start "Edit Atoms"

Press "Select all"

Start "Action → Transform selected atoms"

Use unit transformation matrix and translation vector 1, 0, 0

*This transforms the x coordinates back to the unit cell*

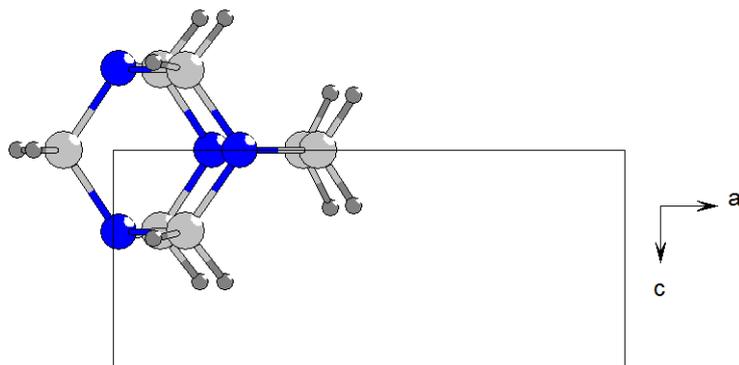
Start "Plot structure"; "Draw + continue"

Use ,  and  to plot atoms from M40

Use Picture → Viewing direction → b

Use  and  to display the unit cell

*This shows the resulting cage of 25 atoms with mirror plane located at z=0*



## 5. Labels

Quit Diamond

Start "Edit Atoms"

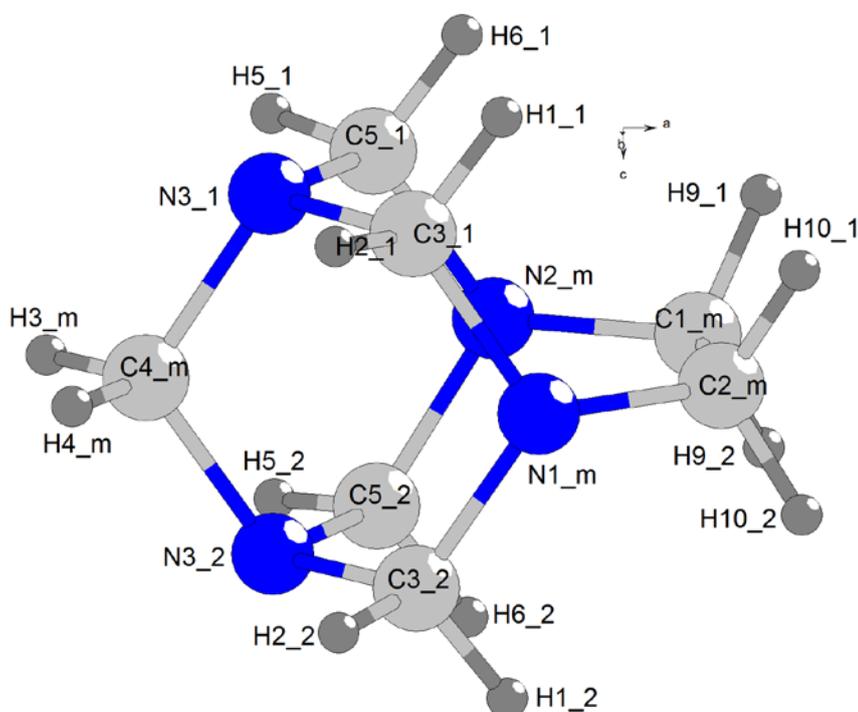
Double-click the first atom

Using "Define" and "Edit" page change the suffix to "m" if z=0, "1" if z<0 and "2" if z>0

Arrows close to the "List" button can be used to move between atoms in the editing mode

*Renaming can also be done in a text editor (Edit/View → Edit of M40 file).*

*The resulting labels will have "m" for atoms at the mirror plane, "1" for atoms below the mirror plane and "2" for atoms above the mirror plane. The suffixes "1" and "2" resulted from the previous expansion by the mirror plane.*



## 6. Text editor

Quit Diamond and Jana

Copy M40 to Magcag-symmC1.m45

Open Magcag-symmC1.m45 in a text editor

Delete five header lines

Delete the s.u. block

Delete every second line (i.e. the lines without atom label)

Add two spaces and "0" at the end of each line

Add the following header lines:

"cell 7.585 10.837 16.065 90 90 90" (this can be copied from M50)

"pgroup C1"

"scdist C-C 1.52"

Save the file and quit the editor.

*This is the resulting file Magcag-symmC1.m45:*

```
cell 7.585 10.837 16.065 90 90 90
pgroup C1
scdist C-C 1.52
N1_m      3  1      1.000000  0.250500  0.132420  0.000000  0
N2_m      3  1      1.000000  0.194100-0.129200  0.000000  0
N3_1      3  1      1.000000  0.011590  0.024260-0.075730  0
N3_2      3  1      1.000000  0.011590  0.024260  0.075730  0
C1_m      1  1      1.000000  0.373700-0.084900  0.000000  0
C2_m      1  1      1.000000  0.403100  0.054200  0.000000  0
C3_1      1  1      1.000000  0.142500  0.125210-0.074590  0
C3_2      1  1      1.000000  0.142500  0.125210  0.074590  0
H1_1      2  1      1.000000  0.219800  0.115500-0.122300  0
H1_2      2  1      1.000000  0.219800  0.115500  0.122300  0
H2_1      2  1      1.000000  0.080600  0.202900-0.081200  0
H2_2      2  1      1.000000  0.080600  0.202900  0.081200  0
C4_m      1  1      1.000000-0.095500  0.035800  0.000000  0
H3_m      2  1      1.000000-0.185600-0.027800  0.000000  0
H4_m      2  1      1.000000-0.154200  0.115300  0.000000  0
C5_1      1  1      1.000000  0.093300-0.099710-0.074750  0
C5_2      1  1      1.000000  0.093300-0.099710  0.074750  0
H5_1      2  1      1.000000  0.000900-0.160900-0.081200  0
H5_2      2  1      1.000000  0.000900-0.160900  0.081200  0
H6_1      2  1      1.000000  0.170800-0.106700-0.122500  0
H6_2      2  1      1.000000  0.170800-0.106700  0.122500  0
H9_2      2  1      1.000000  0.427000-0.121100  0.053300  0
H9_1      2  1      1.000000  0.427000-0.121100-0.053300  0
H10_2     2  1      1.000000  0.473000  0.074000  0.051500  0
H10_1     2  1      1.000000  0.473000  0.074000-0.051500  0
```

*The keyword scdist is used for scaling of the complete object using arbitrary number described with arbitrary identifier (without spaces). In our case the identifier is "C-C" and the number is a typical C-C distance in the cage. But the identifier could be also "scale" and the number could be, e.g., 100.*

*Each line except header lines contains the following items: label, number of chemical type (indicates that chemical types are different - they will be specified during application of the rigid body in Jana2006), unused, site occupancy, x, y, z, symmetry identifier (0 means symmetry independent with respect to the used point group).*

Copy Magcag-symmC1.m45 to Magcag-symmCs.m45

Open Magcag-symmCs.m45 in a text editor

Replace the point group C1 with Cs

For atoms with the suffix "1", i.e. those with z<0, replace "0" at the end of each line with "1". This indicates the atoms are symmetry dependent

For atoms with the suffix "m" change the site occupancy to 0.5, because they are located at mirror plane

*This is the resulting file Magcag-symmCs.m45:*

```
cell 7.585 10.837 16.065 90 90 90
pgroup Cs
scdist C-C 1.52
N1_m      3  1      0.500000  0.250500  0.132420  0.000000  0
N2_m      3  1      0.500000  0.194100 -0.129200  0.000000  0
N3_1      3  1      1.000000  0.011590  0.024260 -0.075730  1
N3_2      3  1      1.000000  0.011590  0.024260  0.075730  0
C1_m      1  1      0.500000  0.373700 -0.084900  0.000000  0
C2_m      1  1      0.500000  0.403100  0.054200  0.000000  0
C3_1      1  1      1.000000  0.142500  0.125210 -0.074590  1
C3_2      1  1      1.000000  0.142500  0.125210  0.074590  0
H1_1      2  1      1.000000  0.219800  0.115500 -0.122300  1
H1_2      2  1      1.000000  0.219800  0.115500  0.122300  0
H2_1      2  1      1.000000  0.080600  0.202900 -0.081200  1
H2_2      2  1      1.000000  0.080600  0.202900  0.081200  0
C4_m      1  1      0.500000 -0.095500  0.035800  0.000000  0
H3_m      2  1      0.500000 -0.185600 -0.027800  0.000000  0
H4_m      2  1      0.500000 -0.154200  0.115300  0.000000  0
C5_1      1  1      1.000000  0.093300 -0.099710 -0.074750  1
C5_2      1  1      1.000000  0.093300 -0.099710  0.074750  0
H5_1      2  1      1.000000  0.000900 -0.160900 -0.081200  1
H5_2      2  1      1.000000  0.000900 -0.160900  0.081200  0
H6_1      2  1      1.000000  0.170800 -0.106700 -0.122500  1
H6_2      2  1      1.000000  0.170800 -0.106700  0.122500  0
H9_2      2  1      1.000000  0.427000 -0.121100  0.053300  0
H9_1      2  1      1.000000  0.427000 -0.121100 -0.053300  1
H10_2     2  1      1.000000  0.473000  0.074000  0.051500  0
H10_1     2  1      1.000000  0.473000  0.074000 -0.051500  1
```

*The created templates, Magcag-symmC1.m45 and Magcag-symmCs.m45, could be accompanied with plots in jpeg format, Magcag-symmC1.jpg and Magcag-symmCs.jpg. In our example we don't need them.*



# Example 2.3.3: MagCag

Solution of simple organometallic structure from powder data, using the rigid body template from M45

Revised: 4 October 2015

Powder data measured with diffractometer Empyrean (PANalytical) using CuK $\alpha$  radiation, focusing mirror and Debye-Scherrer geometry (sample in capillary), at ambient temperature.

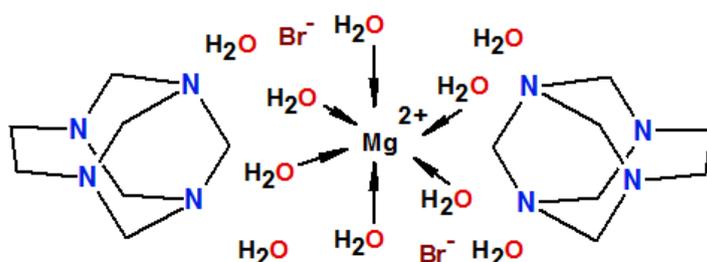
Input files: magcag.xrdml with powder profile

Magcag-symmC1.m45 and Magcag-symmCs.m45: rigid body templates prepared in Example 2.3.2

Additional information:

unit cell 9.19 21.38 8.12 90 113.78 90

Expected scheme:



## 1. Creating new jobname

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click magcag

## 2. Import procedure

Select "Powder data – various CW formats"; NEXT

[On the screen: Powder data form]

Select "PANalytical XRDML"

For method select "Debye-Scherrer"

[On the screen: Complete/correct experimental parameters]

Fill cell parameters

Check the radiation (should be interpreted from the xrdml file as Copper with doublet):

X-rays   
 Neutrons  
 Electrons  
 Kalpha1/Kalpha2 doublet  
 Wave length #1   
 Wave length #2   
 I(#2)/I(#1)   
 Temperature

**Polarization correction:**  
 Circular polarization  
 Perpendicular setting   
 Parallel setting   
 Guinier camera  
 Linearly polarized beam

**Monochromator parameters:**  
 Perfectness   
 Glancing angle

NEXT; FINISH; OK to close data repository; YES to accept the data set

[On the screen: question how to continue]

Select "Yes, I would like to continue with the wizard"; OK

The typical steps for refinement of powder profile will be offered in the wizard. However, all steps can be also done separately from the basic window of Jana2006.

### 3. Refinement of the powder profile

[On the screen: refinement of the powder profile by the Le Bail algorithm]

Press "Show powder profile"

Press "Default" to see more details

Press "Create new" to create a manual background

[On the screen: Options for generating background profile]

For "Number of manual background points" set 60

OK; Quit powder viewer

[On the screen: A manual background has been created]

Select "Accept the new background" and "Reset polynomial coefficients to zero"

The manual background was created because with this data background calculated with Legendre polynomials would not be correct for high angle reflections. (For detail see example 2.4 – PFPhenyl)

Press "Edit profile parameters"

In page "Profile" activate refinement of GW

Unlike for structure parameters, refinement keys of profile parameters are not set automatically

In page Corrections:

Set 30 for "Number of terms" of Legendre polynomials

Polynomial background will be refined in addition to the manual one

Activate refinement of "shift";

OK; Yes to rewrite

Press "Edit refinement commands"

Set 100 refinement cycles

OK

Press "Run Refine"

Refinement of profile slowly converges to the profile R value  $R_p \sim 2.9\%$  and  $GOF \sim 7.3$ .

Waiting for the full convergence is not necessary. Refinement can be interrupted by End or Cancel - in this case End should be used in order to see the latest difference curve in the powder profile viewer.

"Show Powder profile"; "Default"

Move the slider towards low angles; "Fit Y"

*The calculated profile fits quite well with the experimental one but some profiles are too narrow, especially for low angles*

Quit profile viewer

"Edit profile parameters"

In page "Cell" activate refinement of a,b,c,beta

In page "Profile" activate refinement of GV

OK, YES to save changes

Run several cycles of Refine

*Refinement of profile slowly converges to the profile R value  $R_p \sim 2.8\%$  and  $GOF \sim 7$*

*For Gaussian parameters an important rule is that they cannot be refined all together because they are linearly dependent. Usually we refine GW, then GV and finally GU. In our case GU would not improve the fit.*

In page "Profile" change the type of the peak-shape function to "Pseudo-Voigt", activate refinement of LX and LY

OK, YES to save changes

"Run Refine"

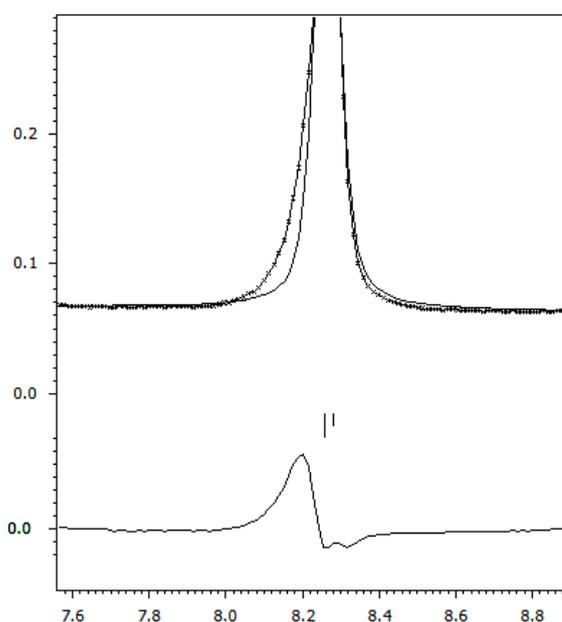
*In case of oscillations press "Parameters" (during the refinement) and change "Damping factor" to 0.5*

*Refinement of profile slowly converges to the profile R value  $R_p \sim 1.7\%$  and  $GOF \sim 4.3$ .*

"Show Powder profile"

Enlarge the profile and investigate details of the fit between the calculated and experimental profile.

*We are especially interesting whether asymmetry of peaks has been correctly described. Not correctly described asymmetry can be found for low angle reflections:*



"Edit profile parameters"

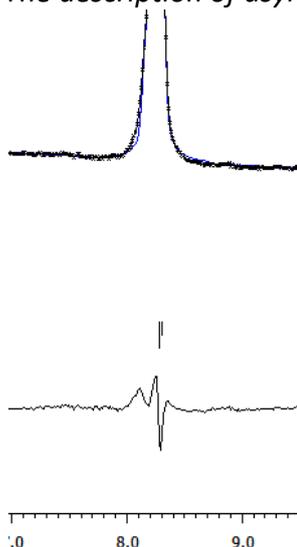
In page "Asymmetry/Diffractometer" select "correction by divergence"

Activate refinement of "HpS/L" (do not refine HmS/L)

"Run Refine"

*Refinement of profile slowly converges to the profile R value  $R_p = 1.4\%$  and  $GOF \sim 3.1$ . "Show Powder profile"*

The description of asymmetry for the low angle peak is considerably improved:



Quit the profile viewer

Press "Save As" and **make a backup copy** of the structure  
FINISH to close the Powder wizard

#### 4. Space group determination

[On the screen: Tolerances for crystal system recognition]

Use default; NEXT

[On the screen: Select Laue symmetry]

Select the highest one – monoclinic; NEXT

[On the screen: Select cell centering]

Select P centering as it gives the best profile fit; NEXT

[On the screen: Select space group]

Select space group  $P21/a$ ; NEXT

[On the screen: Final step of the space group test];

Accept the space group transformed into the original cell; FINISH

YES to refine profile parameters once more.

*This new profile refinement uses only independent Bragg reflections compatible with  $P21/a$ . The results are almost the same like for  $P-1$  but calculation taking into the account the symmetry is faster.*

#### 5. Structure solution

[On the screen: information that the solution wizard will start]

OK

Type formula Mg O10 H40 Br2 N8 C14; Formula units 2

Select "Use Superflip"

Check "Repeat Superflip: Number of runs" and choose 10 runs

*With this setting Superflip will run ten times and a solution with best R value will be used*  
"Run Solution"

*In case that Superflip does not converge interrupt the calculation, discard the results and repeat it. It will start from a new set of random phases and the result may be different. The agreement factors of the symmetry printed at the bottom of the Superflip listing will be between 10-20, indicating rather worse fit for the screw axis.*

Press the button "Draw structure"

The initial structure model contains octahedrally coordinated Mg located in one of inversion centers, isolated Br, two oxygens of the water molecules, a fragment of the  $N_4C_7$  cage and probably some false maxima. For instance:



Press button "Accept last solution"

#### 6. Preparation of the starting Rietveld refinement

Start "Edit atoms" and change chemical types of atoms coordinated to Mg to oxygen  
Change to oxygen also the two carbon atoms, which are in fact lattice water molecules  
Rename the changed atoms according to their chemical types

OK; YES to save changes

Start "Refine commads"; go to page "Basic"

Set 100 refinement cycles with Damping factor 0.1

Uncheck "Make only profile matching"

OK; YES to save changes without starting refinement

Start "Edit profile"

Fix all profile parameters: a, b, c, beta, GW, GP, LX, LY, HpS/L, shift

*This means that only Legendre background will be refined*

OK, YES to save changes

Start File → Structure → Save as and **make a backup copy** named "start"

#### 7. Completing the cage

Start "Refine commands"; go to page "Various"

Press "Fixed commands"

Fix all parameters for O\* Mg\* Br\*; OK

Press "Restrictions"

Restrict ADP of C\* to be the same; OK

*Be careful not to restrict coordinates!*

OK; YES+Start

*During refinement you may change damping from 0.1 to 0.5*

*Refinement converges with  $R \sim 11\%$ ,  $R_p \sim 10\%$ ,  $GOF \sim 23$*

Run difference Fourier, YES to start procedure for inserting atoms

Insert new maxima in reasonable distances to the atoms of the cage

Repeat refinement

Repeat difference Fourier and inserting of maxima until 11 carbon atoms is present

“Reasonable distance” should not be taken too strictly for Fourier maxima from powder data

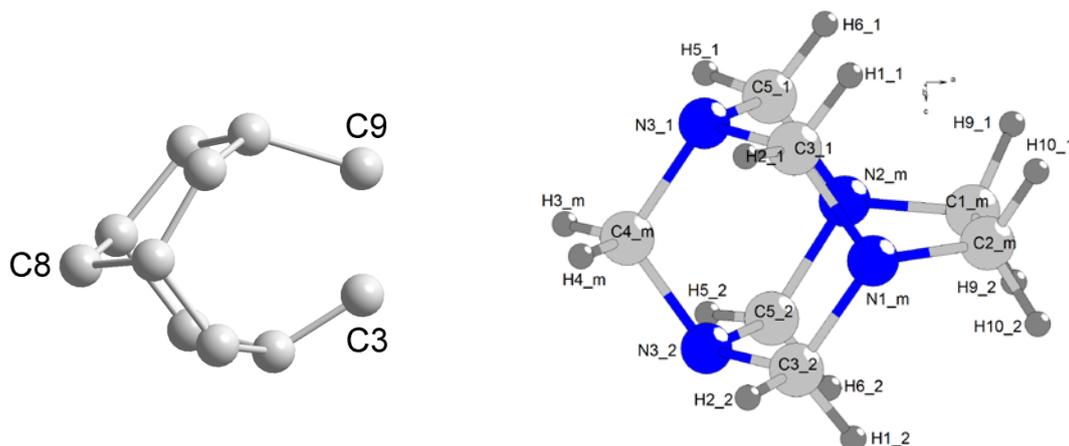
Refinement converges with  $R \sim 5\%$ ,  $R_p \sim 4\%$ ,  $GOF \sim 8$

Start File → Structure → Save as and make a backup copy named “cage\_atomic”

## 8. Placing the cage template with point group symmetry C1

Start “Plot structure”

Using the button  plot the atoms of the cage and ensure they make a symmetry contiguous motif. If not, return to Jana, start Edit atoms and put C\* to symmetry contiguous motif. Otherwise placing of the molecule will not work.



Plot the cage and compare with the template prepared in the previous example. Probably C9 corresponds to C1\_m; C3 corresponds to C2\_m; C8 corresponds to C4\_m (**your labels can be different!**)

Return to Jana2006

Start “Parameters → Molecules → New molecule”

[On the screen: Atoms of the new molecule from:]

Select “Model file”

For name of the molecule type “kage”

We need a name not starting with C, N, O, B, H and M

For “Model name” browse for “Magcag-symmC1.m45” created in the previous example

Keep the scaling distance unchanged

“Show the model molecule” is disabled because we don’t have Magcag-symmC1.jpg

NEXT

[On the screen: Specify atomic types in the model molecule]

Do not change the suggested atomic types; NEXT

[On the screen: Define the molecular reference point]

Select “Explicit”

In “Reference point” textbox type N1\_m

The reference point should be some atom from the mirror plane in order to reflect the symmetry of the molecule. Such atoms in the model molecule have suffix \_m (see Example 2.3.2)

NEXT

[On the screen: Define and complete molecular position #1]

For the pairs “model atoms” – “actual positions” choose c1\_m and C9; C2\_m and C3; C4\_m and C8 (**with actual names taken previously from Diamond**)

For "Maximal coincidence distance" type 0.5

The coincidence ration should be 11/25 but it depends on the previous refinement

Try to adjust the coincidence distance to reach 11 coinciding carbons.

If carbons of the model molecule coincide e.g. with oxygens this means that the cage has been positioned incorrectly, probably because the carbon atoms in the atomic part do not form a symmetry contiguous motif.

Press "Apply+End"

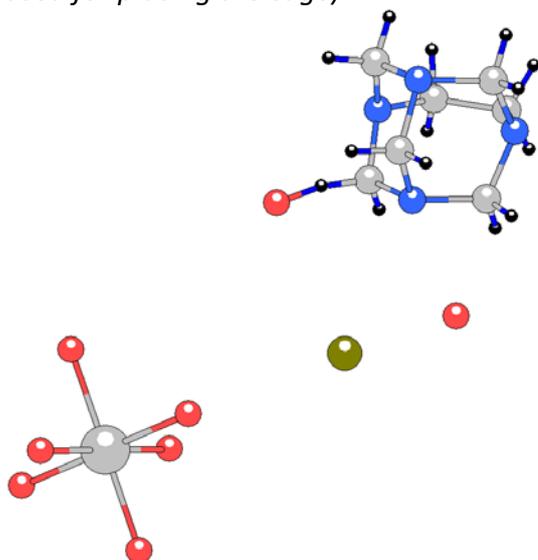
Start "Edit atoms"

Ensure that the atomic part does not contain carbon atoms.

OK, YES to save changes

Start "Plot structure"

The structure with the cage should look like this (depending which carbon positions were used for placing the cage):



In this example one water oxygen is too close to the cage but it may change during the refinement

Return to Jana2006

Start "Refine commands"; go to page "Various"

Press "Fixed commands"

Fix "all parameters" for C\*, H\*, N\* (i.e. for atoms of the cage)

Because the molecule is called "kage", the wild character C\* does not include the molecule and therefore molecular parameters (rotations and translation of the cage), will not be fixed.

OK; OK; YES+START to save changes and start refinement

During refinement you may change damping from 0.1 to 0.5

After many cycles refinement converges with R~4.5%, Rp~4%, GOF~9

Start "Plot structure"

The cage should be now in better position, i.e. without short distances to lattice water

## 9. Refinement of Mg, O and Br

Start "Refine commands"; go to page "Various"

Press "Fixed commands"

Disable or delete the "fixed all" commands for Mg\* O\* Br\*

OK

Go to page "Equations" and define the following equations:

equation : ai[o2]=ai[o1]

equation : ai[o3]=ai[o1]

equation : ai[o4]=ai[o1]

equation : ai[o5]=ai[o1]

*All oxygens belong to water; refinement of their occupancy mimics the missing hydrogens*  
OK

Go to page "Various", press "restrictions"

Define the same ADP for all oxygen atoms (O\*); OK

*Be careful not to make identical coordinates!*

OK; YES to save commands without starting Refine

Start "Edit atoms"

Set harmonic ADP for Br1

*This works because Br is slightly disordered*

Activate refinement of occupancy (ai) of O1

OK, YES to save changes

Start "Refine"

*The refinement converges with R~3%, Rp~2.3%, GOF~5*

## **10. Refinement of atoms of the cage**

Start "Edit atoms"

Select all carbon atoms of the cage (blue carbons)

Press "Action → Adding of hydrogen atoms"

*This procedure will not add hydrogens, because they are already present, but it will introduce Keep commands necessary for fixing of their geometry*

OK; YES to save changes

Start "Refine commads"; go to page "Various"

Press "Restrictions"

Define the same ADP for all nitrogen atoms (N\*)

*Be careful not to make identical coordinates!*

OK

Press "Fixed commands"

Disable or delete the "fixed all" command for C\* N\* H\*

OK; go to page Basic

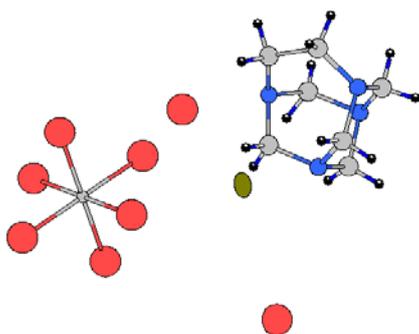
Set "Damping factor" 0.1

OK; YES+START

*The refinement converges with R~2.8%, Rp~2.1%, GOF~4.3*

Start "Plot structure" verify the structure

*Final plot:*



Make backup copy

### 11. Placing the cage template with point group symmetry $C_s$

Now we shall test how the cage with  $C_s$  point symmetry would fit

Start "Edit atoms"

Select the model molecule (blue atoms)

Start "Action → Atoms from molecule to atomic part"

OK; YES to rewrite changes

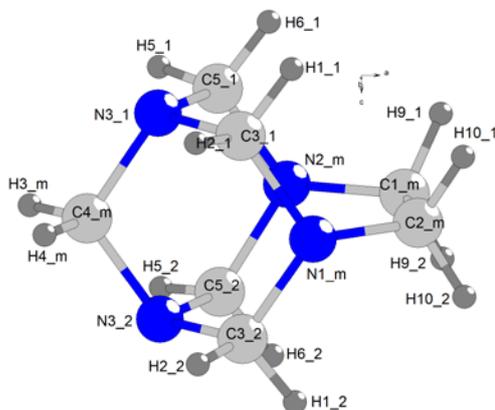
The molecule had only one actual position and therefore this atomic structure model is equivalent with the previous one

Start "Refine"

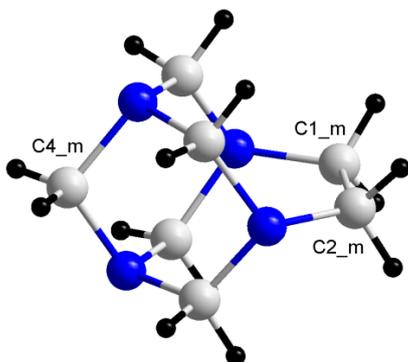
$R$  values must be the same like with the molecule

Now we shall place the template  $C_s$  in such a way that it coincides with the cage present in the atomic part

This is the template how it was created in the example 2.3.2:



Start "Plot structure" and try to orient your cage similarly. Make use of the fact that there is only one C-C bond in the cage.



From the comparison we can see which pairs of atoms should be used for placing the molecule

Return to Jana2006

Start "Parameters → Molecule → New molecule"

[On the screen: Atoms of the new molecule from:]

Select "Model file"

For name of the molecule type "kage"

For "Model name" browse for "Magcag-symmCs.m45" created in the previous example

Keep the scaling distance unchanged

"Show the model molecule" is disabled because we don't have Magcag-symmC1.jpg

NEXT

[On the screen: Specify atomic types in the model molecule]

Do not change the defaults atomic types; NEXT

[On the screen: Define the molecular reference point]

Select "Explicit"

In "Reference point" textbox type N1\_m

This should be some atom from the mirror plane

NEXT

[On the screen: Define and complete molecular position #1]

For the pairs "model atoms" – "actual positions" type the three previously noted pairs

For "Maximal coincidence distance" type 0.6

Press "Show coinciding atoms"

We should see the complete coincidence 25/25 and the coinciding atoms should have the same chemical types.

	Individual atomic positions			distance to	
N1_m	0.773704	0.617148	0.286488	0.068	N2_m
N2_m	0.915984	0.683329	0.081966	0.058	N3_2
N3_1	0.819658	0.573639	0.028719	0.000	N3_1
N3_2	1.046434	0.599749	0.305107	0.020	N1_m
C1_m	0.812606	0.717724	0.144220	0.116	C5_2
C2_m	0.737231	0.682379	0.252867	0.125	C1_m
C3_1	0.715574	0.577568	0.127447	0.047	C5_1
C3_2	0.938936	0.603285	0.399674	0.044	C2_m
H1_1	0.612403	0.593090	0.045690	0.509	H6_1
H1_2	0.978634	0.635256	0.492042	0.139	H10_1
H2_1	0.700096	0.535685	0.163343	0.595	H5_1
H2_2	0.943252	0.563681	0.459695	0.031	H10_2
C4_m	0.977860	0.554390	0.158135	0.137	C3_1
H3_m	1.048065	0.549993	0.096007	0.233	H1_1

Ok

	Individual atomic positions			distance to	
H4_m	0.969985	0.513941	0.207965	0.215	H2_1
C5_1	0.837987	0.634247	-0.048792	0.083	C4_m
C5_2	1.061828	0.660019	0.224019	0.040	C3_2
H5_1	0.898539	0.627373	-0.121264	0.076	H4_m
H5_2	1.141694	0.655369	0.175087	0.047	H2_2
H6_1	0.733458	0.648971	-0.128558	0.118	H3_m
H6_2	1.100287	0.691206	0.318524	0.054	H1_2
H9_2	0.883607	0.752456	0.223110	0.371	H6_2
H9_1	0.723999	0.734079	0.028583	0.155	H5_2
H10_2	0.772972	0.703848	0.372985	0.114	H1c1_m
H10_1	0.618753	0.686092	0.185028	0.391	H2c1_m

Ok

Press "Apply+End"

Start "Edit atoms"

The atomic part should contain only Br1, Mg1 and five oxygens

Start "Plot structure"

The cage should be correctly placed – verify by plotting

In a plot slash "/" means the atoms is transformed by the point group symmetry of the molecule, while "a" indicates the first actual position of the molecule.

## 12. Refinement of the cage with Cs point symmetry

Make backup copy

Start "Refine commands"; go to page "Various"

Press "Keep commands" and delete all of them

OK; OK; YES to save commands without starting Refine  
Start "Edit Atoms"  
Select all carbons  
Start "Action → Adding of hydrogen atoms"  
Select "Try automatic run"  
*The procedure should not add any new hydrogen atoms*  
OK; YES to quit "Edit atoms" and save changes  
Start "Refine Commands"  
Set zero refinement cycles; OK; YES+START  
This applies the previously created keep commands  
Start "Plot structure" and verify hydrogen positions  
Start "Refine commands", set 100 refinement cycles with Damping factor 0.5  
OK; YES+START to save commands and run refinement  
*The refinement has difficulties to reach convergence*  
*The fit is  $R \sim 3.2\%$ ,  $R_p \sim 2.3\%$ ,  $GOF \sim 5$ , 53 structure parameters; i.e. only slightly worse fit comparing with the asymmetric cage*



# Example 2.4: PFPhenyl

Revised: 16 October 2018

Data	Topic	Level
X-ray powder crystal data	organometallic structure from powder data using geometry constrains	Intermediate

## Tasks

Refinement of moderately sized organometallic structure from powder data with help of geometry constrains.

## Initial data

### Data

Powder data measured with diffractometer Empyrean (PANalytical) using CuK $\alpha$ 1 radiation and Debye-Scherrer geometry (sample in capillary), at ambient temperature.

### Input files:

pfphenyl.xrdml with powder profile

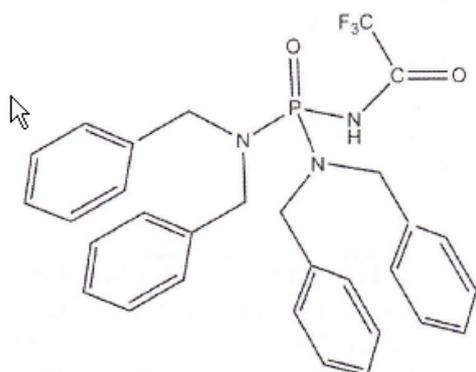
pfphenyl.cif with solution obtained by the program FOX

### Additional information:

unit cell 10.77024 9.957075 26.70771 90 91.683 90

expected symmetry P2<sub>1</sub>/n

Chemical formula: C<sub>30</sub> N<sub>3</sub> H<sub>29</sub> P O<sub>2</sub> F<sub>3</sub> (Z=4)



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# Instructions

## I. Data import

### 1. Creating new jobname

Start Jana2006

"File → Structure → New" opens a file manager (Step 1)

Left pane: locate directory with input files

Right textbox: type "**pfphenyl**"; OK (Step 2)

### 2. Import procedure

[On the screen: Specify type of the file to be imported]

Select "Structure – **from CIF**"; NEXT (Step 1)

[On the screen: select input CIF file]

Select **pfphenyl.cif**; OK (Step 2)

[On the screen: CIF does not contain any reflection block]

**YES** to import data from file

[On the screen: Specify type of the file to be imported]

Select "**various CW formats**"; NEXT

[On the screen: Powder data from:]

Select "**PANalytical XRDML**"

For method select "**Debye-Scherrer**"; NEXT

[On the screen: Complete/correct experimental parameters]

#### Notes

Cell parameters were taken from CIF

Radiation was interpreted from the xrdml file as CuKα1

Complete/correct experimental parameters

Cell parameters: 10.7673 9.9524 26.6946 90 91.679 90

Target dimension: 3 Info about metrics parameters

X-rays X-ray tube

Neutrons

Electrons

Kalpha1/Kalpha2 doublet

Wave length: 1.540598

Temperature: 293

**Polarization correction:**

Circular polarization

Perpendicular setting Info

Parallel setting Info

Gunier camera

Linearly polarized beam

**Monochromator parameters:**

Perfectness: 0.5

Glancing angle: 13.2776 Set glancing angle

NEXT; FINISH; OK to close data repository; **YES** to accept the data set

## II. Le Bail refinement

### 1. Refinement of the powder profile

#### Notes

For refinement of the powder profile we will use the le Bail wizard. All steps of the wizard could also be done without the wizard using the basic tools of Jana2006.

[On the screen: Refinement of the powder profile by the le Bail algorithm]

Press "Profile viewer" – just to see how it looks like

Press "Default" to see more details

Quit powder viewer

Press "Edit profile"

In page "Profile" activate refinement of "GW"

## Notes

Unlike for structure parameters, refinement keys of profile parameters are not set automatically

In page "Corrections":

Activate refinement of "shift";

Change number of "Legendre terms" for background to **30**; (Step 3)

OK; Yes to rewrite

Right click on Refine; select the page "Basic"

Make sure that "Make only profile matching" is activated

The structure previously imported from CIF will not be used in this refinement, only profile parameters will be refined

Set **100** refinement cycles (Step 1)

OK; Yes + start

### Step 1

The screenshot shows the 'Refine commands' dialog box with the 'Basic' tab selected. The 'Number of cycles' is set to 100. The 'Make only profile matching' checkbox is checked. Other options include 'Use dynamical LS method', 'Check for convergence', and 'Disable atoms having too large isotropic ADP parameter'.

## Notes

Refinement finishes with:  $GOF \approx 3.5$ ,  $R_p \approx 2.9$ ,  $wRp \approx 5.1$ .

Waiting for the full convergence is not necessary. Refinement can be interrupted by End or Cancel - in this case End should be used in order to see the latest difference curve in the powder profile viewer.

“Profile viewer”

Press "Default"

Move the theta slider towards high angles

Press "Details ON"; YES to plot many component functions

Press "Fit Y" (Step 2)

## Notes

The calculated profile shows problem with background. The background is too low and the Bragg peaks are too high, giving together good fit between calculated and observed line, which is unfortunately false. We shall therefore use the manual background. This problem only occurs with profile fitting. For Rietveld refinement, this problem cannot happen because intensities of peaks are given by the structure.

Press "Details OFF"

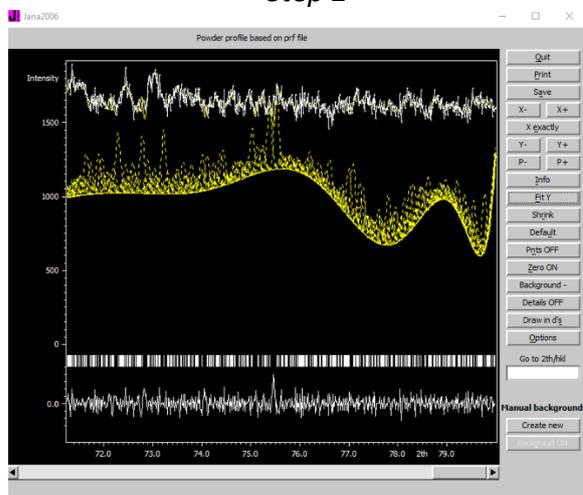
Press "Create new" button (lower right corner of the Powder profile viewer)

[On the screen: Options for generating background profile]

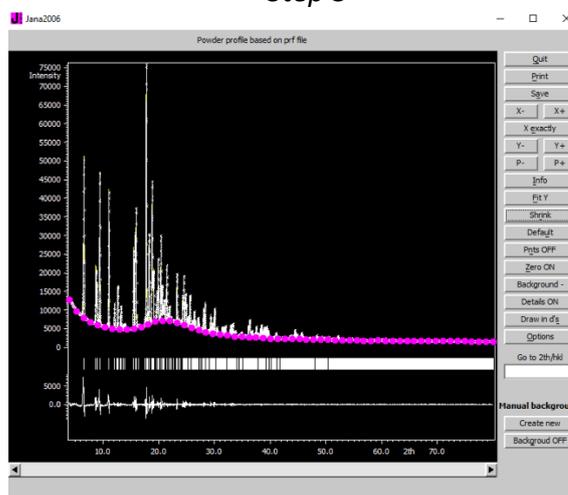
Use 60 background points and significance intensity level 1; OK

Using the slider check the manual background. It can be edited by dragging the points by mouse. (Step 3)

Step 2



Step 3



Press "Quit"

[On the screen: A manual background has been created]

Select "Accept the new manual background" and "Suppress using of polynomial terms"

OK

Run "Refine"

## Notes

Refinement finishes with  $GOF \approx 3.6$ ,  $R_p \approx 2.8$ ,  $wRp \approx 5.2$

“Edit profile parameters”

In page “Cell” activate refinement of “a, b, c, beta”

In page "Profile" **activate** refinement of "**GV**"  
OK, YES to save changes  
Run "**Refine**"

#### Notes

*Refinement finishes with  $GOF \approx 3.1$ ,  $Rp \approx 2.5$ ,  $wRp \approx 4.5$*   
*For Gaussian parameters an important rule is that they cannot be refined all together because they are linearly dependent. Usually we refine GW, then GV and finally GU. In our case GU would not improve the fit.*

"Edit profile parameters"

In page "Profile" change the type of the peak-shape function to "**Pseudo-Voigt**", activate refinement of "**LY**"

OK, YES to save changes

Run "**Refine**"

#### Notes

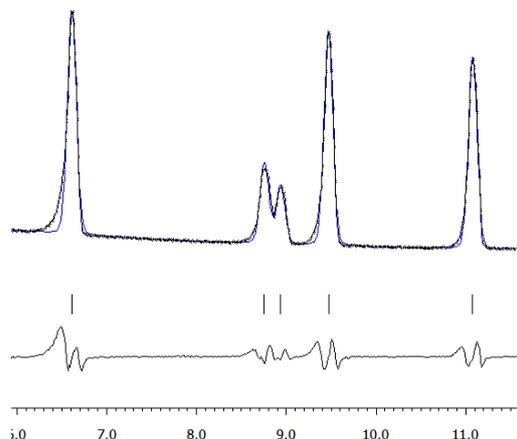
*Refinement finishes with  $GOF \approx 3.0$ ,  $Rp \approx 2.5$ ,  $wRp \approx 4.6$*

"Show Powder profile"

Enlarge the profile and investigate details of the fit between the calculated and experimental profile.

#### Notes

*Some low angle peaks exhibit strong asymmetry:*



"Edit profile parameters"

In page "Asymmetry/Diffractometer" select "**correction by divergence**"

Activate refinement of "**HpS/L**" and fix to zero "**HmS/L**"

OK; YES to save changes

Right click Refine

In page "Basic" set "Damping factor" to **0.5**

OK;

Run "**Refine**"

#### Notes

*Refinement finishes with  $GOF \approx 1.7$ ,  $Rp \approx 1.8$ ,  $wRp \approx 2.5$*   
*Waiting for full convergence is not necessary.*

"Show Powder profile"

Notes

*Asymmetry seems to be well described*

Quit the profile viewer

"File → Structure → Save as → Backup"

**NO** (do not continue with the new structure)

### III. Rietveld refinement

#### 1. Refinement of the free atomic model

Make sure that the backup copy really exists

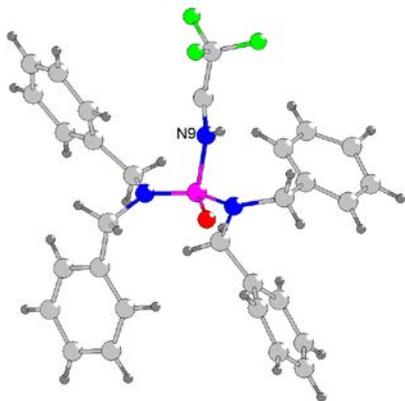
Start "Plot structure"

In Diamond use "Build → Connectivity" and suppress F-H and F-O bonds

Use  to plot the structure

Notes

*The structure from FOX solution is looking like this:*



*Before refinement we have to fix geometry for hydrogen atoms. Hydrogen positions cannot be determined from this powder data set.*

Return to Jana

Start "Edit atoms"

Select **all carbon** atoms and **N9**

Start "Action → **Adding of hydrogen atoms**" (Step 1)

[On the screen: Adding of "hydrogen" atoms"]

Use default settings; OK

Notes

*Hydrogen atoms of carbon have been fixed automatically while for N9 the program offers a dialogue*

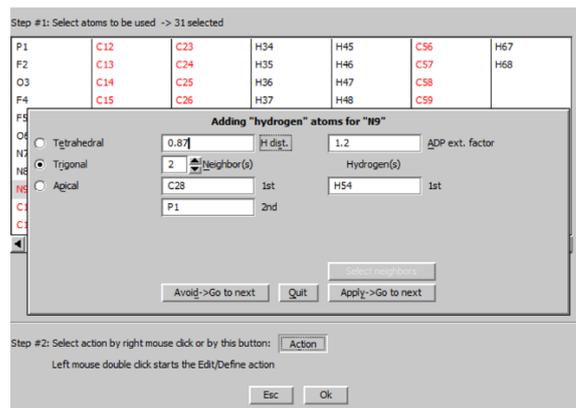
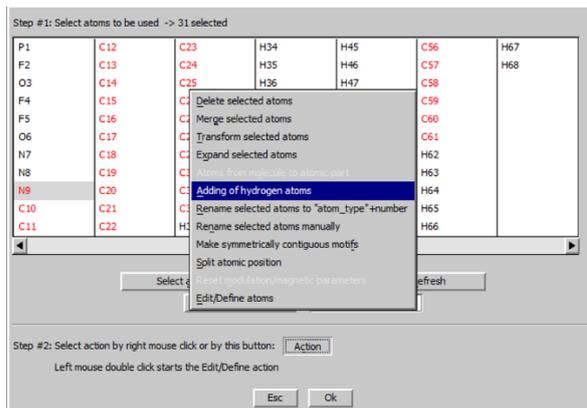
[On the screen: Adding "hydrogen" atoms for "N9"]

Select "**Trigonal**"; C28 and P1 for neighbors; **H54** for hydrogen (Step 2)

Press "Apply → Go to next"

Step 1

Step 2



OK; YES to save changes

### Notes

Adding of hydrogen atoms results in no new atoms in the list of atoms. The reason is that the hydrogen positions calculated by Jana2006 coincide with positions of already existing hydrogens. However, each hydrogen atom has now the corresponding keep command fixing its geometry.

Start **Refinement options** (Right-click on the "Refine" icon)  
 Select the page "**Basic**"  
 Set **0** refinement cycles  
 Uncheck "**Make only profile matching**"

### Notes

This changes *le Bail* fitting into Rietveld refinement, where intensities of the profile points are calculated from the structure model

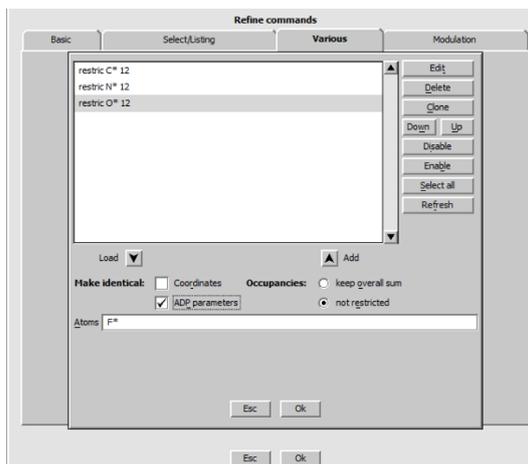
OK; YES+START

### Notes

R values are bad because the scale remains unrefined. However, positions of hydrogen atoms were updated according to the previously introduced keep commands and now we can check in the plotting program correctness of hydrogen positions.

Start "Plot structure"  
**Verify hydrogen positions**  
 Quit Diamond  
 Start "Edit Profile" and **fix all profile parameters: "a, b, c, beta, GV, GW, LY, HpS/L and shift"**.  
 OK, YES to save changes  
 Using "File → Structure → Save as" **make a backup copy named "pfphenyl\_free"**  
**No** (You don't want to continue with the new structure)  
 Start Refinement options; set **100** refinement cycles; set Damping factor **0.2**  
 In page "Various" start "**Restrictions**"  
 Set the **same ADP** for all carbon atoms (**C\***)  
 Set the **same ADP** for all nitrogen atoms (**N\***)  
 Set the **same ADP** for all oxygen atoms (**O\***)  
 Set the **same ADP** for all fluorine atoms (**F\***) (Step 3)

Step 3



OK; YES (i.e. DO NOT start refinement)

Using "File → Structure → Save as→ Backup\_2" make a backup copy

NO (Do not continue with the new structure)

Start "Refine"

#### Notes

Now the structure is refined but the originally obtained profile parameters are fixed

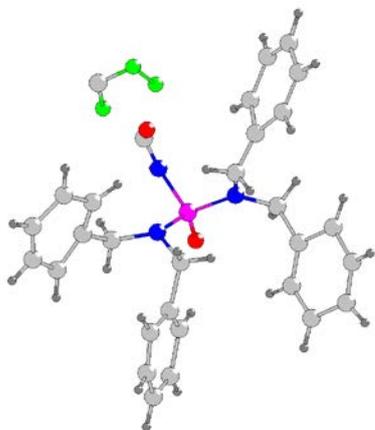
Refinement finish with:

Resulting structure factors  $R(obs) \approx 6.3$ ,  $wR(obs) \approx 5.0$ ,  $R(all) \approx 8.6$ ,  $wR(all) \approx 5.3$

Resulting profile factors  $GOF \approx 2.0$ ,  $R_p \approx 2.1$ ,  $wR_p \approx 2.9$

Start "Plot structure" and plot the refined structure

#### Notes



We can see that the PN3O group has been refined correctly but phenyl groups are not planar and the CF3 group has been destroyed

## 2. Fixing geometry with keep commands

Start "Tools → Recover files"

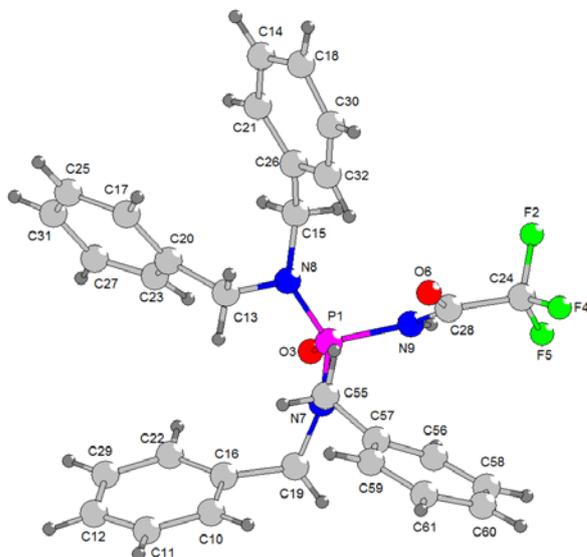
#### Notes

This returns the previous structure model (one step back). In case refinement would be started more than once, "File → Structure → Copy in" would be used for importing the previously created backup file.

Start "Plot structure" in order to see atom labels.

#### Notes

With "Draw+continue" Jana2006 and Diamond run independently, and atom labels seen in Diamond can be immediately used in Jana. Otherwise it is necessary to note the labels in Diamond for later use, or use the figure from the Cookbook.



Start Refine Commands

In page Various start "**Keep commands**"

The already existing 50 commands keep the geometry of hydrogen atoms

Select "**Geometry**" and "**Plane**"

For "List of atoms" type labels of carbons in one of the Phenyl rings (without hydrogens)

**C17 C20 C23 C27 C31 C25** (step 1)

Press "Add"

**Repeat the process** for the remaining Phenyl rings

**C14 C18 C30 C32 C26 C21**

**C57 C56 C58 C60 C61 C59**

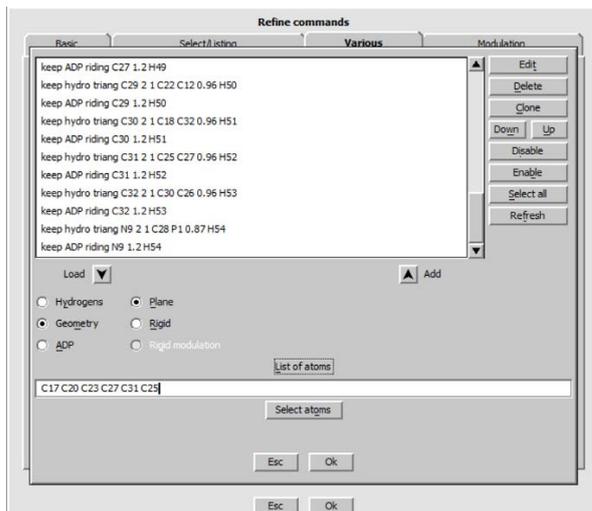
**C10 C11 C12 C29 C22 C16**

Switch from "Plane" to "**Rigid**"

For "List of atoms" type **C28 O6 C24 F2 F4 F5**

*Step 1*

*The introduced keep commands:*



keep geom plane C17 C20 C23 C27 C31 C25  
 keep geom plane C14 C18 C30 C32 C26 C21  
 keep geom plane C57 C56 C58 C60 C61 C59  
 keep geom plane C10 C11 C12 C29 C22 C16  
 keep geom rigid C28 O6 C24 F2 F4 F5

Press "Add"  
 OK; OK; YES+START

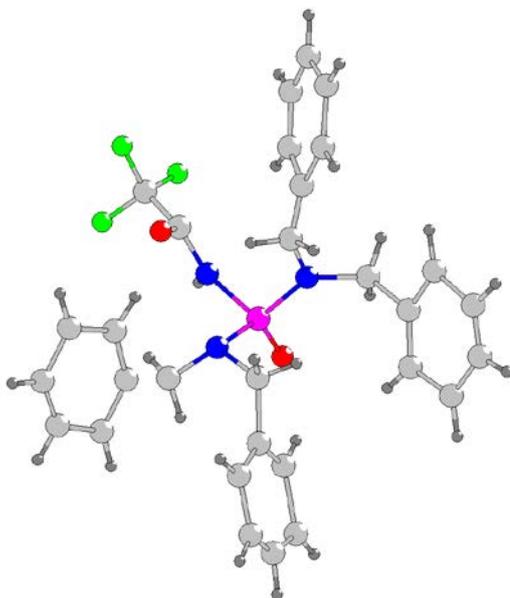
### Notes

*The resulting structure factors:  $R(obs) \approx 7.4$ ,  $wR(obs) \approx 6.6$ ,  $R(all) \approx 10.1$ ,  $wR(all) \approx 7.0$   
 The resulting profile factors:  $GOF \approx 2.3$ ,  $Rp \approx 2.5$ ,  $wRp \approx 3.3$   
 i.e. slightly worse results compared with the unrestricted geometry  
 Damping factor may be changed to 1*

Start "Plot structure" and verify the result

*The geometry is now much more reasonable, but some angles in the phenyl rings are too much different of 120°.*

**Make backup copy** of this refinement named (for instance) phphenyl\_keepgeom  
**NO** (do not continue with the new structure)

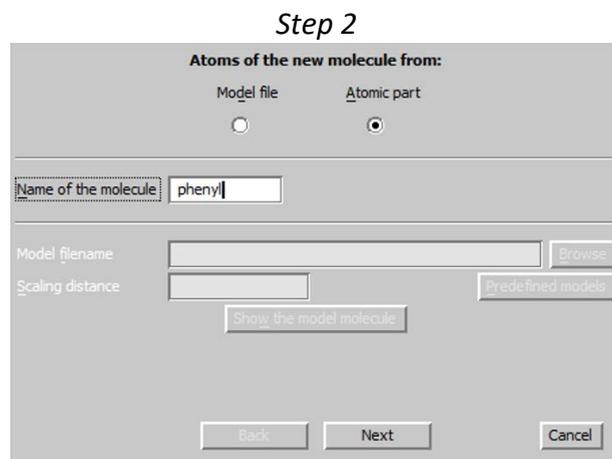
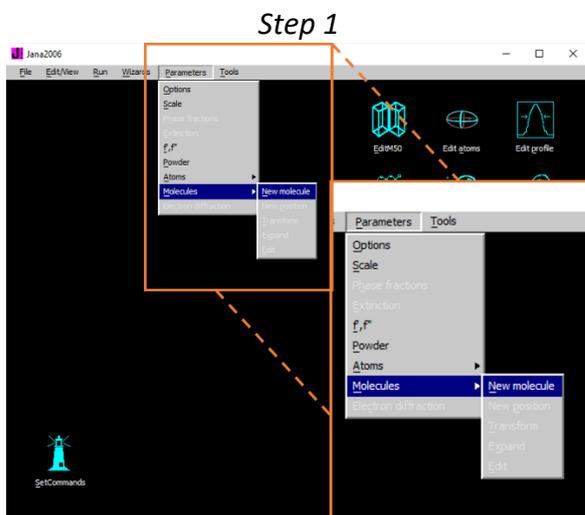


### 3. Application of rigid body to phenyl rings

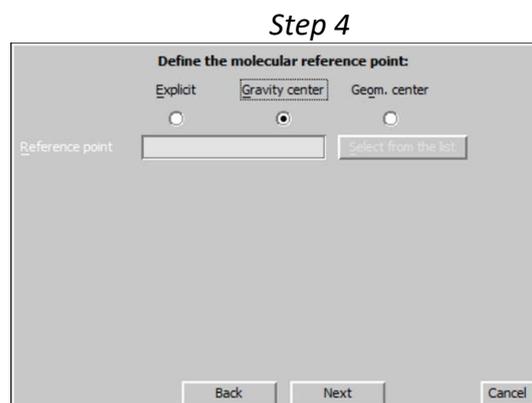
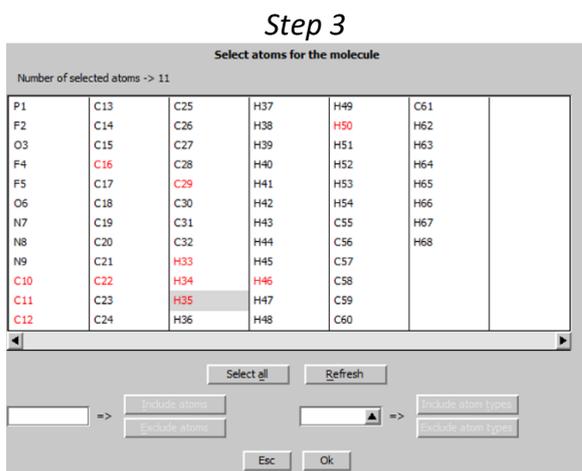
Start "Refinement options", go to the page "Various"

Start "Keep commands" and **delete** or **disable** the four "keep geom plane" commands ("keep geom rigid" should be retained)

OK; OK; **YES** to save commands **without** starting Refine  
 Start "Parameters → Molecules → **New molecule**" (Step 1)  
 [On the screen: Atoms of the new molecule from:]  
 Select "Atomic part"  
 Write "**Phenyl**" for the name of the molecule (Step 2)  
**NEXT**



[On the screen: Select atoms for the molecule]  
 Select "**C10, C11, C12, C29, C22, C16, H46, H50, H33, H34, H35**" (i.e. one of the phenyl rings) (Step 3)  
 OK  
 [On the screen: Define the molecular reference point:]  
 Select "**Geom. Center**" (Step 4)  
**NEXT**



### Notes

*For molecules not located in a special position the position of the reference point is not important. For symmetrical molecules, the reference point is used for derivation of symmetry restrictions and its definition is important.*

[On the screen: Complete molecular position #1:]

Use Occupancy 1

Press "Apply+Next position" (Step 5)

## Notes

The Coincidence ratio 11/11 means that all atoms of the actual position #1 coincide with atoms in the atomic part. This is obviously fulfilled, because the model molecule has been taken from the atomic part

## Step 6

### Step 5

**Complete molecular position # 1:**

**Molecular parameters:**  
Phi = 0.00 Chi = 0.00 Psi = 0.00 determinant = 1  
Translation vector : 0.000000 0.000000 0.000000

Occupancy: 1      Coincidence ratio: 11/11

Apply+Next position    Apply+End    Quit

**Define and complete molecular position # 2:**

Apply inversion

	Model atom	Actual position/atom
1st point	c16	c57
2nd point	c11	c58
3rd point	c29	c61

Select the actual atom  
Fill by a saved point

**Options for removing of atoms from atomic block coinciding with those generated from molecular position # 2:**

Maximal coincidence distance: 0.6      Show coinciding atoms

Calculate molecular parameters

**Molecular parameters:**  
Phi = 97.67 Chi = -0.31 Psi = -73.54 determinant = 1  
Translation vector : -0.554602 0.048572 -0.029251

Occupancy: 1      Coincidence ratio: 11/11

Apply+Next position    Apply+End    Quit

[On the screen: Define and complete the molecular position #2:]

For model atoms select three carbons from the model molecule: **C16, C11 and C29**

For the actual position choose three corresponding carbons from another existing phenyl group, for instance **C57, C58 and C61**

For "Maximal coincidence distance" type **0.6** (in Angstroms) (Step 6)

Press "Show coinciding atoms"

## Notes

It shows that the actual molecular position #2 coincides with another 11 atoms from the atomic part. These atoms will be automatically deleted in the atomic part.

	Individual atomic positions			distance	to
C10	-0.202061	0.389799	0.552940	0.437	C56
C11	-0.298377	0.496468	0.544273	0.226	C58
C12	-0.316706	0.596045	0.568925	0.420	C60
C16	-0.140155	0.429460	0.594416	0.000	C57
C22	-0.145972	0.533765	0.626369	0.406	C59
C29	-0.248215	0.632091	0.612199	0.317	C61
H33	-0.188034	0.310964	0.533202	0.462	H62
H34	-0.352530	0.484228	0.515442	0.193	H63
H35	-0.382990	0.654549	0.558022	0.432	H65
H46	-0.091110	0.544578	0.655067	0.518	H64
H50	-0.264578	0.711780	0.631133	0.316	H66

Ok

Press "Apply+Next position"

For model atoms re-use **C16, C11 and C29**

For actual position #3 use **C26, C30 and C14**

Calculate molecular parameters

Number of coinciding atoms should be again 11

Press "Apply+Next position"

For model atoms re-use **C16, C11 and C29**

For the last actual position #4 use **C20, C25 and C27**

Calculate molecular parameters

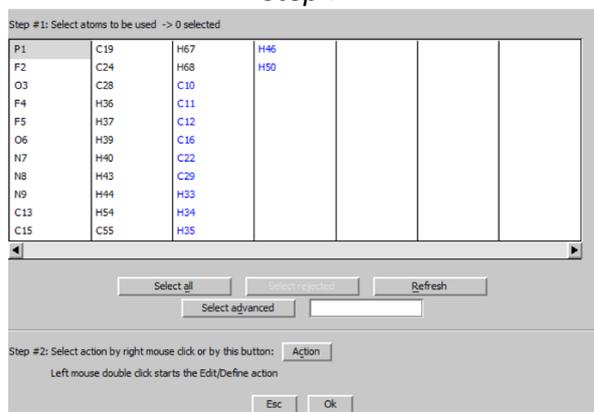
Number of coinciding atoms should be again 11

Press "Apply+End"

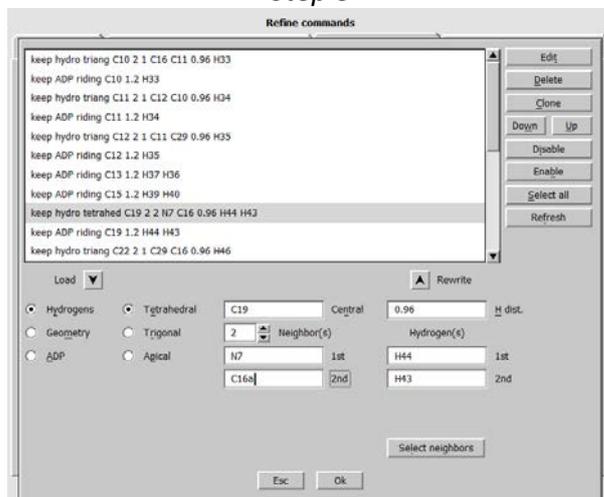
Start "Edit atoms"

The free atoms are black, the atoms of the model molecule are blue (Step 7)

### Step 7



### Step 8



OK

Start "Plot structure"

### Notes

The structure should look more or less like before (with the difference that now we have four identical phenyl groups)

The old keep commands acting for atoms replaced by some of the molecular positions were automatically deleted. Keep commands acting for atoms of the model molecule were retained.

However, we have also used keep commands involving atoms from the phenyl groups and N-CH<sub>2</sub>- group. The command defining positions of two hydrogen atoms bonded to C19 has not been deleted, and it still contains the atom C16, which belongs to the model molecule and not to some actual position. Therefore, C16 must be changed to C16a (atoms of molecular positions #1, #2, #3 and #4 have suffixes a,b,c and d. :

Start Refine Commands

In page Various start "Keep commands" and load the keep command for C19:

Change **C16 to C16a**; Add

OK; OK; YES to save commands without starting Refine

### Notes

The commands for keeping the geometry of hydrogen atoms in N-CH<sub>2</sub>- groups for remaining three atoms (C55, C15 and C13) have to be re-defined, too. Another way how to do it uses the tool for adding hydrogen atoms:

Start "Edit atoms"  
Select **C55, C15 and C13**  
Start "Action → Adding of hydrogen atoms"  
Use default settings; OK  
(number of atoms should not change)

#### Notes

Here are the final keep commands:

```
keep hydro triang C10 2 1 C16 C11 0.96 H33
keep ADP riding C10 1.2 H33
keep hydro triang C11 2 1 C12 C10 0.96 H34
keep ADP riding C11 1.2 H34
keep hydro triang C12 2 1 C11 C29 0.96 H35
keep ADP riding C12 1.2 H35
keep ADP riding C13 1.2 H36 H37
keep ADP riding C15 1.2 H40 H39
keep hydro tetrahed C19 2 2 N7 C16a 0.96 H44 H43
keep ADP riding C19 1.2 H44 H43
keep hydro triang C22 2 1 C29 C16 0.96 H46
keep ADP riding C22 1.2 H46
keep hydro triang C29 2 1 C22 C12 0.96 H50
keep ADP riding C29 1.2 H50
keep ADP riding C55 1.2 H68 H67
keep hydro triang N9 2 1 C28 P1 0.87 H54
keep ADP riding N9 1.2 H54
keep geom rigid C28 O6 C24 F2 F4 F5
keep hydro tetrahed C13 2 2 C16d N8 0.96 H36 H37
keep hydro tetrahed C15 2 2 N8 C16c 0.96 H40 H39
keep hydro tetrahed C55 2 2 C16b N7 0.96 H68 H67
```

OK  
Open the page "Basic"  
Set **number of cycles to 0**; OK; **YES+START** to save commands and start refinement  
*This will apply keep commands without any further changes*  
Start "Plot structure"  
Verify the structure after application of the new keep commands  
*There should be only small changes*  
Start "Refine Commands"  
Change number of refinement cycles back to **100**  
OK; **YES+START** to save commands and start refinement

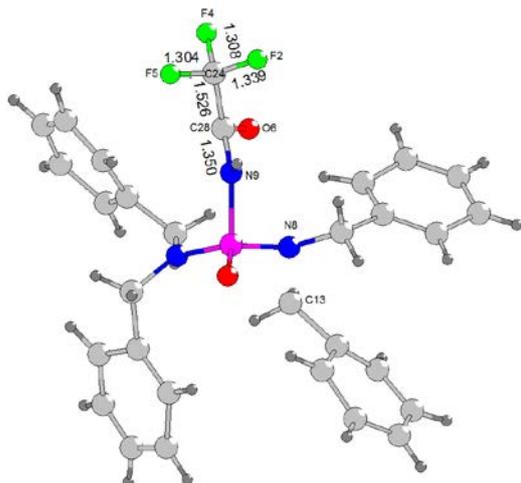
#### Notes

The resulting structure factors:  $R(\text{obs}) \approx 7.9$ ,  $wR(\text{obs}) \approx 7.0$ ,  $R(\text{all}) \approx 10.5$ ,  $wR(\text{all}) \approx 7.3$   
The resulting profile factors:  $GOF \approx 2.4$ ,  $R_p \approx 2.6$ ,  $wRp \approx 3.4$

Start "Plot structure"

#### Notes

The resulting structure has much better geometry of phenyl groups  
 However, the distance C13-N8 is too large



Make backup copy **pfphenyl\_rigid**  
**NO** (do not continue with the new structure)

#### 4. Releasing the geometry of COCF<sub>3</sub>

Start "Refine commands"

In page "Various" start "Keep commands"

Delete or disable the "keep geom rigid" command; OK (Step 1)

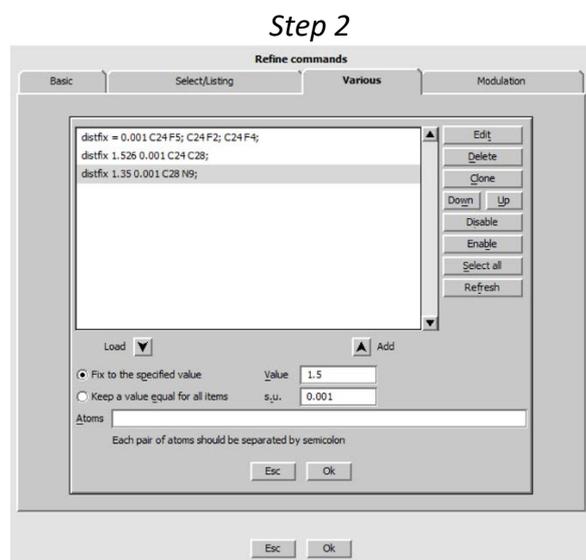
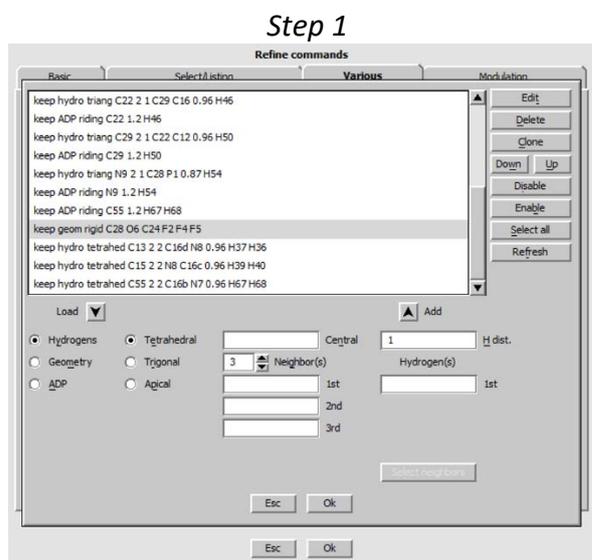
Start "Distance restrains"

Define the following restrains (with default s.u.):

"Keep a value equal for all items": C24 F5; C24 F2; C24 F4

"Fix to the specified value": C24 C28 to 1.526

"Fix to the specified value": C28 N9 to 1.35 (Step 2)



OK; OK; YES+START to save commands and start refinement  
 "Use all"

#### Notes

The resulting structure factors:  $R(\text{obs}) \approx 7.4$ ,  $wR(\text{obs}) \approx 6.6$ ,  $R(\text{all}) \approx 10.0$ ,  $wR(\text{all}) \approx 6.9$   
The resulting profile factors:  $GOF \approx 2.2$ ,  $R_p \approx 2.5$ ,  $wR_p \approx 3.3$

Start "Plot structure"

Notes

The geometry is correct and (as a side effect) the distance N8-C13 is now also correct

Make backup copy as **phenyl\_rigid\_final**

## 5. Refinement of structure and profile parameters together

Notes

Up to now the profile parameters were fixed on values obtained in Le Bail refinement

Start "Edit profile"

**Activate** refinement of "a, b, c, beta, GW, GV, LY, HpS/L and shift"

OK; YES to save changes

Start "Refine"

Notes

The refinement finish with:  
the structure factors  $R(\text{obs}) \approx 7.9$   $wR(\text{obs}) \approx 7.0$   $R(\text{all}) \approx 10.5$   $wR(\text{all}) \approx 7.3$   
the profile  $GOF \approx 2.4$   $R_p \approx 2.6$   $wR_p \approx 3.4$

Start "Edit profile"

Go to page "Corrections"

Change number of Legendre polynomial terms to **20**

OK; YES to save changes

Start "Refine"

Notes

Now the manual background is combined with the polynomial background  
The problem with the background refinement, which we have seen at the beginning of this example, cannot occur with Rietveld refinement because the intensities of the profile points are calculated from the structure factors  
The resulting structure factors:  $R(\text{obs}) \approx 7.4$ ,  $wR(\text{obs}) \approx 6.5$ ,  $R(\text{all}) \approx 10.0$ ,  $wR(\text{all}) \approx 6.8$   
The resulting profile factors:  $GOF \approx 2.2$ ,  $R_p \approx 2.4$ ,  $wR_p \approx 3.2$

## 6. Fixing planarity of phenyl

Start "Plot structure"

Notes

The structure is correct except that the phenyl rings are not perfectly planar

Start "Profile viewer"

Notes

The profile is correctly described

Start "Refine commands"

In page "Various" start "Keep commands"

Define "keep - geometry - plane" for C10, C11, C12, C16, C22 and C29, i.e. for the carbon atoms of the model molecule  
OK; OK; YES+START

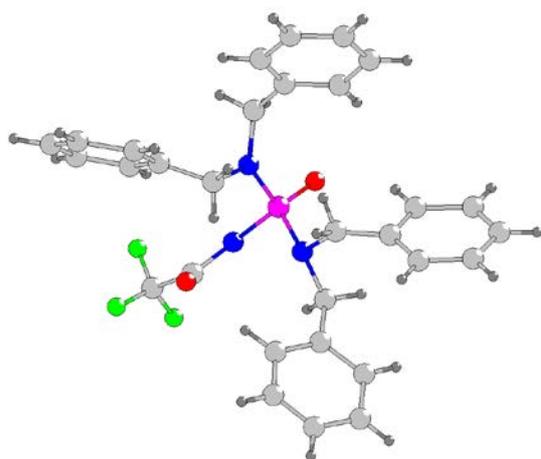
#### Notes

The resulting structure factors:  $R(\text{obs}) \approx 7.6$ ,  $wR(\text{obs}) \approx 6.7$ ,  $R(\text{all}) \approx 10.2$ ,  $wR(\text{all}) \approx 7.0$   
The resulting profile factors:  $GOF \approx 2.3$ ,  $R_p \approx 2.5$ ,  $wRp \approx 3.3$

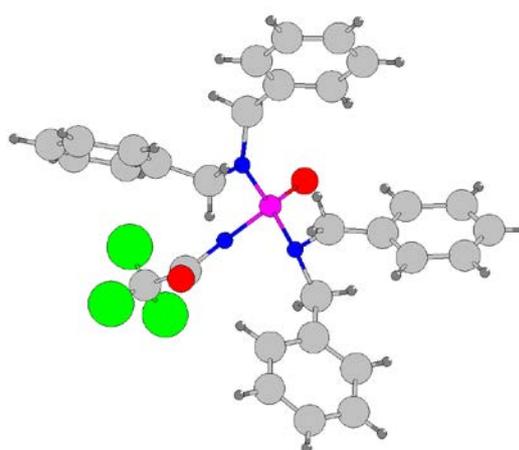
Start "Plot structure"

#### Notes

The phenyl rings are now perfectly planar, with reasonable distances and angles, although only the planarity has been kept.



Plot with default radii



Plot with radii scaled by isotropic ADP

## References

Favre-Nicolin, Vincent & Cerny, Radovan. (2002). FOX, 'free objects for crystallography': A modular approach to ab initio structure determination from powder diffraction. *Journal of Applied Crystallography*. 35. 734-743. 10.1107/S0021889802015236.

# Example 2.5.1: Twoph

Revised: 16 October 2018

Data	Topic	Level
X-ray powder crystal data	Multiphase powder refinement	Intermediate

## Tasks

Multiphase powder refinement  
Entering two phases in Jana2006 manually  
Refinement using Le Bail method  
Entering two phases in Jana2006 from cif file  
Refinement using Rietveld method  
Rigid body refinement  
Preferential orientation

## Initial data

### Data

Powder measurement was done with Empryan (PANalytical) using CuK $\alpha$  radiation, focusing mirror and Debye-Scherrer geometry (sample in a capillary)

### Input files:

**twoph.xrdml** with powder profile

**RT.cif** crystal structure of the room temperature phase solved and refined from single-crystal

**LT.cif** crystal structure of the low temperature phase solved from powder data by FOX.

### Additional information:

Room temperature (RT) phase of this sample is known from single crystal data. At cooling, a phase transition occurred, which was repeatedly destroying the single crystals. Therefore, the low temperature (LT) phase was measured at 150K as a powder. The powder sample at 150K still contained an admixture of the room temperature phase.

Unit cell of the LT phase was determined with CRYSFIRE 2004. Its structure was solved by direct methods implemented in the program FOX, using the RT structure as a starting template.

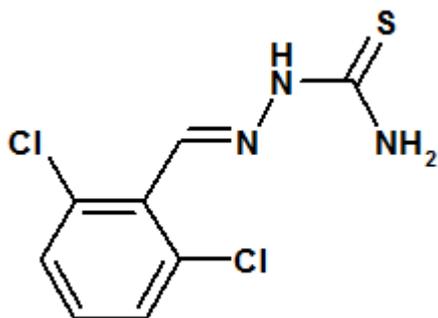
RT phase unit cell: 6.81 8.56 17.78 90 96.8 90

RT phase symmetry:  $P2_1/n$

LT phase unit cell: 8.54 17.68 7.15 90 111.25 90

LT phase symmetry:  $P2_1/a$

Chemical formula: RT and LT



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# Instructions

---

## I. Data import

### 1. Creating new job name

Start Jana2006

"File → Structure → New" opens the file manager

Left pane: locate directory with input files

Right pane: double-click **twoph**

OK;

### 2. Import procedure

*[On the screen: Specify type of the file to be imported]*

Select "Powder data – various CW formats"; NEXT

*[On the screen: Powder data from:]*

Select "**PANalytical XRDML**"

Select "**Debye-Scherrer method**"; NEXT

*[On the screen: Complete/correct experimental parameters]*

For "Cell parameters" type "**6.81 8.56 17.78 90 96.8 90**"

*(cell parameters of the RT phase)*

X-ray tube **Cu**

**Check** the radiation **Kalpha1/Kalpha2 doublet** (Step 1)

*(should be interpreted from the xrdml file as Copper with doublet):*

NEXT; FINISH;

OK to close data repository

YES to accept the data set

*[On the screen: question how to continue]*

Select "**No, I shall go by my own way**"; OK

### Step 3

The screenshot shows the 'Complete/correct experimental parameters' dialog box. The 'Cell parameters' field contains '6.81 8.56 17.78 90 96.8 90'. The 'Target dimension' is set to '3'. The 'X-ray tube' is set to 'Cu'. The 'Polarization correction' section has 'Parallel setting' selected. The 'Monochromator parameters' section has 'Perfectness' set to '0.5' and 'Glancing angle' set to '13.2776'. The 'Temperature' is set to '293'. There are 'Back', 'Next', and 'Cancel' buttons at the bottom.

## II. Le Bail refinement

### I. Powder profile indicates a multiphase

Start "Tools → Powder → Make Le Bail" (Step 1)

YES to start "profile viewer"

Press "Default" and move the slider to beginning of the powder profile (Step 2)



#### Notes

Some peaks, for example at  $12.22^\circ$ , do not have corresponding Bragg position. This is the indication of a multiphase (we believe our unit cell)

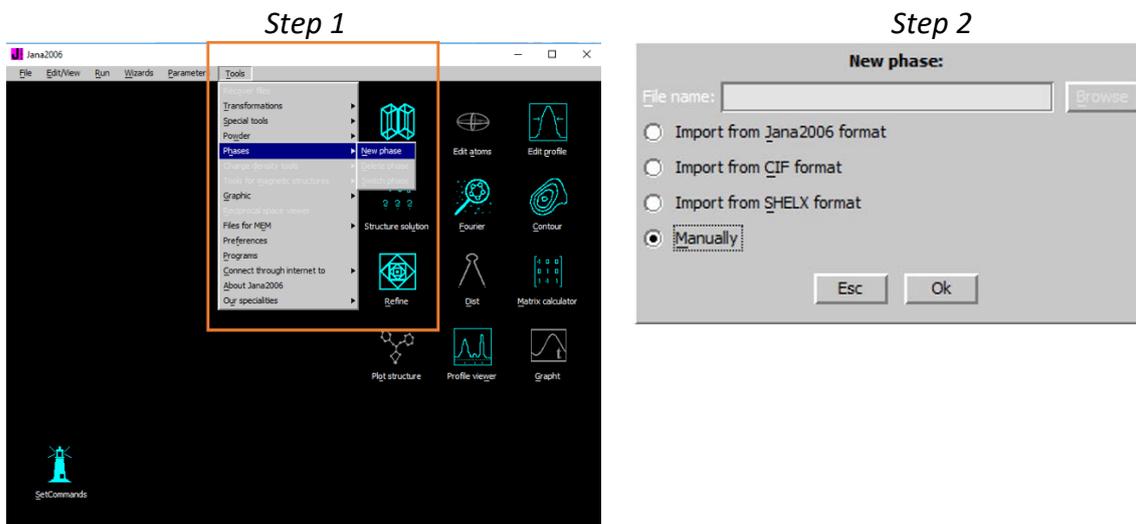
Quit

### 2. Importing of the second phase

Start "Tools → Phases → New phase" (Step 1)

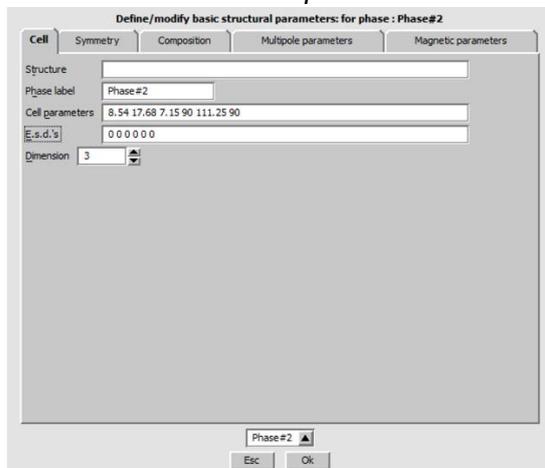
[On the screen: New phase]

Select "Manually"; OK (Step 2)

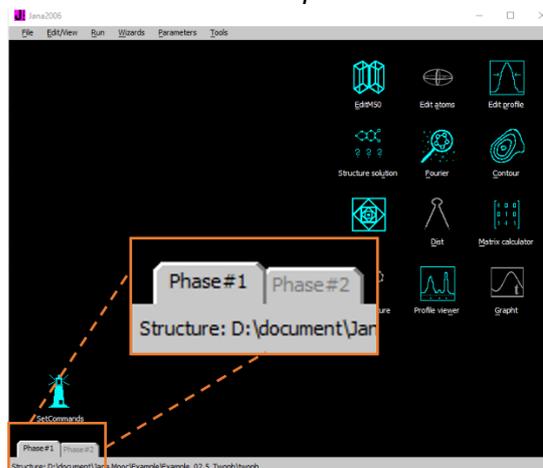


[On the screen: Define/ modify basic structural parameters for phase: Phase#2]  
 For "Cell parameters" type "8.54 17.68 7.15 90 111.25 90" (unit cell of the LT phase);  
 For E.s.d.'s "0 0 0 0 0" (Step 3)  
 OK; YES to rewrite M50

### Step 3



### Multiphase

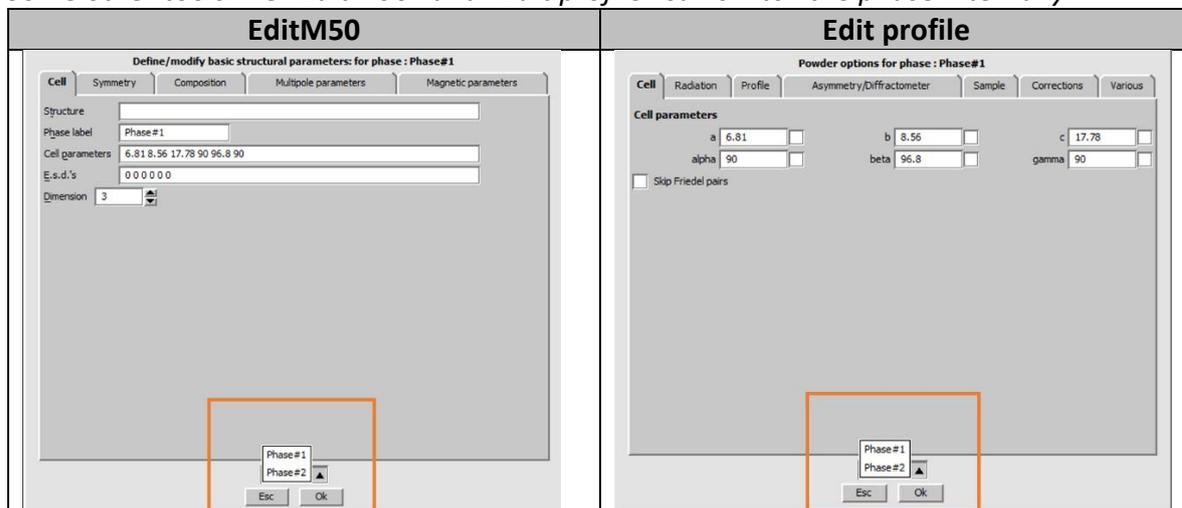


### Notes

In the lower left corner of the Jana2006 basic window two new thumbnails appear: "Phase#1" and "Phase#2".

They are used for switching between the two phases. Many tools of Jana2006 work only with the active phase, for instance "Fourier", "Dist", "Contour" and "Plot structure". Before starting these tools, the required phase must be activated.

Some other tools like "EditM50" and "Edit profile" can switch the phase internally.



"Refine" and "Profile viewer" work independently on the active phase.



The tool "Structure solution" places results to the first phase and deletes atoms of the other phases.

### 3. Set Phase labels and symmetry

Start "EditM50"

[On the screen: Define/ modify basic structural parameters for phase: Phase#1]

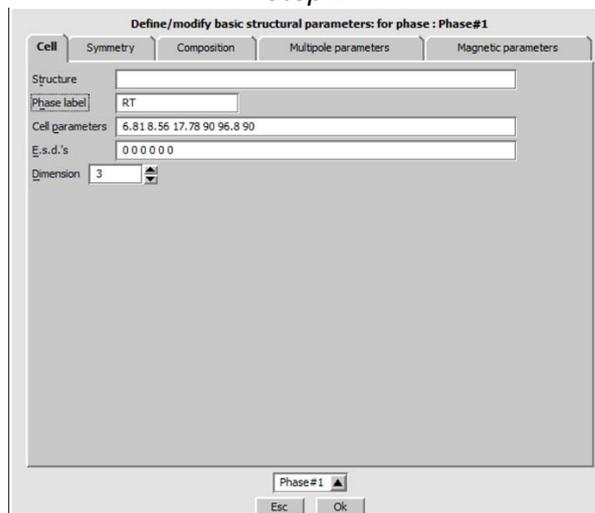
Ensure that **Phase#1** is selected at the bottom of the EditM50 window.

For "Phase label" type "RT" (Step 1)

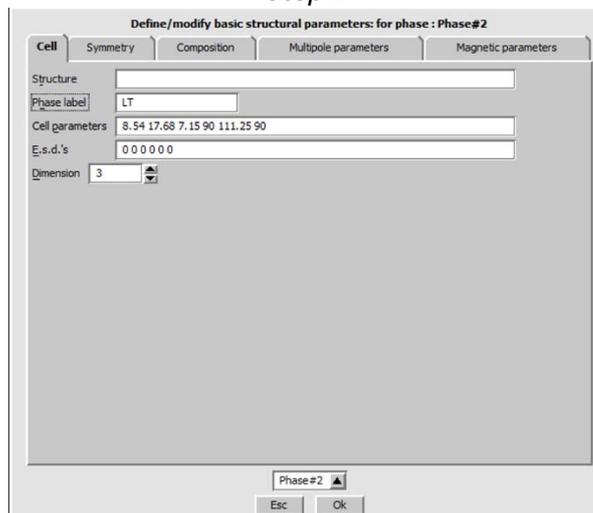
Still in the EditM50 window, switch to the **Phase#2**

For "Phase label" type "LT" (Step 2)

Step 1



Step 2

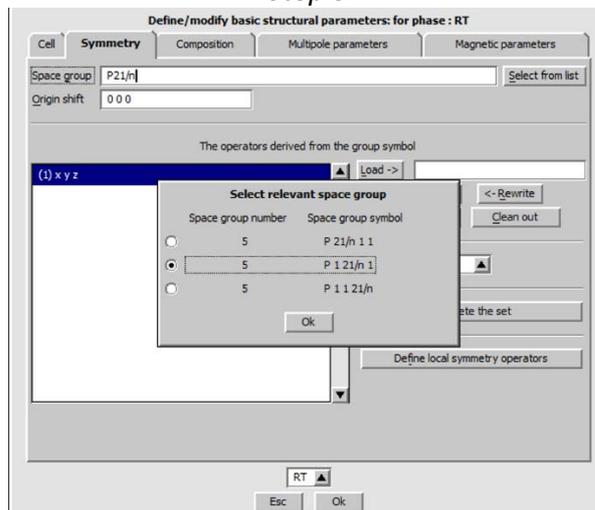


Go to the page "Symmetry"

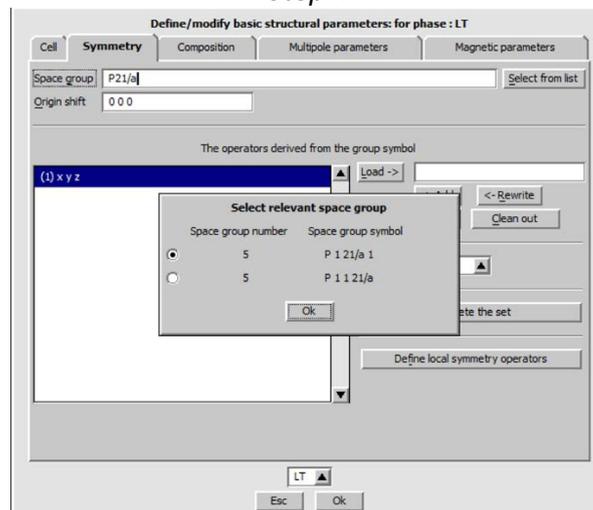
Select the phase **RT** and for "Space group" type "**P21/n**"; choose 21 along b; TAB; OK (step 3)

Select the phase **LT** and for "Space group" type "**P21/a**"; choose 21 along b; TAB (step 4)

Step 3



Step 4



OK; YES to rewrite M50

### 4. Le Bail refinement

Start "Edit profile"

[On the screen: Powder options for phase: RT]

Ensure that the RT phase is selected at the bottom of the form.

In page "Cell" activate refinement of "a, b, c and beta" (RT phase) (Step 1)

Select LT phase

In page "Cell" activate refinement keys of "a, b, c and beta" (LT phase) (Step 2)

Go to the page "Profile"

### Step 1

Powder options for phase: RT

Cell parameters

a	6.81	<input checked="" type="checkbox"/>
b	8.56	<input checked="" type="checkbox"/>
c	17.78	<input checked="" type="checkbox"/>
alpha	90	<input type="checkbox"/>
beta	96.8	<input checked="" type="checkbox"/>
gamma	90	<input type="checkbox"/>

RT

Esc Ok

### Step 2

Powder options for phase: LT

Cell parameters

a	8.54	<input checked="" type="checkbox"/>
b	17.68	<input checked="" type="checkbox"/>
c	7.15	<input checked="" type="checkbox"/>
alpha	90	<input type="checkbox"/>
beta	111.25	<input checked="" type="checkbox"/>
gamma	90	<input type="checkbox"/>

LT

Esc Ok

For each phase, select page "Profile"; "Pseudo-Voigt"; activate refinement keys for GW and LY

Go to the page "Corrections"

Corrections are independent on a phase selection

For "Background", select "Legendre polynomials" and for "Number of terms" type 25 (Step 6)

OK; YES to rewrite changes

Right-Click on "Refine"

[On the screen: Refine commands]

Set "Number of cycles" to 30

Select LeBail refinement for each phase; OK (Step 6)

OK; Yes+start

### Step 5

Powder options for phase: RT

Background

Legendre polynomials  Number of terms

Chebyshev polynomials  Use  $1/x$  term

Cos-ortho background

Cos-GSAS background

Shift parameters

shift	0	<input type="checkbox"/>
sycos	0	<input type="checkbox"/>
syain	0	<input type="checkbox"/>

RT

Esc Ok

### Step 6

Refine commands

Basic

Number of cycles: 30  Use Marquart technique  Sigma weight:  Instability factor:

Damping factor: 1  Fudge factor:   Instability factor from reflection statistics

Use Wilson's modification  Unit weight

Use dynamical LS method => if R<sub>w</sub> is increased by 10% reduce the damping by a factor 2

After 3 cycles try to enlarge it back.

Check for convergence => stop if max(change/s.u.) ≤ 0.05 in 1 consecutive cycles.

Disable atoms having too large displacement

Refinement:  Rietveld  Le Bail  ...

RT  LT

Automatic refinement keys

Automatic symmetry restrictions

Refinements on F(obs)\*\*2

Apply electroneutrality

Simulation run

After last cycle call Fourier

Correct for lambda/2 effect

Correct for lambda effect

Randomize atomic coordinates  Random seed:  Maximal random displacement in Ang:

Warning: the randomize procedure will be applied just once during the next run.

Esc Ok

## Notes

Refinement [5788/37+1] finishes with  $GOF \approx 3.3$ ,  $Rp \approx 1.3$ ,  $wRp \approx 2.0$

## 5. Correction for asymmetry

Start "Profile viewer" and investigate the powder profile

### Notes

*The peaks at low angles are slightly asymmetric, otherwise the profile fits very well  
Two rows of Bragg positions correspond to two phases, the second phase (LT) is the top row. Clicking on some of the Bragg positions gives information about  $h k l$ ,  $2\theta$  position and about the corresponding phase.*

Quit the profile viewer

Start "Edit profile"

[On the screen: Powder options for phase: RT]

Go to "Asymmetry/Diffractometer"

Select "correction by divergence"

Enable refining of  $HpS/L$ , set  $HmS/L$  to 0 and do not refine it.

Go to "Corrections"

Check "shift"

OK; YES;

Right click on Refine

In page "Basic" change the Damping factor to 0.5. OK; Yes + Start

### Notes

*Refinement finishes with  $GOF \approx 2.8$ ,  $Rp \approx 1.2$ ,  $wRp \approx 1.7$*

*Waiting for the full convergence is not necessary*

*The Le Bail fitting is now complete, create a backup copy!*

Start "File → Structure → Save as"

Make a backup copy "twoph\_lebail"

OK; **NO** (Do not continue with the new structure)

## III. Rietveld refinement

### 1. Importing structure models for RT and LT

#### Notes

*In this example, we could have imported the structure models of both phases at the beginning and make Le Bail fit with "Make only profile matching" refinement option. However, we want to demonstrate that structures can also be imported later on, e.g., in case when we need to test more structure models.*

*Structure models cannot be imported through "File - Import model from" because this would destroy the phases.*

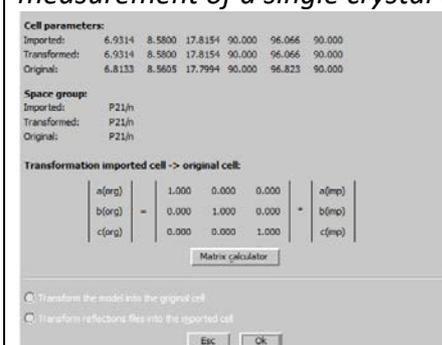
*In next steps, we rely on the previously created backup copy!*

Start "Tools → Phases → Delete Phase" and delete the phase LT

Start "File → Structure → Import model from CIF" and import the file "RT.cif"

#### Notes

The program retains the original unit cell, i.e. the one refined by the previous Le Bail fitting. This is important because the unit cell in RT.cif corresponds to the room temperature measurement of a single crystal while the powder data set was acquired at 150K



Start "Tools → Phases → **New Phase**"

[On the screen: *New phase*"]

Select "**Import from CIF format**"

Import the file "**LT.cif**"; OK; OK

Start "EditM50" and rename "**Phase#1**" to "**RT**", "**Phase#2**" to "**LT**"

Start "File → Structure → Copy In" and copy **only** M41 from the backup copy "**twoph\_lebail**"

By this, we obtain the previously refined profile parameters

Start refinement options, page "**Basic**", press "Select leBail/Rietveld refinement for each phase"; select **le Bail for both phases**

OK; Yes+Start

#### Notes

*Refinement results should be the same like in previous profile refinement:*

*GOF ≈ 2.7, Rp ≈ 1.2, wRp ≈ 1.7*

Start "File → Structure → **Save as**"

Make a backup copy "**twoph\_rietveld\_start**"

OK; **NO** (Do not continue with the new structure)

## 2. Rietveld refinement of both phases with fixed parameters

#### Notes

*In this example, we will use combination of rigid body with bond and bond-angle restraints. The rigid body approach will be applied on the RT phase because (i) this phase was known from single-crystal measurement and (ii) this is the minor phase. In fact, we are refining the RT phase only to get better results for the LT phase.*

Start "Edit profile"

**Uncheck a, b, c and beta for both phases**

**Uncheck GW and LY for both phases**

**Uncheck asymmetry correction**

**uncheck shift**

OK; YES

Right-Click on Refine

[On the screen: *Refine commands*]

Set "Number of cycles" to **100**

“Select leBail/Rietveld refinement for each phase” select **“Rietveld”** for both phases

Go to "Various" and open **“Fixed commands”**

For Atoms/Parameters” type \*; select **“All parameters”**; “Add”

By this, we created command **“fixed all \*”** fixing all structure parameters except scales  
OK; OK; YES (saving new refinement commands without starting refinement)

Parameters->Phase fraction (Step 7)

**Check phvol2**

**“Refine”**

Notes
Refinement finishes with RT [627=624+3/2]: $R(obs) \approx 10.2$ $wR(obs) \approx 11.9$ $R(all) \approx 10.3$ $wR(all) \approx 11.9$ LT [609=609+0/2]: $R(obs) \approx 9.7$ $wR(obs) \approx 13.0$ $R(all) \approx 9.7$ $wR(all) \approx 13.0$ Profile [5788/25+2]: $GOF \approx 13.9$ , $R_p \approx 5.8$ , $wRp \approx 8.6$ The factor <i>phvol2</i> refines to 0.83

### 3. Keep commands for hydrogen atoms of the LT phase

[On the screen: Basic window of Jana2006]

Go to "Edit Atoms"

“Switch phase” - Select **LT** phase

Select **“all carbon atoms, N2\_2 and N3\_2”** → action → **adding of hydrogen atoms”**

*N1\_2, Cl1\_2 and Cl2\_2* should not be selected

OK

[On the screen: Adding "hydrogen" atoms for "N2\_2"]

Geometry is **“Trigonal”** and neighbors are (**C7\_2, N1\_2**); "Apply->Go to next"(Step 1)

[On the screen: Adding "hydrogen" atoms for "N3\_2"]

Geometry is **“Trigonal”** and there is only **one** neighbor **C7\_2**; "Apply " (Step 2)

OK; YES

Step 1

Step #1: Select atoms to be used ; Phase : LT -> 9 selected

C5_2	N3_2				
C4_2	Cl1_2				
C6_2	Cl2_2				
C9_2					

Adding "hydrogen" atoms for "N2\_2"

Tetrahedral  Trigonal  Apical

H dist.: 0.87 ADP ext. factor: 1.2 Hydrogen(s): 2

Neighbor(s): C7\_2 1st N1\_2 2nd

Buttons: Avoid->Go to next, Quit, Apply->Go to next

Step #2: Select action by right mouse click or by this button: Action  
Left mouse double click starts the Edit/Define action  
Buttons: Esc, Ok

Step 2

Step #1: Select atoms to be used ; Phase : LT -> 9 selected

C5_2	N3_2				
C4_2	Cl1_2				
C6_2	Cl2_2				
C9_2					

Adding "hydrogen" atoms for "N3\_2"

Tetrahedral  Trigonal  Apical

H dist.: 0.87 ADP ext. factor: 1.2 Hydrogen(s): 1

Neighbor(s): C7\_2 1st

Buttons: Locate position in map, Avoid, Quit, Apply

Step #2: Select action by right mouse click or by this button: Action  
Left mouse double click starts the Edit/Define action  
Buttons: Esc, Ok

## Notes

By this we have generated fixed commands for hydrogen atoms. Total number of atoms should be 21

### 4. Rigid body for the RT phase

Right-Click on Refine

[On the screen: Refine commands]

Go to the page "Basic"

Set Damping factor to **0.1**

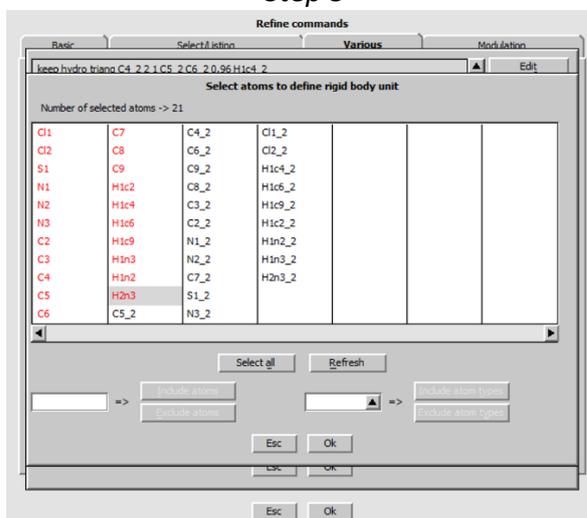
Go to the page "Various"; start "**Keep commands**"

Select "**Geometry**" and "**Rigid**" and click "**Select atoms**" button.

[On the screen: "Select atoms to define rigid body unit"]

Select **all atoms of the RT phase** (atoms **without** "\_2") (Step 1); OK; Add

#### Step 3



## Notes

The new keep command has the following form: "keep geom rigid C1 C2 S1 N1 N2 N3 C2 C3 C4 C5 C6 7 C8 C9 H1c2 H1c4 H1c6 H1c9 H1n3 H1n2 H2n3"

OK;

### 5. Set bond and bond-angle restraints for LT phase

## Notes

In the next we will use pre-prepared "distfix" and "anglefix" commands based on the geometry of the RT phase. RT phase was solved from single crystal; hence, we suppose that its geometry is correct. The format of the commands is: key word, value of the restraint, sigma (connected to the weight of the restraint in the refinement), list of atoms

[On the screen: Refine commands]

Go to "Distance restraints"

Click "Edit" to open the text file editor.

Paste all lines from distfix.txt or from this Cookbook

Close the text file editor and save changes

OK

Notes

```
distfix 1.736 0.001 C5_2 Cl1_2
distfix 1.401 0.001 C3_2 C5_2
distfix 1.376 0.001 C4_2 C5_2
distfix 1.460 0.001 C2_2 C3_2
distfix 1.400 0.001 C8_2 C3_2
distfix 1.369 0.001 C6_2 C4_2
distfix 1.265 0.001 N1_2 C2_2
distfix 1.741 0.001 Cl2_2 C8_2
distfix 1.375 0.001 C9_2 C8_2
distfix 1.371 0.001 C9_2 C6_2
distfix 1.371 0.001 N2_2 N1_2
distfix 1.345 0.001 C7_2 N2_2
distfix 1.685 0.001 S1_2 C7_2
distfix 1.313 0.001 N3_2 C7_2
```

[On the screen: Refine commands]

Go to "**Angles restraints**"

Click "Edit" to open the text file editor.

Paste all lines from the file anglefix.txt or from this Cookbook)

Close the text file editor and save changes

OK

Notes

```
anglefix 121.977 0.01 C3_2 C5_2 Cl1_2
anglefix 115.676 0.01 C4_2 C5_2 Cl1_2
anglefix 122.347 0.01 C4_2 C5_2 C3_2
anglefix 126.236 0.01 C2_2 C3_2 C5_2
anglefix 114.761 0.01 C8_2 C3_2 C5_2
anglefix 120.262 0.01 C6_2 C4_2 C5_2
anglefix 118.989 0.01 C8_2 C3_2 C2_2
anglefix 124.469 0.01 N1_2 C2_2 C3_2
anglefix 120.003 0.01 Cl2_2 C8_2 C3_2
anglefix 123.439 0.01 C9_2 C8_2 C3_2
anglefix 119.969 0.01 C9_2 C6_2 C4_2
anglefix 116.048 0.01 N2_2 N1_2 C2_2
anglefix 116.553 0.01 C9_2 C8_2 Cl2_2
anglefix 119.211 0.01 C6_2 C9_2 C8_2
anglefix 119.412 0.01 C7_2 N2_2 N1_2
anglefix 119.203 0.01 S1_2 C7_2 N2_2
anglefix 116.961 0.01 N3_2 C7_2 N2_2
anglefix 123.835 0.01 N3_2 C7_2 S1_2
```

## 6. ADP for the RT and LT phase

*[On the screen: Refine commands]*

Start "**Fixed commands**"

Delete the "**fixed all \***" command created previously

Select "**ADP harmonic parameters**"

For "Atoms/Parameters" type "**Cl1 Cl2 S1 N1 N2 N3 C2 C3 C4 C5 C6 C7 C8 C9 H1c2 H1c4 H1c6 H1c9 H1n3 H1n2 H2n3**"

Add; OK

Notes

*This fixes ADP of all atoms of the RT phase to the values refined from the single crystal data*

*[On the screen: Refine commands]*

Go to "**Restrictions**"

Notes

*We will define one common ADP parameter for all non-hydrogen atoms of LT phase*

Uncheck "**Make identical coordinates**"

Check "**For atoms/molecules**"

Check "**Make identical ADP parameters**"

For occupancies use "**not restricted**"

For "Atoms/Parameters" type "**C5\_2 C4\_2 C6\_2 C9\_2 C8\_2 C3\_2 C2\_2 N1\_2 N2\_2 C7\_2 S1\_2 N3\_2 Cl1\_2 Cl2\_2**" (Step 1)

Add; OK

### Step 1

Load

For atoms/molecules  For powder profiles

**Make identical:**  Coordinates **Occupancies:**  keep overall sum  
 ADP parameters  not restricted

Atoms: C5\_2 C4\_2 C6\_2 C9\_2 C8\_2 C3\_2 C2\_2 N1\_2 N2\_2 C7\_2 S1\_2 N3\_2 Cl1\_2 Cl2\_2

OK; OK; **YES**; (saving refinement commands without starting refinement)

**Make a backup copy**

**"Refine"**

Press **"Use all"** as a reply to the message about significant discrepancy

#### Notes

*Refinement finishes with*

*RT [627=622+5/8]: R(obs) ≈ 4.2 wR(obs) ≈ 4.9 R(all) ≈ 4.2 wR(all) ≈ 4.9*

*LT [609=608+1/45]: R(obs) ≈ 3.7 wR(obs) ≈ 5.0 R(all) ≈ 3.7 wR(all) ≈ 5.0*

*Profile [5788/25+51]: GOF ≈ 6.3, Rp ≈ 2.6, wRp ≈ 3.9*

*Plot both structures by "Plot structure" and check them*

*[On the screen: main windows Jana2006]*

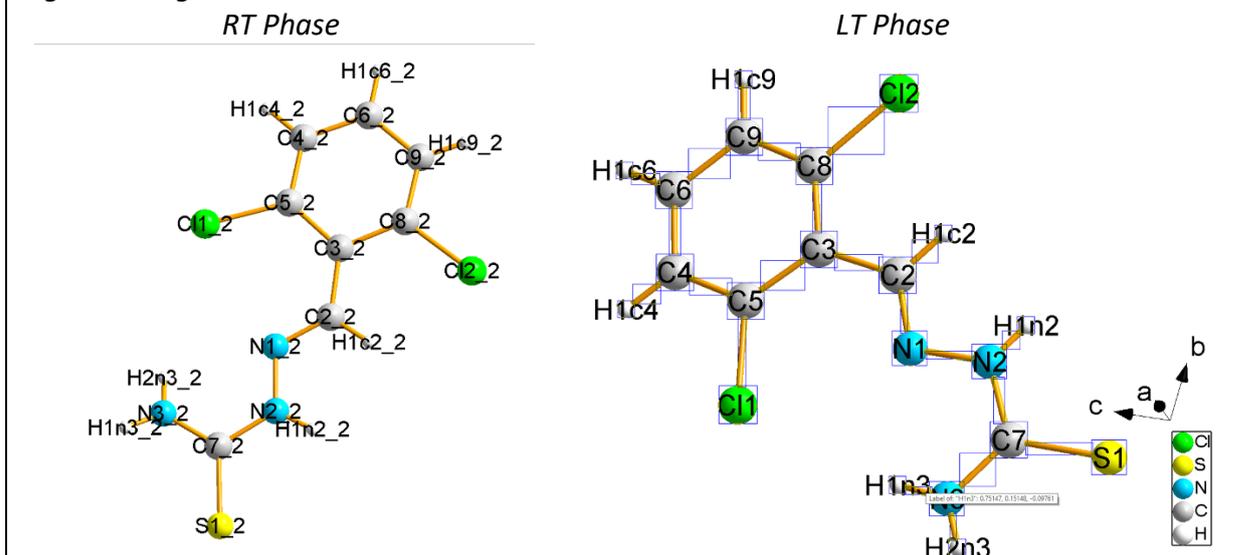
Select **RT** phase -> Plot structure-> Draw+continue

Repeat the procedure for **LT** phase

[On the screen: window of Diamond]

To draw the structure press  then right click on an atom and select all molecule(s).

Right click again then Add -> Atom labels



## 7. Fine tuning the profile parameters

Start **"Edit Profile"**

Switch to the **"LT"** phase

Activate refinement of "a, b, c, and beta"  
 Go to the page "Profile"  
 Activate refinement of "GW" and "LY" of LT phase  
 Go to the page "Corrections"  
 Activate refinement of "shift"  
 Go to the page "Sample"  
 For Preferred orientation select "March-Dollase"  
 Set "pref1" to 1, activate its refinement and for "Direction" type "0 1 0"

#### Notes

*This corresponds to the longest unit cell parameter of the LT phase*

Still in the Sample page, switch to the RT phase  
 For Preferred orientation select "March-Dollase"  
 Set "pref1" to 1, activate its refinement and for "Direction" type "0 0 1"  
 Activate refinement of "a, b, c, and beta"  
 Go to the page "Profile"  
 Activate refinement of "GW" and "LY" of LT phase

#### Notes

*This corresponds to the longest unit cell parameter of the RT phase*

OK; YES (to save profile parameters)  
 Run "Refine"  
 Yes Use all

#### Notes

*Refinement finishes with*  
*RT :R(obs)  $\approx$  3.7, wR(obs)  $\approx$  4.3, R(all)  $\approx$  3.7, wR(all)  $\approx$  4.3*  
*LT :R(obs)  $\approx$  3.2, wR(obs)  $\approx$  4.3, R(all) = 3.2, wR(all)  $\approx$  4.3*  
*Profile:GOF  $\approx$  5.5, Rp  $\approx$  2.4, wRp  $\approx$  3.4*

## 8. The final model

#### Notes

*Finally, we will remove ADP restrictions for heavy atoms of the LT phase*

Right-click on Refine  
 [On the screen: Refine commands]  
 Go to the page "Various" and start "Restrictions"  
 Load the restriction command, delete Cl1\_2, Cl2\_2 and S1\_2, rewrite the command  
 OK; OK; Yes+start

#### Notes

*Refinement finishes with*  
*RT :R(obs)  $\approx$  3.6 wR(obs)  $\approx$  4.2 R(all)  $\approx$  3.6 wR(all)  $\approx$  4.2*  
*LT :R(obs)  $\approx$  3.1 wR(obs)  $\approx$  4.3 R(all)  $\approx$  3.1 wR(all)  $\approx$  4.3*  
*Profile : GOF  $\approx$  5.5, Rp  $\approx$  2.4, wRp  $\approx$  3.3*

*In case the convergence is too slow, Marquardt refinement can be activated by pressing "Parameters" during the refinement. In such case damping factor can be increased to 0.5.*



## References

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# Example 2.5.2: CandAt

Revised 6 March 2019

Data	Topic	Level
Simulated X-ray powder data	Refinement of the mixture	Basic

## Tasks

---

Multiphase powder refinement of a mixture of calcite with aragonite

Load data and known crystal structure of calcite from the cif file

Adding second phase with unknown crystal structure manually

Le Bail refinement of both phases

Structure solution of the unknown phase

Rietveld refinement of the unknown phase

## Initial data

---

### Data

Powder diffraction profile was simulated by program JANA2006 for Debye-Scherrer geometry (capillary), Cu K $\alpha$ 1 and focusing mirror.

### Input files:

CandAt.xy

calcite.cif

### Additional information:

unit cell of the unknown phase is 4.96 7.97 5.74 90 90 90, *Pm**cn*

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## Instructions

---

### I. Data import

#### 1. Creating new jobname

Start Jana2006  
"File -> Structure -> New" opens the file manager  
Left pane: locate directory with input files  
Right pane: double-click **CandAt**  
OK;

#### 2. Import wizard

*[On the screen: Specify type of the file to be imported]*  
Select "from CIF"; NEXT  
*[On the screen: Select input CIF file]*  
Double-click on calcite.cif;  
YES (to import data from file)  
*[On the screen: Specify type of the file to be imported]*  
Select "Powder data – various CW formats"; NEXT  
*[On the screen: Powder data from:]*  
Browse and double-click on CandAt.xy file  
Select "Free format of 2th, I, [sig(I)]"  
Select "Debye-Scherrer method"; NEXT  
*[On the screen: Complete/correct experimental parameters]*  
Click on "X-ray tube" and select Cu  
(unit cell should be loaded from the cif file as 4.9907 4.9907 17.0634 90 90 120)  
NEXT;FINISH;OK;YES  
(You should be in the main JANA's window)

### II. Le Bail refinement

#### 3. Fast check of the powder diffraction profile

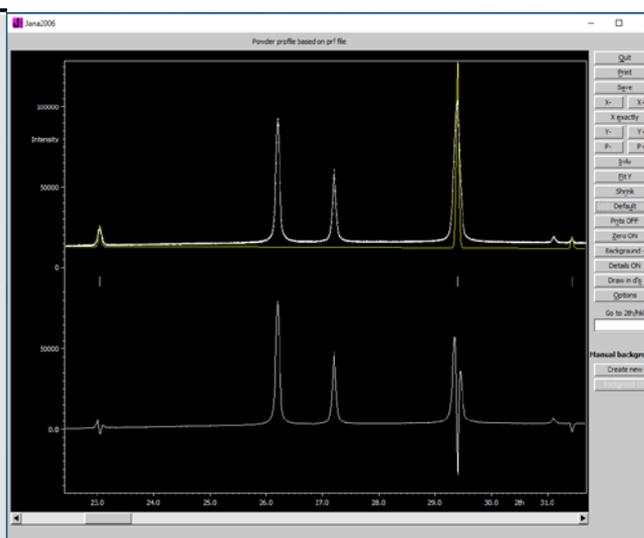
*[On the basic JANA2006 window]*  
Right-click on "Refine"  
*[On the screen: Refine commands]*  
Check "Make only profile matching (le Bail refinement)" (Step 1)  
OK; YES+start  
Let it converge and press NO  
*[On the basic JANA2006 window]*  
Double click in "Profile viewer"  
Zoom for example to the low angles and see unexplained reflections (Step 2)

## Step 1

**Refine commands**

Basic	Select/Listing	Various	Modulation
Number of cycles: 10	<input type="checkbox"/> Use Marquart technique	<input checked="" type="radio"/> Sigma weight	Instability factor: 0.01
Damping factor: 1	<input type="checkbox"/> Fudge factor	<input type="checkbox"/> Instability factor from reflection statistics	
		<input type="checkbox"/> Use Wilson's modification	
		<input type="radio"/> Unit weight	
<input checked="" type="checkbox"/> Use dynamical LS method => if R <sub>w</sub> is increased by 10% reduce the damping by a factor 2	After 3 cycles try to enlarge it back.		
<input checked="" type="checkbox"/> Check for convergence => stop if max(change/s.u.) ≤ 0.05 in 1 consecutive cycles.			
<input checked="" type="checkbox"/> Disable atoms having too large isotropic ADP parameter => ADP(iso) limit for disabling 0.2			
<input checked="" type="checkbox"/> Automatic refinement keys	<input type="checkbox"/> Apply Berar's correction		
<input checked="" type="checkbox"/> Automatic symmetry restrictions	<input checked="" type="checkbox"/> Make only profile matching (ie Ball refinement)		
<input type="checkbox"/> Refinements on F(obs)**2	1 Frequency of le Ball decomposition		
<input type="checkbox"/> Apply electroneutrality			
<input type="checkbox"/> Simulation run			
<input type="checkbox"/> After last cycle call Fourier			
<input type="checkbox"/> Correct for lambda/2 effect			
<input type="checkbox"/> Correct for lambda effect			
<input type="checkbox"/> Randomize atomic coordinates	Random seed: <input type="text"/>	Maximal random displacement in Ang: <input type="text"/>	
Warning: the randomize procedure will be applied just once during the next run.			
Esc Ok			

## Step 2



### Notes

*Some peaks do not have corresponding Bragg position. This is the indication of a multiphase (we believe our unit cell)*

Leave profile viewer by "QUIT"

## 4. Importing the second phase

Start "Tools -> Phases -> New phase" (Step 3)

[On the screen: New phase]

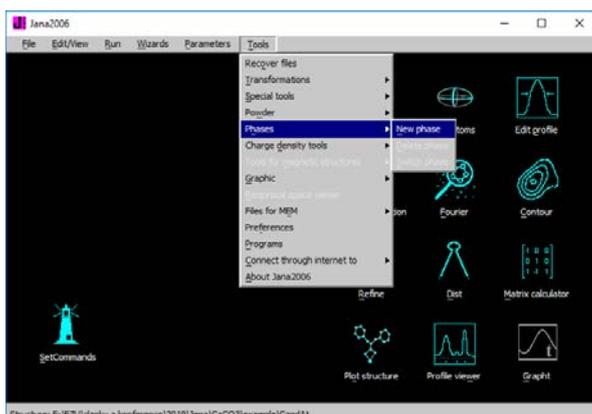
Select "Manually"; OK (Step 4)

[On the screen: Define/ modify basic structural parameters for phase: Phase#2]

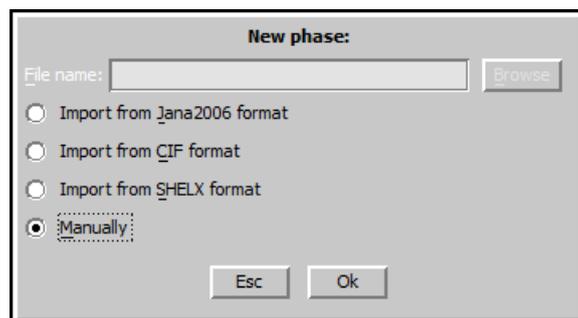
For "Cell parameters" type "4.96 7.97 5.74 90 90 90";

OK; YES to rewrite M50

### Step 3



### Step 4



#### Notes

In the lower left corner of the Jana2006 basic window two new thumbnails appear: "Phase#1" and "Phase#2".

They are used for switching between the two phases. Many tools of Jana2006 work only with the active phase, for instance "Fourier", "Dist", "Contour" and "Plot structure".

Before

starting these tools, the required phase must be activated.

Some other tools like "EditM50" and "Edit profile" can switch the phase internally.

EditM50 Edit profile

"Refine" and "Profile viewer" work independently on the active phase.

## 5. Set Phase labels and symmetry

Start "EditM50"

[On the screen: Define/ modify basic structural parameters for phase: Phase#1]

Ensure that Phase#1 is selected at the bottom of the EditM50 window.

For "Phase label" type "CA" like calcite (Step 1)

Still in the EditM50 window, switch to the Phase#2

For "Phase label" type "AR" like aragonite (Step 2)

[On the tab: Composition]

Switch to the CA phase and check the composition (Formula – list of atomic types).

It should be there "C Ca O3"

Switch to the AR phase and write the composition (Formula – list of atomic types) in the same atomic order "C Ca O3".

(Keep the same order of atomic types!)

OK; YES to rewrite M50

## 6. Le Bail refinement

Start "Edit profile"

*[On the screen: Powder options for phase: CA]*

Ensure that the CA phase is selected at the bottom of the form.

In page "Cell" activate refinement of a and c

Select AR phase

In page "Cell" activate refinement keys of a, b and c

*[On the tab: Profile]*

Go to the page "Profile"

For each phase select "Pseudo-Voigt" and activate refinement keys for GW and LY

*[On the tab: Asymmetry/Diffractometer]*

Asymmetry is independent on a phase selection

Select asymmetry model for "correction by divergence"

Set HpS/L to 0.03

Set HmS/L to 0

*[On the tab: Corrections]*

Corrections are independent on a phase selection

For "Background", select "Legendre polynomials" and for "Number of terms" type 15

Activate refinement of "shift"

OK; YES to rewrite changes

*[On the basic JANA2006 window]*

Right-Click on "Refine"

*[On the screen: Refine commands]*

Set "Number of cycles" to 15

Set Damping factor to 0.5

Press "Select LeBail/Rietveld refinement for each phase" and choose le Bail for both; OK

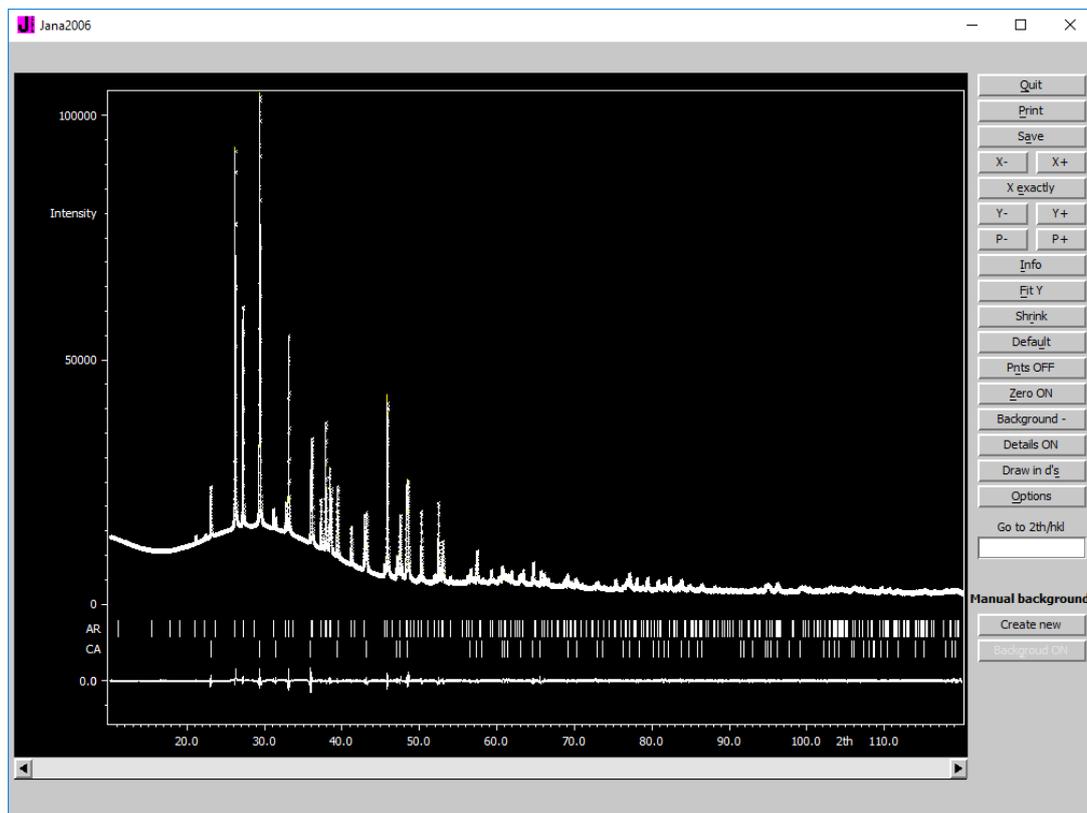
OK; Yes+start

Notes
<i>Refinement finishes with GOF = 2.27 , Rp = 1.73, wRp = 2.72</i>

*[On the basic JANA2006 window]*

Go to the "Profile viewer" and check the resulted profile fit (Step 5)

Step 5



The Le Bail fitting is now complete, create a backup copy!

Start "File -> Structure -> Save as"

Make a backup copy "CandAt\_lebail"

OK; NO (Do not continue with the new structure)

### III. Structure solution of the AR phase

#### Notes

*In our case, calcite represents impurity and it is also the known phase. Aragonite represents the unknown phase, that we would like to solve and refine. To start the structure solution process in Superflip, we have to eliminate contribution of reflections from the impurity (calcite) to the reflections of the unknown phase (aragonite). There are basically two possibilities, how to do that: (i) in the case of negligible peak overlap or without the knowledge of the crystal structure of the impurity, we can simply remove the contribution of the impurity by pure Le Bail refinement where all intensities are extracted just from the measured pattern. (ii) However, it is much better to use the known crystal structure of the impurity and remove its contributions according to its calculated intensities. Combined Rietveld and Le Bail refinement can do this. We are going to do the second (ii) method.*

## 7. definition of the combined Rietveld/Le Bail refinement

[On the basic JANA2006 window]

Right-click on "Refine"

[On the screen: Refine commands]

Set "Number of cycles" to 30

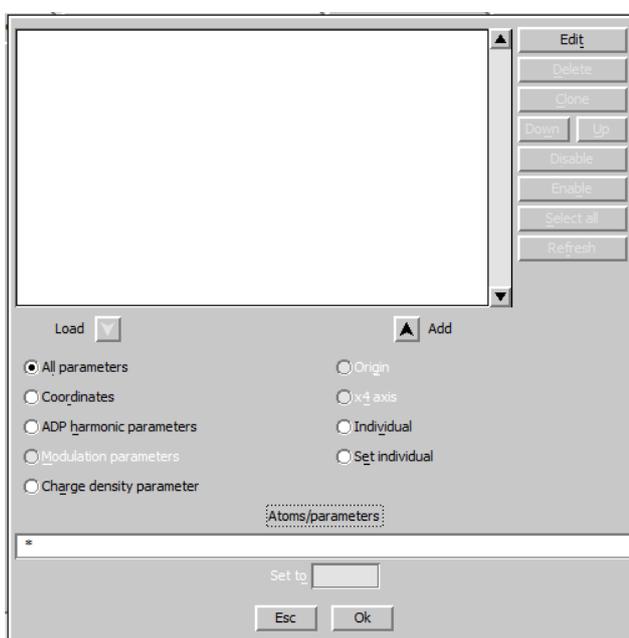
Press "Select LeBail/Rietveld refinement for each phase" and choose Rietveld for Ca phase and Le Bail for AR phase; OK

[On the tab: Various]

Go to "Fixed commands"

Write "\*" to the Atoms/parameters and press "Add" to fix all atomic parameters (to fix structure of the CA phase for this moment) (Step 1)  
OK; OK; Yes+start

### Step 1



### Notes

*Refinement finishes with GOF = 2.30 , Rp = 1.77, wRp = 2.75*

## 8. Structure solution of the AR phase

[On the basic JANA2006 window]

**Important:** Switch to the **AR phase** (left bottom).

Go to “Structure solution” to solve structure of AR

[On the screen: Structure solution]

Check “Repeat Superflip: Until the convergence detected”

Set “Maxcycles” to 2000

Press “Run solution”

OK (accept the error message, that AR phase does not contain any atom)

### Notes

Check the Superflip's output file and find there the derived space group. It should be Pmcn.

Close

[On the screen: Structure solution]

Press “Change the space group”

[On the screen: Define space group]

Write “Pmcn” to Space group

OK; YES

### **REPEAT**

[On the screen: Structure solution]

Check “Repeat Superflip: Until the convergence detected”

Set “Maxcycles” to 2000

Select “EDMA – fixed number of atoms” for the peaks search method and leave there the default value of 40.

Press “Run solution”

OK (accept the error message, that AR phase does not contain any atom)

[After finishing Superflip]

Press “Draw structure”; “Draw+continue”

If the crystal structure does not contain CO<sub>3</sub> groups and Ca cation is not coordinated by 9 oxygen atoms return to **REPEAT** and try to solve it again. Result of structure solution process is unpredictable and it may happen that you end up with some partial solution, which will complicate you the rest part of the example.

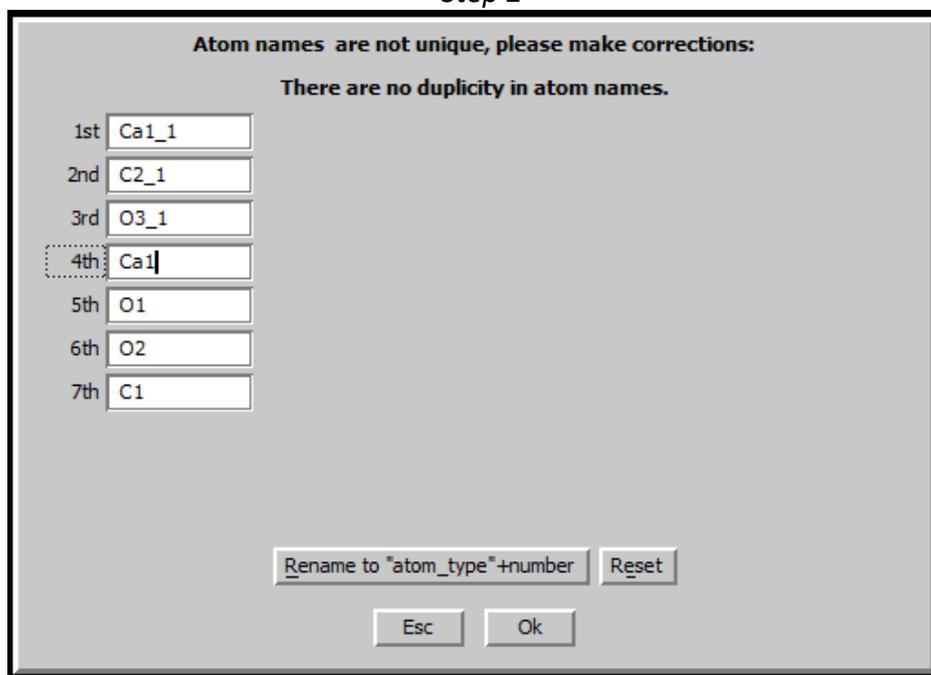
Press “Accept last solution”

[On the screen: Atom names are not unique, please make corrections:]

Change atom names of first three atoms to Ca1\_1, C2\_1, O3\_1 that correspond to calcite phase (Step 2)

OK

### Step 2



The structure solution is now complete, create a backup copy!

Start "File -> Structure -> Save as"

Make a backup copy "CandAt\_solution"

OK; NO (Do not continue with the new structure)

## IV. Rietveld refinement

### 9. Carefully initialize Rietveld refinement – refine scale, phase fraction and background

[On the basic JANA2006 window]

Go to "Edit Profile"

[On the screen: Powder options for phase: AR]

Go to Cell tab:

Uncheck refinement of unit cell parameters for both phases CA and AR

Go to Profile

Uncheck all profile parameters for both phases CA and AR

OK; YES

[On the basic JANA2006 window]  
Menu -> Parameters -> Phase fraction  
[On the screen: Edit phase fraction]  
Allow refinement of the phvol2  
OK; YES

[On the basic JANA2006 window]  
Right-click on "Refine"  
[On the screen: Refine commands]  
Press "Select LeBail/Rietveld refinement for each phase" and choose Rietveld for both phases; OK  
[On the tab: Various]  
Go to "Fixed commands"  
Ensure, that the command for fixing all atomic parameters is still there, otherwise create it:  
Write "\*" to the Atoms/parameters and press "Add" to fix all atomic parameters of both phases  
OK; OK; Yes+start

#### Notes

*Refinement finishes with GOF = 3.19 , Rp = 2.31, wRp = 3.83*

### 1. Perform Rietveld refinement of the AR phase

[On the basic JANA2006 window]  
Right-click on "Refine"  
[On the tab: Various]  
Go to "Fixed commands"  
Delete the previous fixed command  
Write "\*\_1" to the Atoms/parameters and press "Add" to fix all atomic parameters of CA phase (because all atomic labels in this phase ended up with \_1)  
OK; OK; Yes+start

#### Notes

*Refinement finishes with GOF = 2.39 , Rp = 1.84, wRp = 2.86*

[On the basic JANA2006 window]  
Go to "Edit Profile"  
[On the screen: Powder options for phase: AR]  
Go to Cell tab:  
Allow refinement of unit cell parameters for both phases  
Go to Profile  
Allow GW and LY parameters for both phases  
OK; YES

[On the basic JANA2006 window]

Right-click on "Refine"

[On the screen: Refine commands]

Set "Number of cycles" to 30

OK; Yes+start

#### Notes

*Refinement finishes with  $GOF = 2.36$ ,  $Rp = 1.83$ ,  $wRp = 2.83$*

*If the refinement does not converge, disable refinement of the unit cell and profile parameters of the CA phase*

[On the basic JANA2006 window]

Go to "Plot structure"; "Draw+continue" to draw the crystal structure

[On the basic JANA2006 window]

Menu -> Edit/View -> View of Refine

Phase ratio is on the last page of the log file (Step 3)

#### Step 3

```
Jana2006
-----
Find Find_next Go to Print PgTop Open in editor Close
su 0.000000 0.000000 0.000579 0.000610 0.001468
=====
There were no correlations larger than 0.900 in the last refinement cycle
Relative phase amounts in mass
CA 0.3584(9)
AR 0.6416(10)

Refinement program
structure :

Program started at 16:40:57 ended at 16:42:10 cpu time : 73.02
```

# Example 2.6: CaTeO<sub>3</sub> cyclic

Revised: 8 March 2019

Data	Topic	Level
X-ray Powder data	Cyclic refinement	Intermediate

## Tasks

We will study the dehydration of CaTeO<sub>3</sub>(H<sub>2</sub>O) as function of the temperature.

**Room temperature phase:  $\alpha$ -CaTeO<sub>3</sub>(H<sub>2</sub>O):**

Cell parameters: 14.78125 6.78762 8.059512 90 90 90, Space group: *P2<sub>1</sub>cn*

**High temperature phase at 330°C:  $\delta$ -CaTeO<sub>3</sub>**

Cell parameters: 13.32299 6.528064 8.171151 90 90 90, Space group: *P2<sub>1</sub>ca*

## Initial data

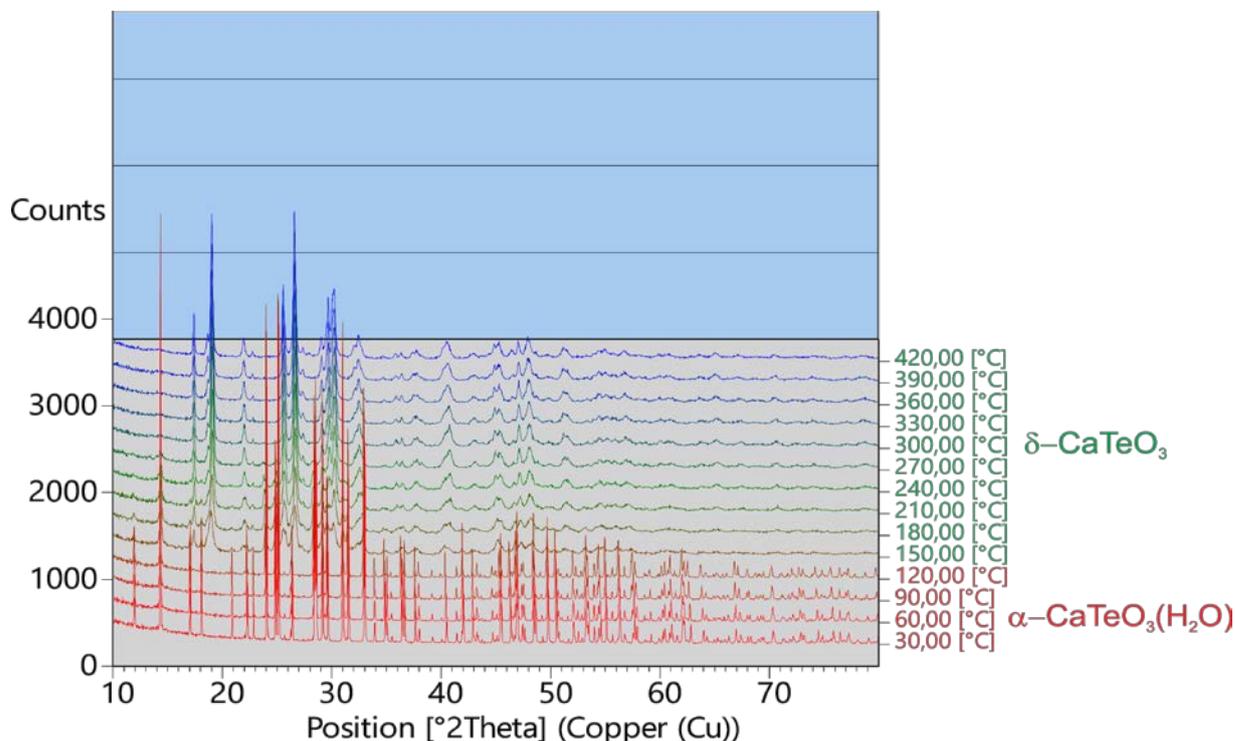
### Data

Laboratory diffractometer Bruker D8,  $\lambda$  CuK $\alpha$ 1

### Input files:

NB-LM01MO\_030, NB-LM01MO\_060, NB-LM01MO\_090, NB-LM01MO\_120, NB-LM01MO\_150, NB-LM01MO\_180, NB-LM01MO\_210, NB-LM01MO\_240, NB-LM01MO\_270, NB-LM01MO\_300, NB-LM01MO\_330, NB-LM01MO\_360, NB-LM01MO\_390, NB-LM01MO\_420,  
+ two directories with pre-refined structures of both phases

### Additional information – powder profiles:



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## Instructions

---

### I. Data import

#### 1. Creating new jobname for cyclic refinement

Start Jana2006

[On the screen: Basic Jana window]

“File → Cyclic refinement → New” opens a file manager

[On the screen: New : Select the master file for cyclic refinement]

Left pane: locate directory with input files

Right pane: Use any job name, for example “CaTeO3”;

OK;

#### 2. Creation of the master file and specifying data files for cyclic refinement

[On the screen: Create the master file and define/import data files]

Press “Define/Copy data files”;

#### Notes

All files for cyclic refinement must be present in the working directory. In the case, that files are located in different directory, the program will copy them to the actual working directory.

[On the screen: Select/import data files”]

Select all files with extension “XRDML”; OK

[On the screen: Create the master file and define/import data files]

Change the units from K to C;

Press “Define individual temperatures”;

[On the screen: Define temperature for imported files]

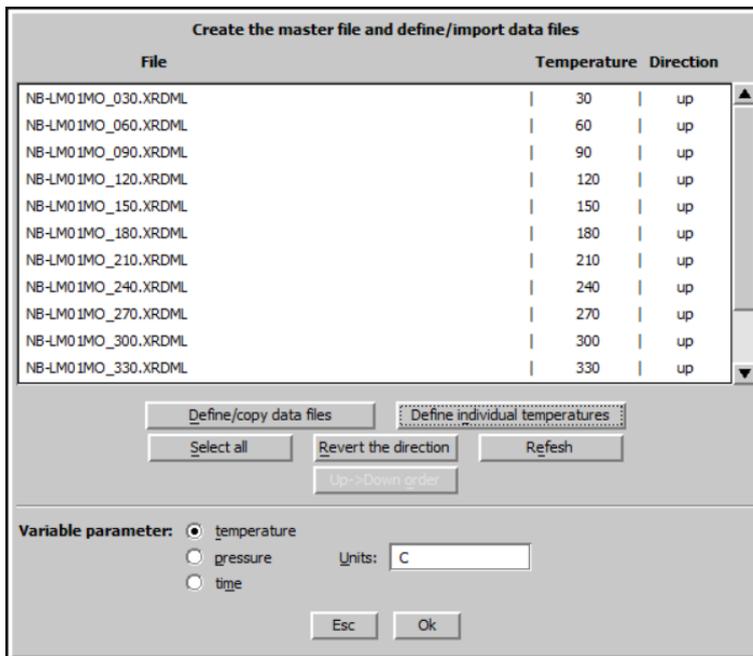
Select “Derive them from file names”;

Rewrite the substring in the file name, which defines the actual temperature by the question marks: NB-LM01MO\_030.XRDML→ NB-LM01MO\_???.XRDML;

OK;

#### Notes

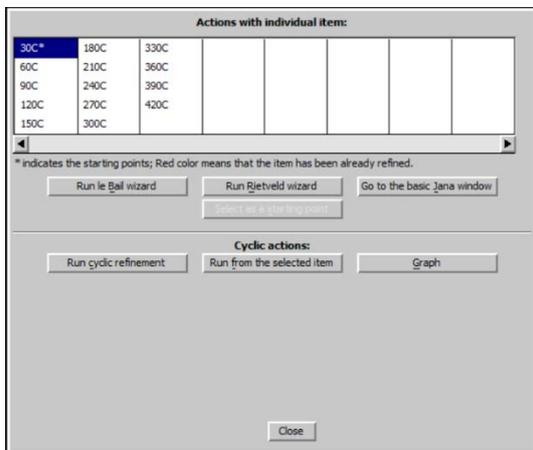
Once you define the place in the file name where the temperature is located, Jana will assign the temperature to every input file automatically, see the following figure.



OK; YES to continue with cyclic refinement right now.

## II. Le Bail refinement

### 1. Preparing the starting point based on the $\alpha$ phase



[On the screen: Actions with individual item:]

Select the data labeled as **30C**;

Press "Run le Bail wizard";

[On the screen: Specify type of the file to be imported:]

Select "various CW formats"; Next;

Select "PANalytical XRDML";

For method select "**Bragg-Brentano method- Fixed Divergence Slit**"; Next;

[On the screen: Complete/correct experimental parameters]

Enter cell parameters: 14.78125 6.78762 8.059512 90 90 90;  
 Radiation: X-ray; Cu wavelength is **1.540598**  
 Uncheck Kaplha1/Kalpha2 doublet;  
 Press "Set glancing angle"; for Material select **Ge**; for Reflection plane type **1 1 1**; Press  
 "=>" to calculate the glancing angle; OK  
 Rewrite temperature to 303 (it is in Kelvins); Next; Finish; OK;  
 "Yes" to accept made changes;  
 "Yes" to continue with wizard;

#### Notes

*The le Bail refinement for the starting point can be done manually step by step by using the wizard. However, as the main purpose of this example is to show how the cyclic refinement works, we shall import the already completed refinement that was made in advance. This will save the time for now. Importing can be made from the subdirectory "alpha" by using "copy in" button.*

*[On the screen: Refinement of the powder profile by the le Bail algorithm]*

Press the button "Copy in";

*[On the screen: Select the name from where to read]*

Go to the subdirectory "alpha" and select the structure "NB-LM01MO\_030";

OK

*[On the screen: Refinement of the powder profile by the le Bail algorithm]*

Press "Edit profile parameters"; Go to page "Asymmetry/Diffractometer" to see parameters used for fundamental approach:

*fundamental approach:*

The screenshot shows the 'Powder options' dialog box with the 'Asymmetry/Diffractometer' tab selected. The 'fundamental approach' radio button is selected. The parameters are as follows:

Parameter	Value	Checked
No correction		<input type="radio"/>
Howard (Boole's rule)		<input type="radio"/>
Berar-Baldinozzi correction		<input type="radio"/>
correction by divergence		<input type="radio"/>
fundamental approach		<input checked="" type="radio"/>
Debye-Scherrer integration		<input type="radio"/>
Primary radius [mm]	217.5	
Secondary radius [mm]	217.5	
RS width [mm]	0.2	<input checked="" type="checkbox"/>
FDS angle [deg]	0.2	<input checked="" type="checkbox"/>
Source length [mm]	12	
Sample length [mm]	16	
RS length [mm]	12	
Primary soller [deg]	2.5	<input checked="" type="checkbox"/>
Secondary soller [deg]	2.5	<input checked="" type="checkbox"/>

In page "correction" unselect "shift" and select "sycos"

In page "profile" allow refinement of **CSizeL** (value around 552) and **StrainG** (0.2), keep fixed **CSizeG** (10000) and **StrainL** (0)

In page "Cell" allow refinement of the unit cell

OK  
Press "Edit refine parameters";  
Number of cycle 15; Damping factor 0.5  
OK; YES to save changes  
"Run Refine";

#### Notes

*The refinement result shows that we have properly described profile.*

When the refinement is done, go to Edit Profile again and uncheck Csize and StrainG.  
Uncheck "sycos"; OK; YES  
Finish; "Yes" to close the refinement tool.

## 2. Cyclic refinement with a single-phase starting point

*[On the screen: Actions with individual item]*

Press "Run cyclic refinement";

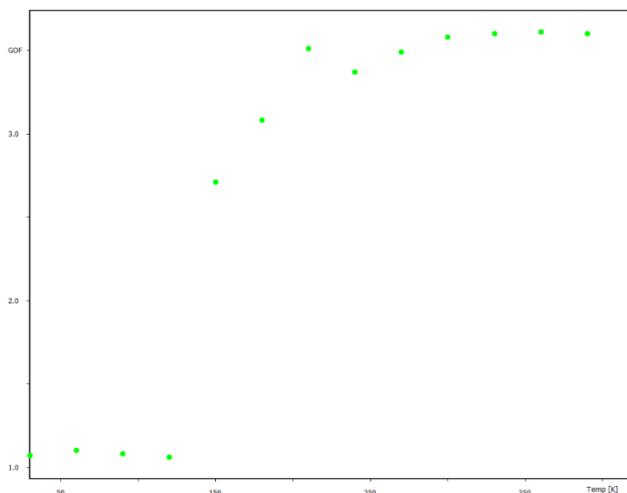
*After several minutes, all powder profiles are refined.*

Press "Graph";

Press "New graph";

*[On the screen: Define parameter to be drawn]*

Select "R factors" and "GOF";



#### Notes

*The GOF values for the range of temperatures 30-120 °C indicate a very good fit GOF~1. For higher temperatures, the fit is considerably worse GOF~3. This means the profile parameters refined at 30 C are not good starting point for higher temperatures.*

Select the temperature 120C;

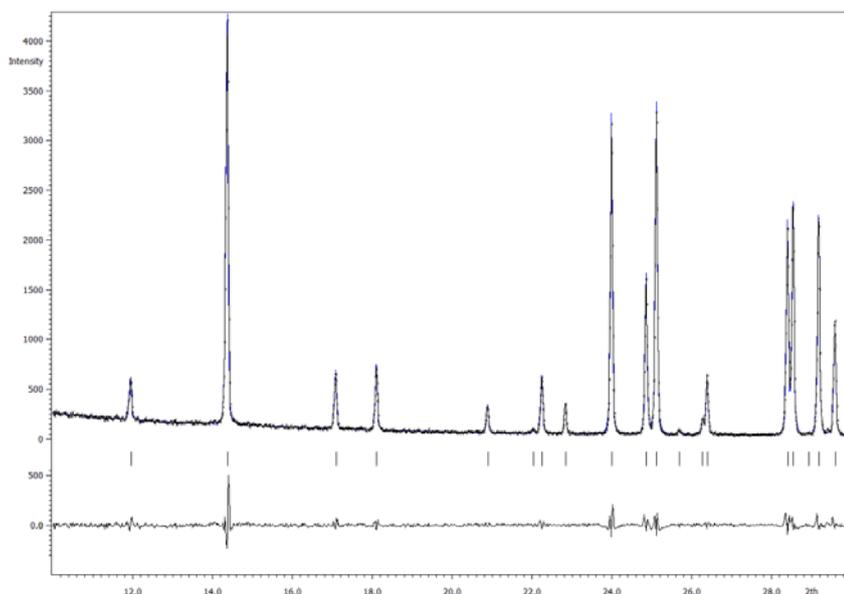
Press "Go to the basic Jana window";

Run "Profile viewer";

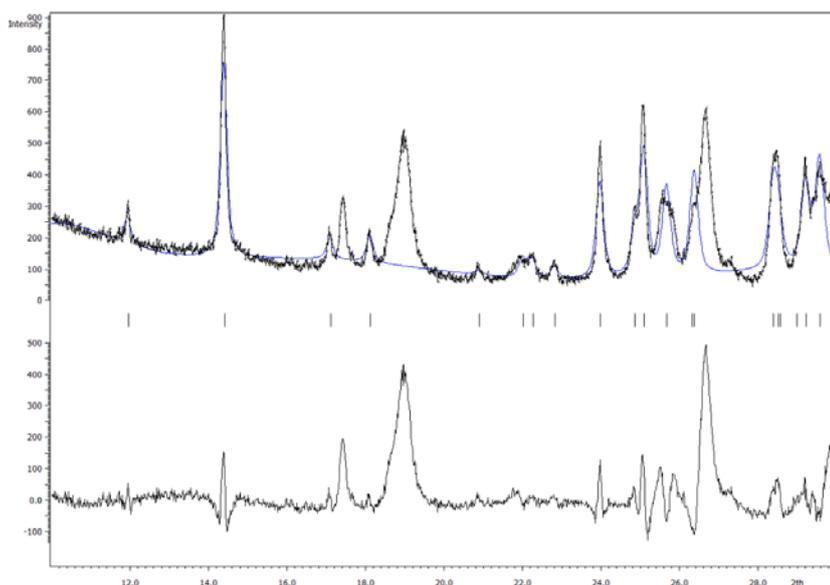
Press "X exactly" and select the range 10-30 in 2th:

QUIT

Press "Return to cyclic wizard" in the lower right corner of the Jana2006 basic window



Repeat the same for the temperature 150C:



#### Notes

*This clearly indicates the presence of the second phase in the pattern, that has to me introduced. Check also the diffraction patterns at other temperatures. This will show you that the phase transition due to dehydration runs over a certain range of temperatures.*

Quit; Return to cyclic wizard;

### 3. Cyclic refinement with a multi-phase starting point

*[On the screen: Actions with individual item:]*

Select the temperature 30C;

Press the button "Go to the basic Jana window";

*[On the screen: Basic Jana window]*

Run "Tools→Phases→New phase;"

[On the screen: New phase]

Use "Import from Jana2006 format";

Browse for the directory "delta" and select the file NB-LM01MO\_330.m50;

OK; OK

Right-Click on Refine

[On the screen: Refine commands]

Set number of cycle 15; Damping factor 0.3

Go to "Various" and open "Restrictions"

Select "For powder profile";

Write to the window of phases with identical profiles: Phase#1 Phase#2; "Add";OK

#### Notes

*This restriction will make the profile parameters of both phases identical.*

In page "Basic" press "Select leBail/Rietveld refinement for each phase" and select "leBail" for both phases

OK; Yes; (to save refinement commands without starting refinement);

Run "Edit profile"

On the page "Cell" ensure that for the Phase#2 the refinement of cell parameters is not allowed;

On the page "Profile" enable refinement of Csize and StrainG for both phases.

Ok; "Yes" to rewrite files;

Run "Refine";

#### Notes

*This makes multiphase refinement of the low temperature phase (despite the high temperature phase is missing at this temperature)*

press "Return to the cyclic wizard";

"Run cyclic refinement";

*After a few minutes, all powder profiles are refined like a multiphase.*

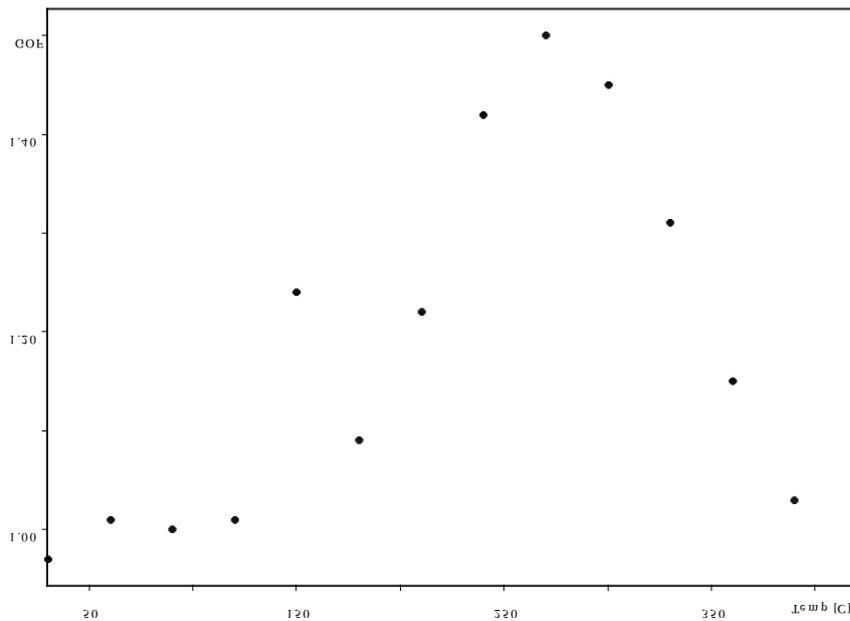
Press "Graph";

Press "New graph";

[On the screen: Define parameter to be drawn]

Select "R factors" and "GOF";

OK



#### Notes

*The GOF values are between 0.95 to 1.24 which indicates a good fit. However, as mentioned above, cell parameters of the phase#2 were fixed and profile parameters of both phases were kept equal. In order to make more accurate refinement, we have to find regions where occupations of the  $\alpha$  or  $\delta$  phase are negligible, and the region where both phases are coexisting.*

#### 4. Cyclic refinement with three multi-phase starting points

Quit (leave the graph)

[On the screen: Action with individual item:]

Select the temperature 30C;

Press the button "Go to the basic Jana window";

[On the screen: Basic Jana window]

Run "Profile viewer"; Press "X exactly" and select the range 10-30 in 2th;

Quit,

Press "Return to cyclic wizard"

[On the screen: Action with individual item:]

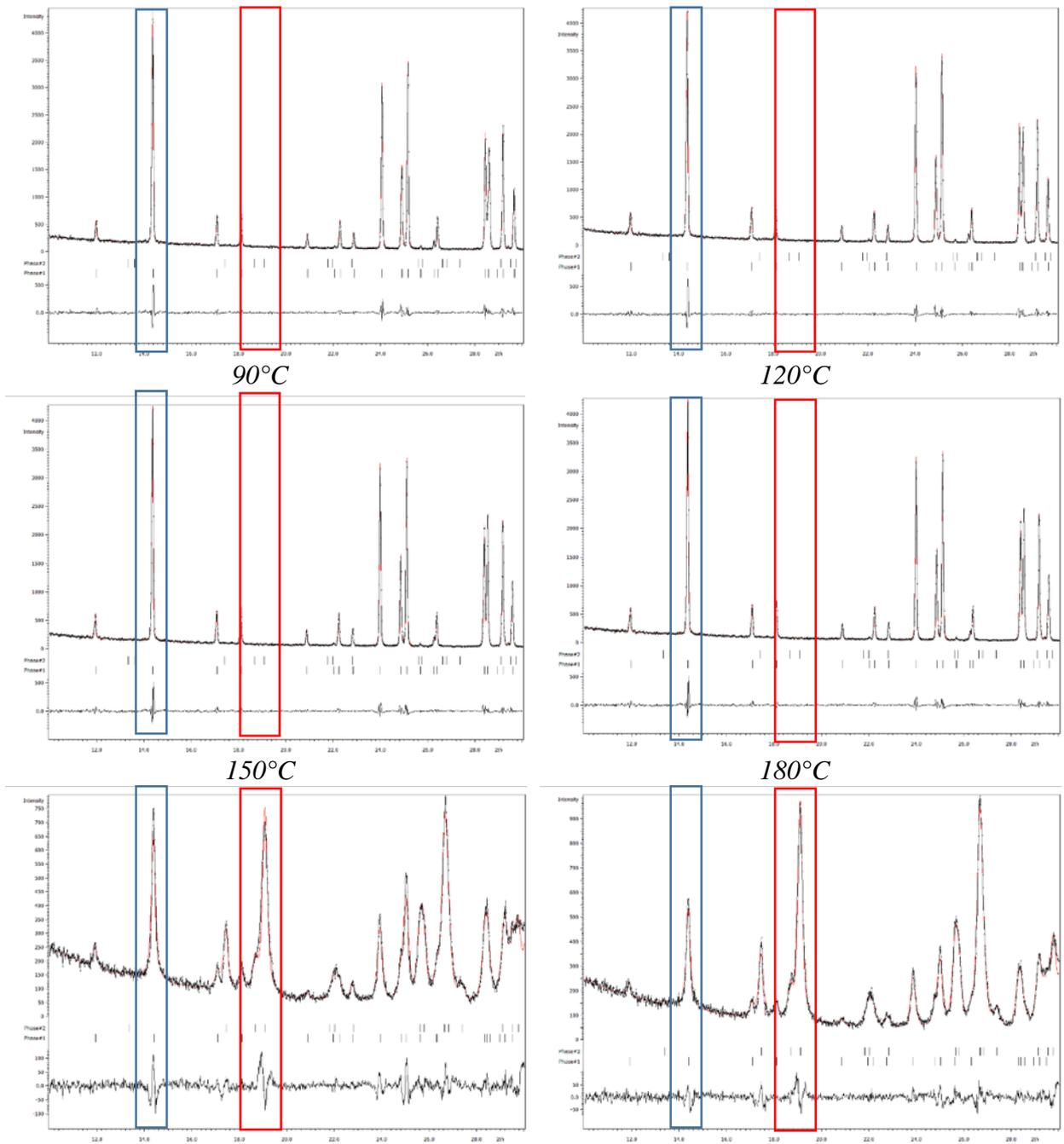
Select another temperature to see difference;

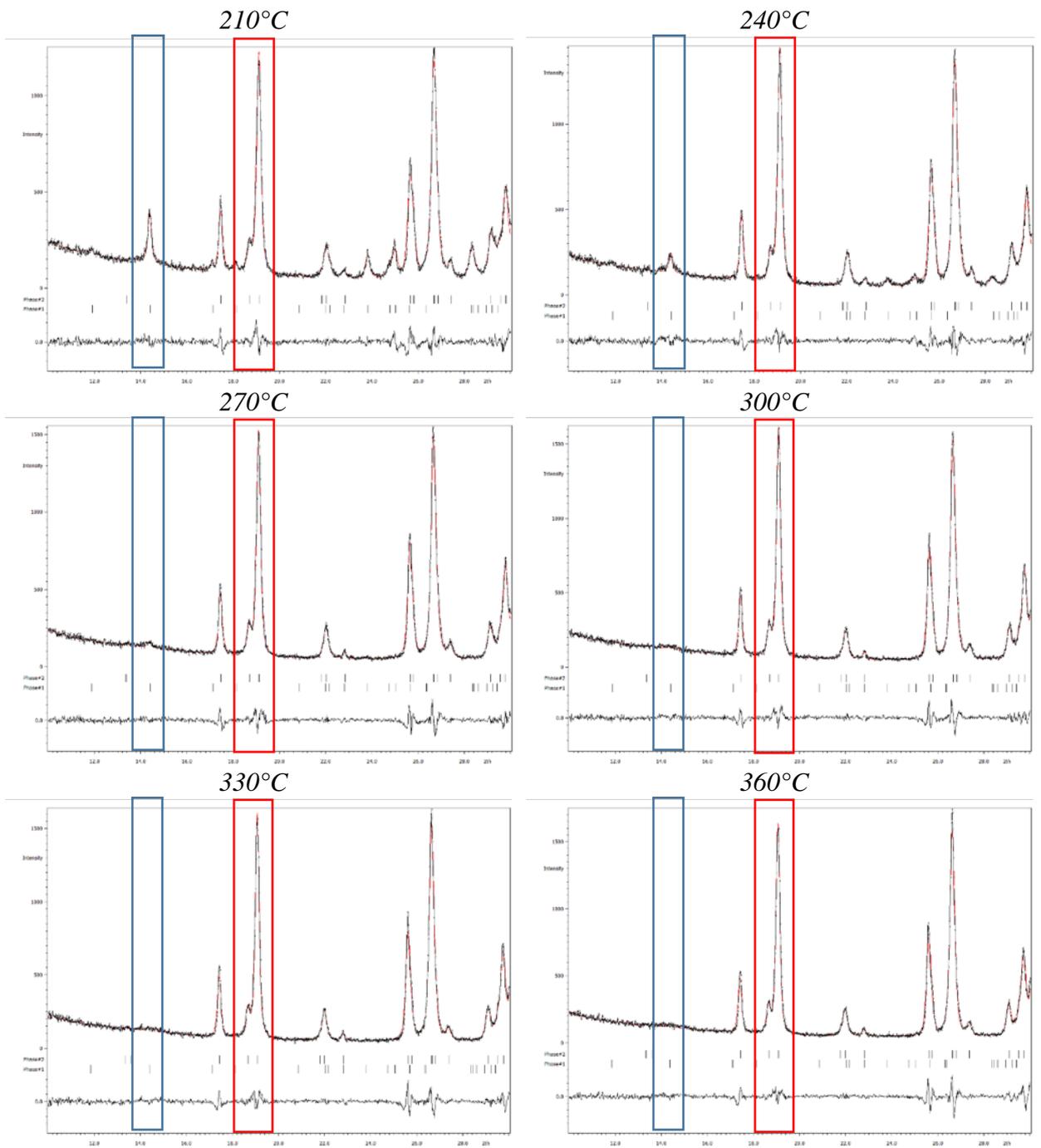
Repeat the process several times to find the above mentioned regions;

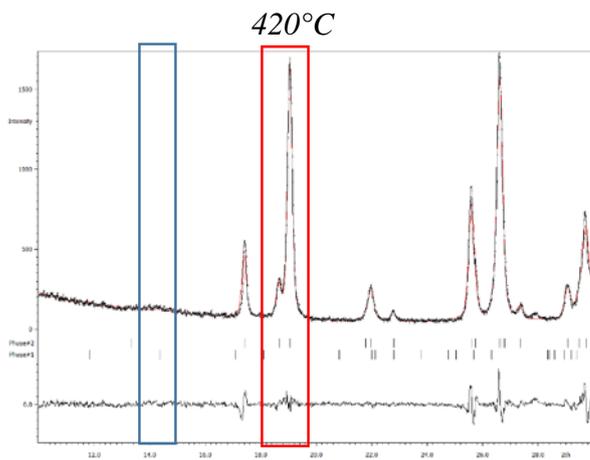
Here are the powder profiles for all temperatures:

30°C

60°C







#### Notes

*The reflection in the blue rectangle is (1,1,0) of the  $\alpha$  phase and the two reflections in the red rectangle are (1,1,1) and (2,1,0) of the  $\delta$  phase.*

*From these figures follows:*

*in the region (30-120) only the  $\alpha$  phase exists.*

*in the region (150-270) both phases are present*

*in the region (330-420) the  $\delta$  phase exists*

*In order to make the full cyclic refinement, two other starting points will be introduced – for 150 °C and for 300 °C.*

[Return to cyclic wizard;](#)

#### **Set starting point for the region (30-120) where only the $\alpha$ phase is present**

Select the temperature 30C;

Press “Run le Bail wizard”

Press “Edit refinement commands”;

In the page “Basic” change “Number of cycles” to 30 (damping factor 0.3)

In the page “Various”; Press “Restrictions”; **Delete** or disable the command “**restric Phase#1 profile Phase#2**”;

OK; OK;

Press “Edit profile parameters”

In page “Profile” and **ensure** that refinement of **StrainG** and **CSizeL** is activated for the **Phase#1**; **ensure** that refinement of **StrainG** and **CSizeL** is **not** activated for the **Phase#2**

OK; Yes to save changes;

Press “Run Refine”;

Finish;Yes

#### **Starting point for the region (150-270) where both $\delta$ and $\alpha$ -phases coexist**

[On the screen: Action with individual item:]

Select the temperature 150C;

Press “Run le Bail wizard”;

[On the screen: Refinement of the powder profile by the le Bail algorithm]

Press "Edit refinement commands";

In the page "Basic" change "Number of cycles" to 30 (damping factor 0.3)

In the page "Various"; Press "Restrictions"; **Delete** or disable the command "**restric Phase#1 profile Phase#2**";

OK; OK;

Press "Edit profile parameters" and

In page "Cell", **activate** the refinement of cell parameters **a,b,c** for the **Phase#2** and **check Skip Friedel** pairs (Unit cell parameters for Phase#1 are already activated)

In page "Profile", **activate** the refinement of **StrainG** and **CSizeL** for **both phases**

OK; YES to save changes;

Press "Run Refine";

#### Notes

*Repeat the refinement if the changes of parameters are too large;  
Interrupt the refinement by pressing "End" if changes are small (about 3 s.u.)*

OK; Finish; YES to close the refinement tool;

YES to the question "Do you want to use this file as a new starting point?"

**Starting point for the region (330-420) where only the  $\delta$  phase is present**

[On the screen: Action with individual item:]

Select the temperature 330C;

Press "Run le Bail wizard";

[On the screen: Refinement of the powder profile by the le Bail algorithm]

Press "Edit refinement commands";

In the page "Basic" change "Number of cycles" to 30 (damping factor 0.3)

In page "Various", "Restrictions", delete command "restric Phase#1 profile Phase#2"

OK; OK;

Press "Edit profile parameters" and

In page "Cell", **deactivate** refinement of cell parameters **a,b,c** for the **Phase#1** and **activate** refinement of cell parameters **a,b,c** for the **Phase#2**; check **Skip Friedel** pairs for the Phase#2;

In the page "Profile", **activate** refinement of **StrainG** and **CSizeL** for the **Phase#2**; and **deactivate** refinement of these parameters for the **Phase#1**. For Phase#1, change the StrainG value to 1.164657 and CSizeL value to 125.5208 for the Phase#1

#### Notes

*This change will have no effect on refinement because manout of the Phase#1 is negligible at this temperature. These values will be aproximately refined values at the 300°C temperature and will be helpful only for drawing the results at the end of this example.*

Yes to save changes;

OK;

Press “Run Refine”;

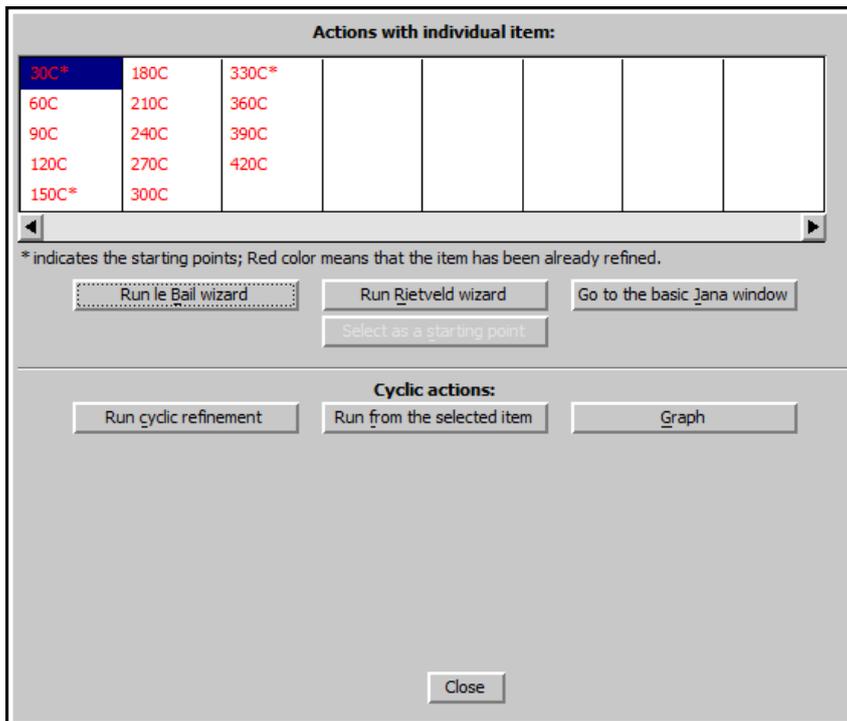
#### Notes

*Repeat the refinement if the changes of parameters are too large;  
Interrupt the refinement by pressing “End” if changes are small (about 3 s.u.);*

OK; Finish; “Yes” to close the refinement tool;

[On the screen: Action with individual item:]

“Yes” to the question “Do you want to use this file as a new starting point?”



“Run cyclic refinement”;

#### Notes

*Most probably the refinement resulted with an error at 300°C due to the unrealistic profile parameters of the Phase#1. In such a case, continue by adding the fourth starting point at 300C. Otherwise continue by “**Analyse results**”*

### **Add the fourth starting point at 300C**

*[On the screen: Action with individual item:]*

Select the temperature 270C;

Press "Run le Bail wizard";

*[On the screen: Refinement of the powder profile by the le Bail algorithm]*

Press "Edit profile parameters" and

In the page "Profile", just **remember StrainG (0.21) and CSizeL (35) parameters of Phase#1.**

ESC;YES;

NO – don't set it as a new starting point

*On the screen: Action with individual item:]*

Select the temperature 300C;

Press "Run le Bail wizard";

*[On the screen: Refinement of the powder profile by the le Bail algorithm]*

Press "Edit profile parameters" and

In the page "Profile", set **StrainG and CSizeL** according to the temperature 270C (0.21 and 35) and disable its refinement

OK; YES;

FINISH; YES

*[On the screen: Action with individual item:]*

YES to create a new starting point

Press "Run cyclic refinement"

*After several minutes, all powder profiles are refined.*

### **Analyse results**

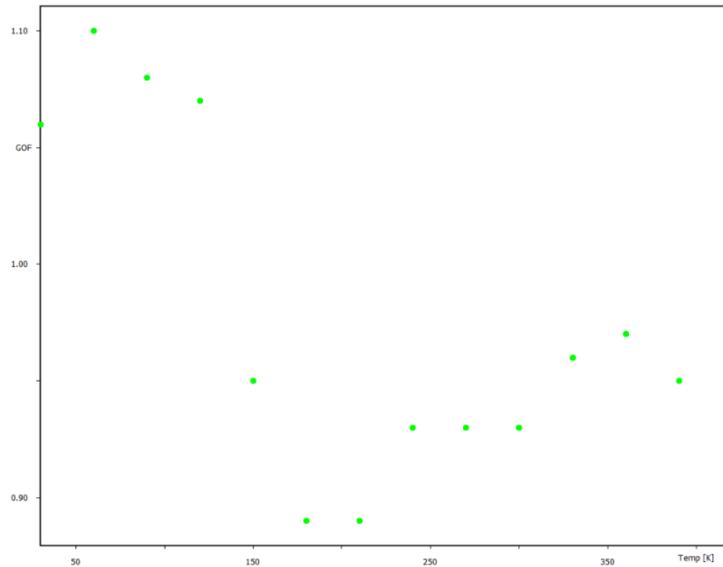
*[On the screen: Action with individual item:]*

Press "Graph";

Press "New graph";

*[On the screen: Define parameter to be drawn]*

Select "R factors" and "GOF";

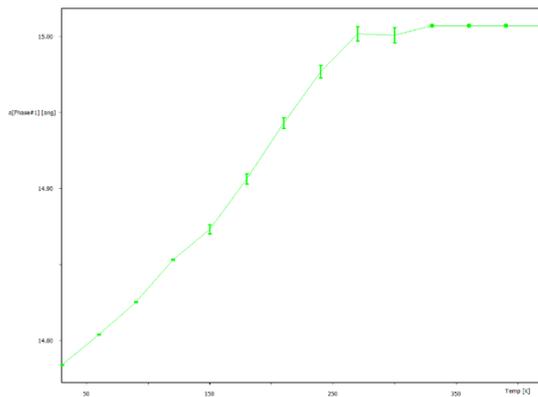


The GOF values are in the interval 0.89 to 1.1 which means slightly better results than in the previous cyclic refinement.

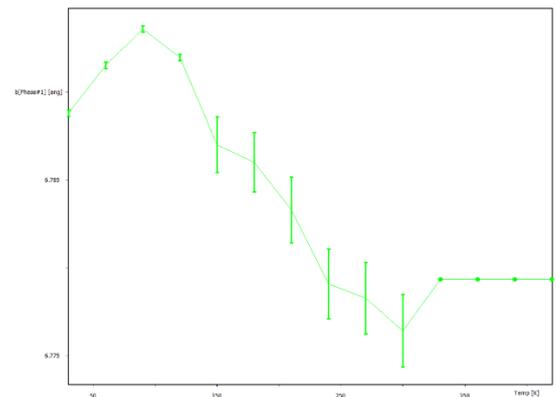
Press "New graph";

Select "Cell parameter", "a", "b" and "c" for the Phase#1:

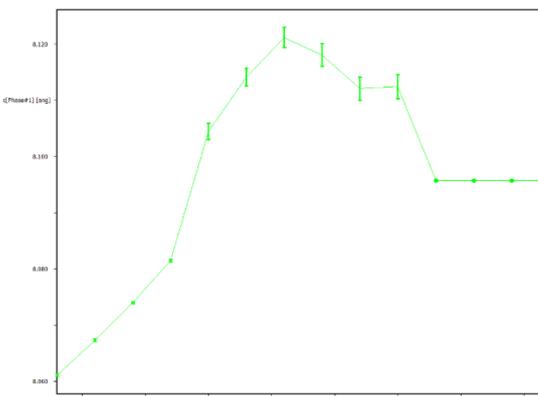
*a* parameter



*b* parameter

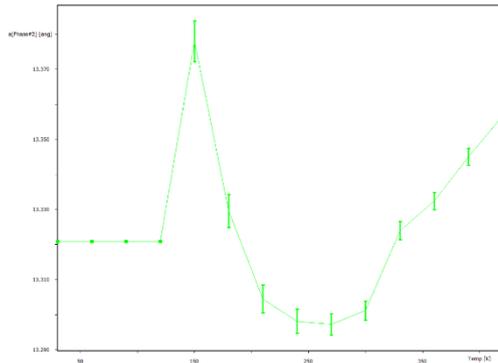


*c* parameter

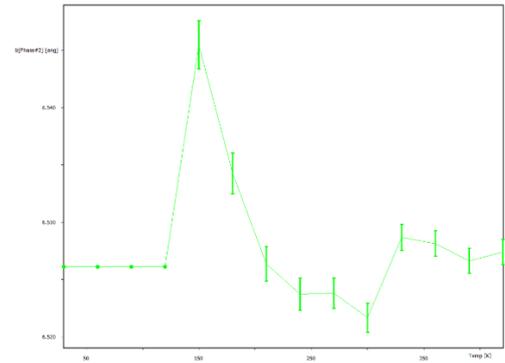


Repeat the process for the Phase#2:

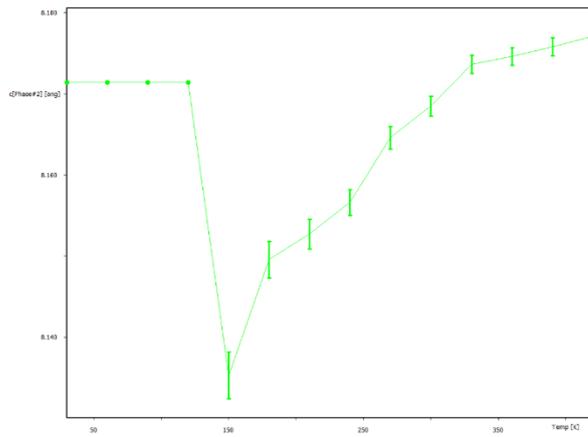
*a parameter*



*b parameter*

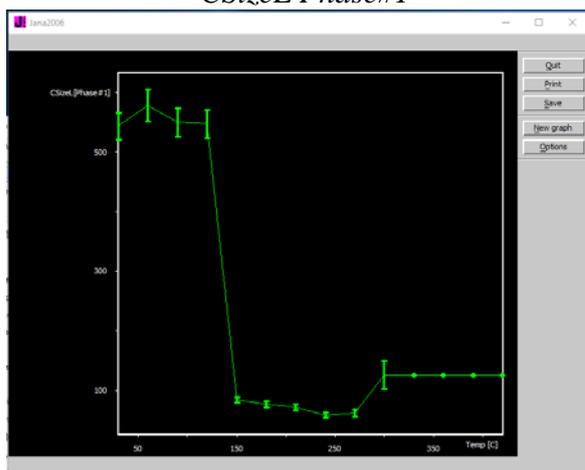


*c parameter*

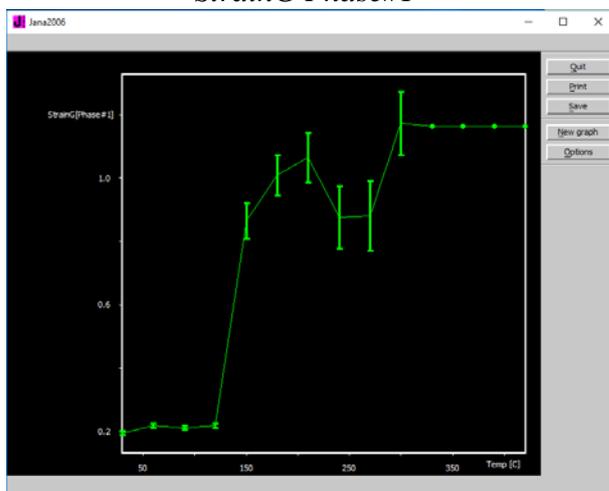


Select "Profile parameter", "CSizeL" and "StrainG" for both Phase#1 and Phase#2

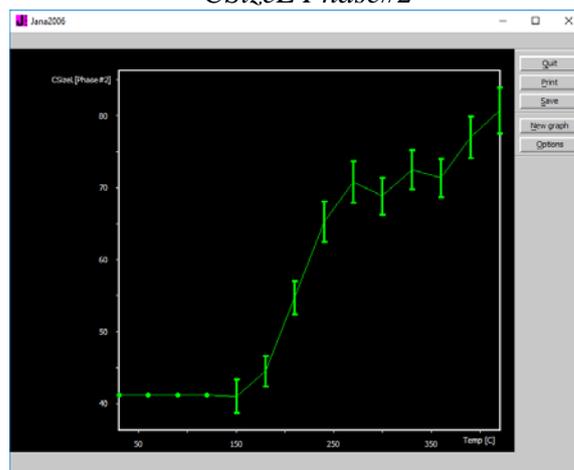
*CSizeL Phase#1*



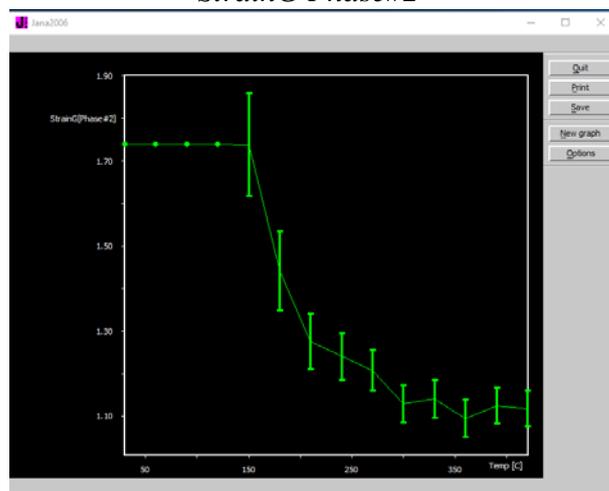
*StrainG Phase#1*



*CSizeL Phase#2*



*StrainG Phase#2*



## Notes

*The crystallite size of phase#1 is stable until 150°C, then due to the dehydration occurring at this temperature, it decreases below 100 nm. The value after 330 deg has no meaning since this phase has completely disappeared. Regarding Phase#2, the crystallite size below 150 deg has no meaning for the same reasons. At this temperature the phase appears and its crystallite size increases due to the temperature from 40 nm to 80 nm.*

*The strain for the phase#1 is stable until 150°C as expected. Then, the value of strain increases during the dehydration (150-330) The value after 330 deg has no meaning since this phase has completely disappeared. Regarding Phase#2, the strain below 150 deg has no meaning for the same reason. Above 150°C, the strain decreases as a function of temperature.*

*For phase#2, both the crystallite size and microstrain evolution indicate an improvement of the crystallite quality.*

## References

*Inorg. Chem.*, **2015**, 54 (12), pp 5660–5670

# Example 2.7.1: LaPO<sub>4</sub>

Revised: 17 October 2018

Data	Topic	Level
X-ray Powder data	Crystallite size by Fundamental approach	intermediate

## Tasks

Determine the crystallite size (coherent diffraction domain length)

A.Coelho and R.W.Cheary developed the fundamental parameter approach to fit the instrumental part of the diffraction pattern of a conventional diffractometer. The aim of this method is to model the instrumental part in order to extract microstructural information of the sample: crystallite sizes and strain.

In case of divergent beam, Bruker D8 ADVANCE configuration, we should take into account:

- the aperture of the divergence slit (fixed FDS angle or variable VDS angle)
- the width (RS width) and axial length (RS length) of receiving slit
- the length (Source length) and projected width of the X-ray source
- the absorption coefficient and axial length (Sample length) of the sample
- angular aperture of Soller slit (Primary Soller and Secondary Soller)
- emission x-ray profile (File with radiation profile)

The LAM subfolder of Jana2006 installation folder contains emission profile files for different wavelengths as well as for different monochromators.

## Initial data

### Data

Bruker D8 ADVANCE Diffractometer Cu K<sub>α1</sub> = 1.540598 Å

Johansson monochromator Ge(111)

Bragg-Brentano method- Fixed Divergence slit

Primary/Secondary radius: 217.5 mm

Receiving slit width = 0.2 mm

Fixed divergence slit = 0.3°

Source length = 12 mm

Sample length = 15 mm

Receiving slit length = 16 (192\*0.075 for Lynxeye detector)

Primary/Secondary Soller slit = 2.5° (0.02 rad\*2)

### Input files:

LaPO4-SharpLines.xy

LaPo4-Nano.xy

### Additional information:

The structural information is given in the following cif file:

LaPO4-ICSD.cif (this file comes from the ICSD database)

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## Instructions

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### I. Data import

#### 1. Creating new jobname

Start Jana2006  
"File → Structure → New" opens the file manager  
Left pane: locate directory with input files  
Right pane: **LaPO4-SharpLines**

#### 2. Import Wizard

Select "structure – from cif"; NEXT  
Select "**LaPO4-ICSD.cif**" in the directory; OK  
YES to import data from file  
*CIF does not contain the powder profile, it must be imported from other file*  
Select "Powder data – **various CW formats**"; NEXT  
*[On the screen: Powder data from]*  
Select "**Free format of 2th, I, [sig(I)]**"  
For method select "**Bragg-Brentano method- Fixed Divergence slit**";  
For "Filename" type or browse for **LaPO4-SharpLines.xy**  
NEXT

#### Notes

*For this example, the difference between Fixed Divergence Slit (FDS) or Variable Divergence Slit (VDS) is important. In case you would select. If here you would select Another/unknown method, the program will request the slit type later on.*

*[On the screen: Complete/correct experimental parameters]*

Radiation: X-ray; Cu wavelength is **1.540598**;  
Press "Set glancing angle"; for Material select **Ge**; for Reflection plane type **1 1 1**; Press "**=>**" to calculate the glancing angle; OK  
Keep the perfectness at **0.5**  
NEXT; FINISH; OK to close data repository;  
Do you want to accept made changes? **Yes**

### II. Rietveld refinement

#### 1. The fundamental approach

#### Notes

*The structure is already known. Hence, the refinement can be directly done the Rietveld instead of Le Bail method. At the beginning, the structure model will be fixed and only profile parameters will be refined.*

*[On the screen: Basic Jana window]*

**Check the profile:** "Profile viewer" – just to see how it looks like  
**Quit** powder pattern profile  
Right click on "**Refine**"

In page “Various” select “Fixed commands”; select “All parameters”; in Atoms/parameters write \*, press “Add”; OK; OK

This fixes all parameters of the structure model except scales.

YES to save refinement commands without starting refinement

Add; OK; OK

Press “Edit profile”

In page “Asymmetry/Diffractometer” select “fundamental approach” and enter following parameters (Step 1)

Primary/Secondary radius: 217.5 mm

Receiving slit width = 0.2 mm

Fixed divergence slit angle = 0.3°

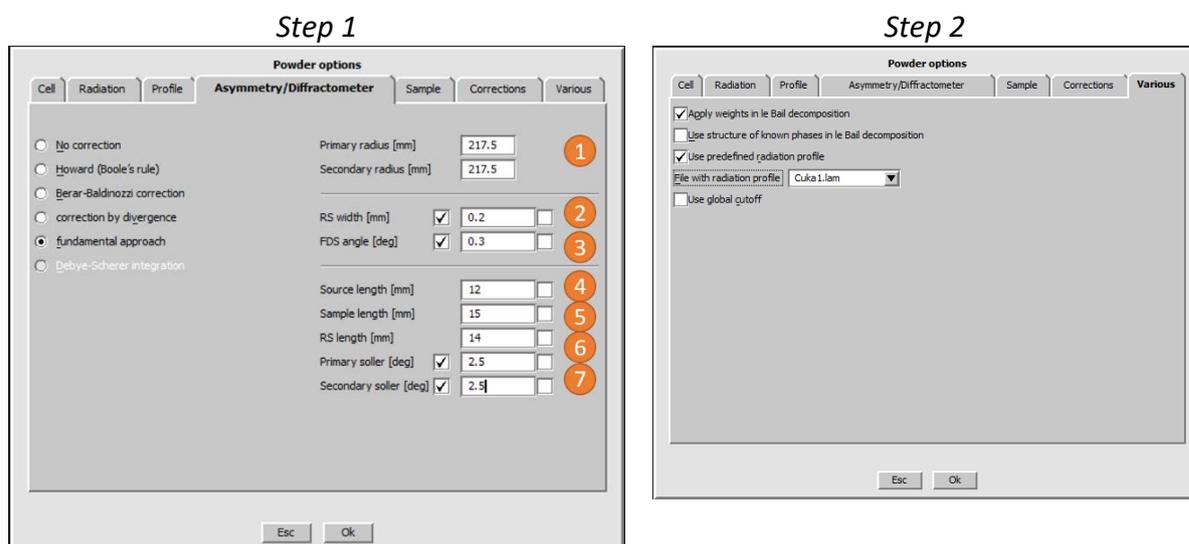
Source length = 12 mm

Sample length = 15 mm

Receiving slit length = 14 (192\*0.075 = Lynxeye detector)

Primary/Secondary Soller slit = 2.5°

In page “Various” check “Use predefined radiation profile” and select from the list CuKa1.lam (Step 2)



## Notes

*The fundamental parameter depends on the used diffractometer*

- 1) Primary and Secondary radii are given in **mm** and correspond to the goniometer radius. In conventional diffractometers, both radii are identical

Example:

Empyrean PANalytical 240 mm,

Smartlab Rigaku 310 mm,

Bruker D8 217.5 mm

- 2) Receiving slit (RS) width is given in **mm**. This value depends on your detector. In case of a scintillator detector (or OD mode of other detectors), the width will correspond to the width of the receiving slit placed just before the detector. This slit reduces the horizontal divergence of the beam due to the flat sample. The

Fundamental approach parameter was originally developed for OD detectors. In case of Lynxeye (or 1D mode of other detectors) the width of RS should be estimated using a standard with known crystallite size, e.g., LaB<sub>6</sub>.

Example:

Lynxeye detector: 0.2 mm

- 3) The Fixed Divergence Slit (FDS) or the Variable Divergence Slit (VDS) is given in **deg**.

Example:

Smartlab Rigaku: value of FDS is given like a value of the Incidence slit (deg)

Bruker: value of the fixed divergence slit is defined directly(deg)

- 4) The source length is given in **mm**, and its value lies between 10 and 14 mm. This parameter has a negligible effect on the refinement; you can use the default value.

- 5) Sample length is given in **mm**, and corresponds to the illuminated part of the sample. This value has a negligible effect; you can use the default value.

- 6) Receiving slit (RS) length is given in **mm**. This value depends on the detector. In case of a scintillator detector (or OD mode of other detectors), the length will correspond to the length of the receiving slit placed just in front of the detector. This slit reduces the vertical divergence of the beam due to the flat sample. The Fundamental approach parameter was originally developed for OD detectors. In case of Lynxeye (or 1D mode of other detectors) the RS length can be calculated as a product of the number of pixels in one silicone strip and the pixel size (Pixel 3D detector) or the product of the spatial resolution and the number of channels on silicon strips (Lynxeye detector).

Example:

Pixel 3D : 0.055 mm\* 256 pixels -> 14 **mm**

D/teX Ultra 250: 0.075 mm\*256 channels -> 19.2 **mm**

Lynxeye detector: 0.075 mm\* 192 channels -> 14.4 **mm**

- 7) Primary and Secondary Soller slit angles are given in **deg**. The primary Soller slit is placed before the sample while the secondary one after the sample. You should be careful as a function of the constructor the definition of the angle is different. This slit reduces the axial divergence due to the beam divergence.

Example:

Empyrean Panalytical 0.02 rad = 1.14deg\*2 = 2.3 deg,

Smartlab Rigaku 2.5 deg

Bruker D8 2.5 deg

The predefined radiation profiles:

For Copper radiation, Jana2006 offers nine different radiation profiles

Name	Ratio between wavelength	Wavelength Å	Lorentzian halfwidth
Cuka1.lam	1	1.5405960	0.5000000
Cuk1sharp.lam	1	1.5405960	0.4018440
Cuka2.lam	0.6538	1.5405960	0.5018440

	0.3462	1.5444930	0.6265790
CuKa2_analyt.lam	0.6605 0.3395	1.5405980 1.5444426	0.5000000 0.5000000
CuKa4_holzer.lam	0.5790 0.0800 0.2360 0.1050	1.5405909 1.5410639 1.5443990 1.5446855	0.4374157 0.6432140 0.5128764 0.6872322
Cuka5.lam	0.0159 0.5791 0.0762 0.2417 0.0871	1.5347530 1.5405960 1.5410579 1.5444100 1.5447210	3.5999999 0.4370000 0.6000000 0.5200000 0.6200000
Cuka5_berger.lam	0.0159 0.5691 0.0762 0.2517 0.0871	1.5347530 1.5405960 1.5410579 1.5444100 1.5447210	3.6854000 0.4370000 0.6000000 0.5200000 0.6200000
Cuka5_t.lam	0.0159 0.5791 0.0762 0.2417 0.0871	1.5347530 1.5405960 1.5410579 1.5444100 1.5447210	3.5999999 0.2370000 0.4000000 0.3200000 0.4200000
CuKb4_holzer.lam	0.4850 0.2480 0.1100 0.1000 0.0550	1.3922160 1.3925949 1.3917581 1.3934906 1.3913004	0.5502872 0.5505868 0.5546122 1.2654732 0.8290293

*The two first profiles are used for diffractometers with monochromator, the others except CuKb4) for diffractometers without monochromator*

In page "Profile" select "**Pseudo Voigt**" with **CSizeL = 100, StrainL = 0, CSizeG = 10000 and StrainG = 0 (Step 3)**  
OK; YES

#### Notes

*The peak broadening due to the small size of crystallites is fitted with a Lorentzian function whereas the peak broadening due to micro strain inside the crystallite is fitted with a Gaussian function. In the case of LaPO<sub>4</sub>, no strain is present, and we use zero for both strain components. We also want to suppress the Gaussian component of the profile by setting a very large crystallite size (Csize G= 10000).*

### Step 3

### Step 4

Right click "Refine"

Set **50 refinement cycles** and set **Damping factor to 0.8** (Step 4)

OK; YES to save refinement commands without starting refinement

"Edit Profile"

In page "Cell" activate refinement of unit cell parameters **a, b c and beta** (Step 5)

In page "Corrections": Activate refinement of "sycos"

In page "Profile" activate "**Csize L**" (Step 6)

OK; Yes to save profile parameters

"Refine"

### Step 5

### Step 6

The refinement converges with

Structural factor  $R(obs) \approx 3.0$   $wR(obs) \approx 3.1$   $R(all) \approx 3.0$   $wR(all) \approx 3.1$

Profile factor  $GOF \approx 1.4$   $RP \approx 3.6$   $Rwp \approx 4.7$

The refined crystallite size  $CSizeL \approx 36$  nm

## 2. Structure refinement

### Notes

*Lanthanum is the heaviest atom in the structure, therefore its position will be refined first.*

Right click "Refine"

In page "Various", press "Fixed commands" and delete "fixed all \*"

Select "ADP harmonic parameters", in "Atoms/parameters" type \*, press "Add" (at that point the ADP are fixed for all the atoms)

Select "coordinates", in "Atoms/parameters" type P\* O\*, press "Add" (to keep the position of phosphorus and oxygen atoms fixed)

OK; OK; Yes+Start

Right click "Refine"

In page "Various" in "Fixed commands" delete "fixed xyz P\* O\*"

OK; OK; Yes+Start

*At this stage, profile plot at low angles shows that we need more background parameters*

"Edit profile"

In page "Corrections" change number of terms for 10; OK; YES

Run "Refine"

Check profile using "Profile viewer"

Check structure using "plot structure"

### Notes

*The refinement converges with*

*R factors [242=239+3/19]: R(obs)≈2.4; wR(obs) ≈ 2.6 R(all) ≈2.4 wR(all) ≈2.6*

*Profile R factors [2723/16+19]: GOF ≈ 1.2, Rp ≈ 3.2, Rwp ≈ 4.3*

## 3. Refinement of nano-powder

*In the following, we will use the structure and profile refined for the standard powder as a template for refinement against the nano-powder.*

File → structure → Save as → LaPo4-nano

"Yes" (You want to continue with the new structure)

*(At that point the observed pattern is still LaPo4-SharpLines. It has to be changed for LaPo4-Nano)*

File → Reflection file → Import/modify the reflection file

Select "Reimport", Browse for the new pattern "LaPo4-nano.xy"

NEXT; NEXT; FINISH; OK

Right click on "Refine"

In page "Various" select "Fixed commands"

Select "All parameters"; in Atoms/parameters write "\*"; "Add"; OK; OK ("fixed all \*" is not in contradiction with "fixed u \*", therefore both commands can be retained)

Yes + Start (to run refine)

### Notes

*The refinement converges with*

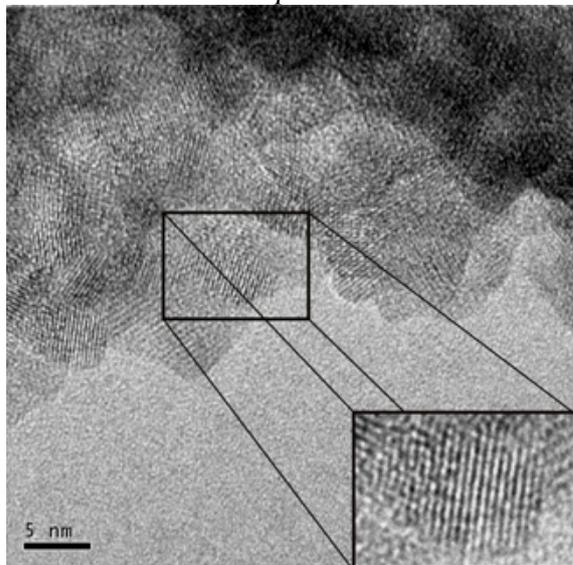
Structural factor  $R(\text{obs}) \approx 1.0$   $wR(\text{obs}) \approx 1.0$   $R(\text{all}) \approx 1.0$   $wR(\text{all}) \approx 1.0$   
Profile factor  $GOF \approx 1.3$   $RP \approx 2.6$   $Rwp \approx 3.3$

Press "Edit profile"

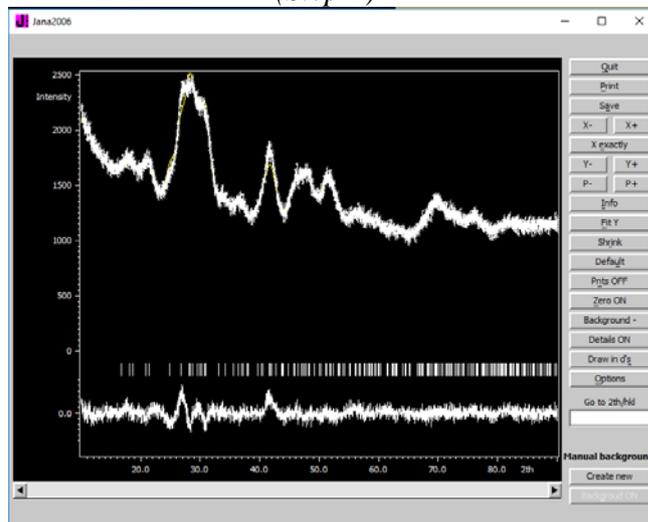
Go to the page "Profile" to see the new refined crystallite size:  $CSizeL \approx 4$  nm

Check the profile using "Profile viewer" (Step 1)

TEM picture



(Step 1)

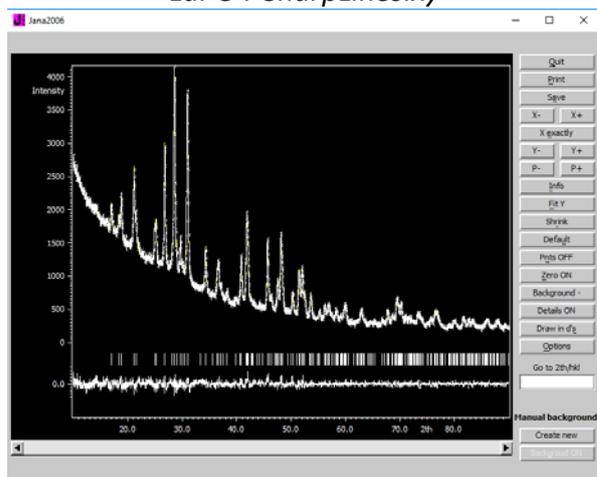


## Notes

Because of severe overlaps of Bragg reflections and low intensity, the structure refinement cannot be done

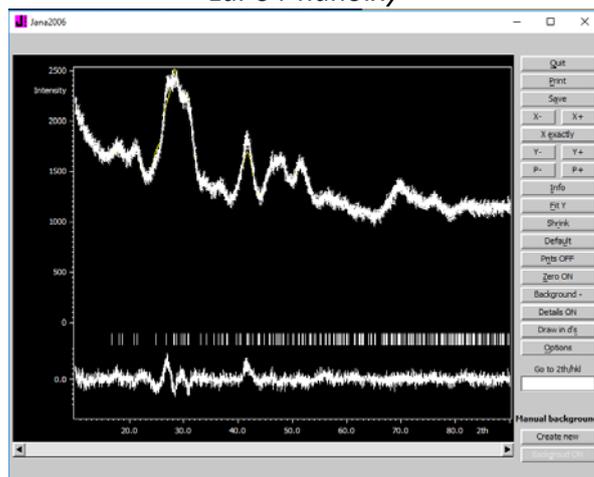
Final result

LaPO4-SharpLines.xy



Crystallite size = 36 nm

LaPO4-nano.xy



Crystallite size = 4 nm

## References

*J. Appl. Cryst.* (1992). **25**, 109-121.

*J. Appl. Cryst.* (1998). **31**, 851-861.

*J. Appl. Cryst.* (1998). **31**, 862-868.



# Example 2.7.2: MnWO<sub>4</sub>

Revised: 17 October 2018

Data	Topic	Level
X-ray Powder data	Strain by Stephens' formalism	Intermediate

## Tasks

Using the Stephens' formalism to model the anisotropic broadening due to the microstrain

## Initial data

### Data

Bruker D8 ADVANCE Diffractometer Cu K<sub>α1</sub> = 1.540598 Å

Johansson monochromator Ge(111)

Bragg-Brentano method- Fixed Divergence slit

Primary/Secondary radius: 217.5 mm

Receiving slit width = 0.2 mm

Fixed divergence slit = 0.3°

Source length = 12 mm

Sample length = 15 mm

Receiving slit length = 16 (192\*0.075 = *Lynxeye detector*)

Primary/Secondary Soller slit = 2.5° (0.02 rad\*2)

### Input files:

MnWO4.m50; MnWO4.m40; MnWO4.m41; MnWO4.m90; MnWO4.m95

### Additional information:

Cu<sub>x</sub>Mn<sub>(1-x)</sub>WO<sub>4</sub> is a solid solution. The actual composition of the compound under study was determined from chemical analysis (Cu<sub>0.3</sub>Mn<sub>0.7</sub>WO<sub>4</sub>). A phase transition occurs for x = 0.3. At this composition, the compound experiences huge anisotropic microstrain. The monoclinic MnWO<sub>4</sub> structure presents the same arrangement of atoms as that of the triclinic CuWO<sub>4</sub>. The two structures are mainly related by a stretching along the 1 1 0 direction.

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# Instructions

## I. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → open” opens a file manager

Left pane: locate directory with input files

Right pane: double-click **MnWO4**

## II. Rietveld refinement

### 1. Rietveld refinement using fundamental approach only

Select “Edit profile”

In page “Cell” select unit cell parameter **a, b, c and beta** (Step 1)

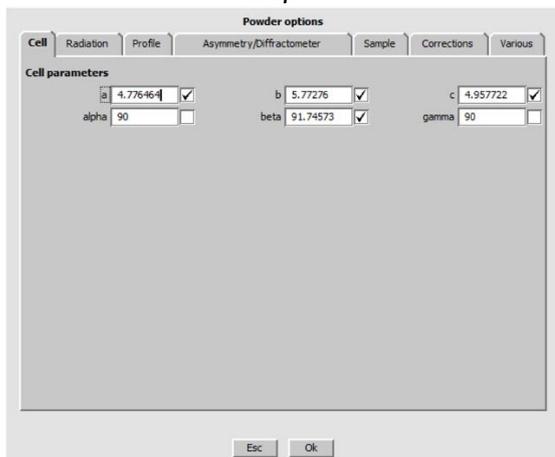
In page “Profile” select CSizeL (Step 2)

In page “Asymmetry/Diffractometer” use “fundamental parameters” (Step 3)

In page “Corrections” type 5 for “Number of terms”; check **syncos** (Step 4)

OK

**Step 1**



Powder options

Cell Radiation Profile Asymmetry/Diffractometer Sample Corrections Various

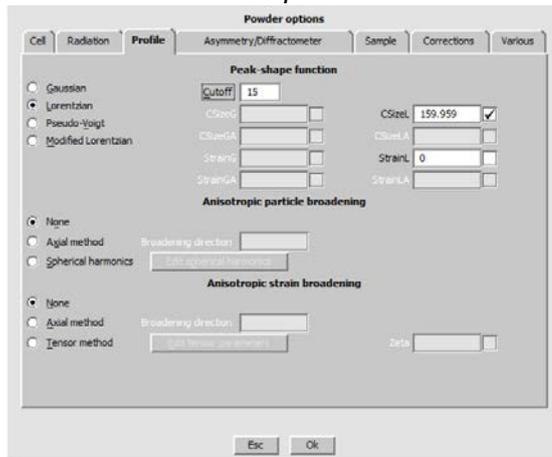
Cell parameters

a 4.776464  b 5.77276  c 4.957722

alpha 90  beta 91.74573  gamma 90

Esc Ok

**Step 2**



Powder options

Cell Radiation Profile Asymmetry/Diffractometer Sample Corrections Various

Peak-shape function

Gaussian  Lorentzian  Pseudo-Voigt  Modified Lorentzian

Cutoff 15

CSizeL  CSizeL 159.959

CSizeA  StrainL 0  StrainLA

Anisotropic particle broadening

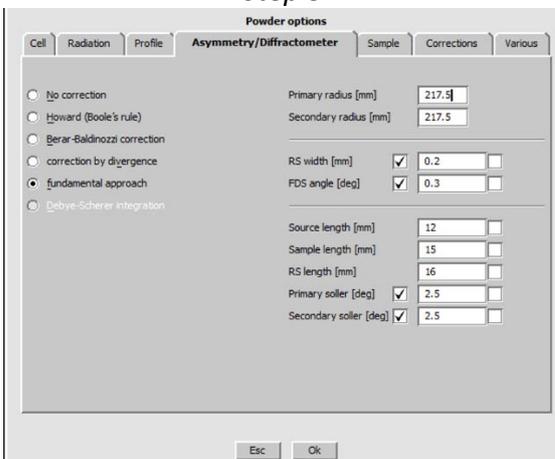
None  Axial method  Spherical harmonics

Anisotropic strain broadening

None  Axial method  Tensor method

Esc Ok

**Step 3**



Powder options

Cell Radiation Profile Asymmetry/Diffractometer Sample Corrections Various

No correction  Howard (Boole's rule)  Berar-Baldinozzi correction  correction by divergence  fundamental approach  Debye-Scherrer integration

Primary radius [mm] 217.9

Secondary radius [mm] 217.5

RS width [mm]  0.2

FDS angle [deg]  0.3

Source length [mm] 12

Sample length [mm] 15

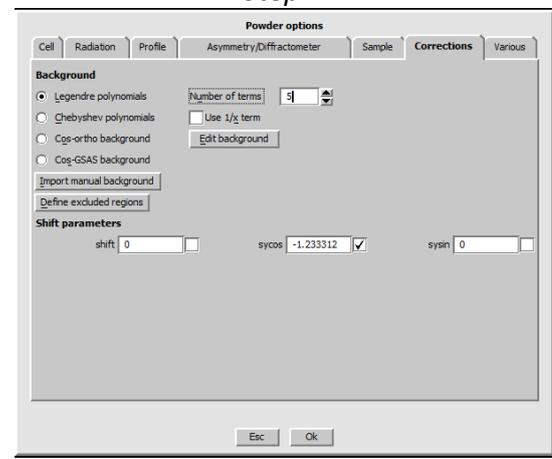
RS length [mm] 16

Primary soller [deg]  2.5

Secondary soller [deg]  2.5

Esc Ok

**Step 4**



Powder options

Cell Radiation Profile Asymmetry/Diffractometer Sample Corrections Various

Background

Legendre polynomials  Chebyshev polynomials  Cos-ortho background  Cos-GSAS background

Number of terms 5  Use 1/g term

Import manual background  Define excluded regions

Shift parameters

shift 0  syncos -1.233312  sysin 0

Esc Ok

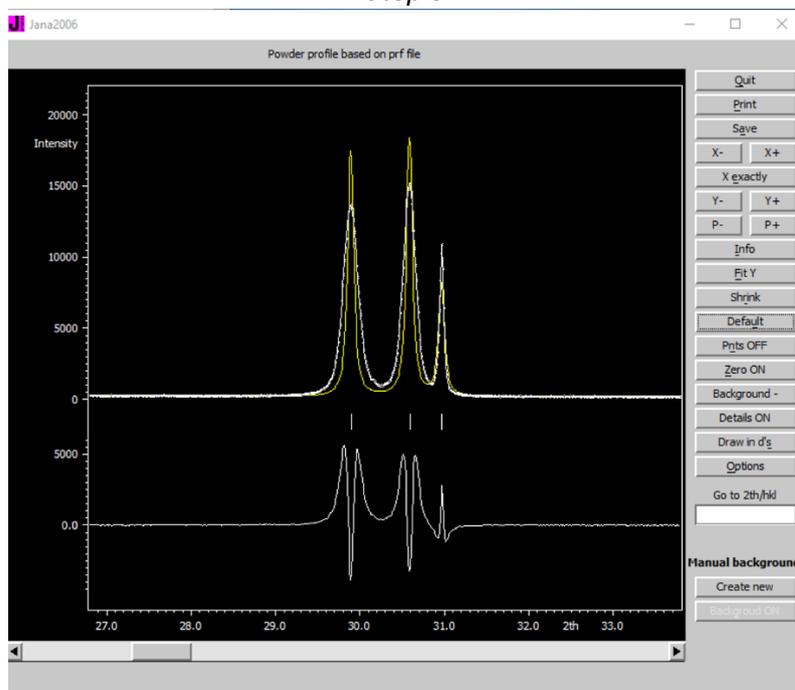
Right click on "Refine"  
 Uncheck "Make only profile matching"  
 In page "Various" go to "Fixed commands"; select "All parameters"; for  
 "Atoms/parameters" write \*; "Add" (This fixes all structure parameters except scales)  
 OK; OK; "Yes+start"

Notes
<p>The refinement converge with            Structure factors: <math>R(\text{obs}) \approx 10.2</math>, <math>wR(\text{obs}) \approx 15.7</math>, <math>R(\text{all}) \approx 10.2</math>, <math>wR(\text{all}) \approx 15.7</math>            Profile factors: <math>\text{GOF} \approx 8.3</math>, <math>R_p \approx 27.3</math>, <math>wRP \approx 34.4</math></p>

Start "Profile viewer"; press "Default" and examine peaks between 27 and 33 degrees (Step 5)

Notes
<p>We can see two different types of peak broadening. It is impossible to fit it using only the fundamental parameters. In this case, the different peak broadening is caused by an anisotropic strain broadening.</p>

### Step 5



## 2. Rietveld refinement using fundamental approach and axial method

Notes
<p>In Powder options, page Profile, we can see possibilities available for description of anisotropic strain broadening.</p> <p>The axial method cannot work because the strain broadening is not due to a simple uniaxial strain. Try to see if it is possible to find a simple hkl value presenting a broadening peaks.</p>

### 3. Le Bail refinement using fundamental approach and tensor method (Stephens' method)

Notes		
<p>The Stephens' method is used to describe anisotropic strain broadening taking into account the crystal symmetry.</p> <p>The maximum number of <math>S_{HKL}</math> parameters to be refined is given in the right column</p> <p><math>M_{hkl}</math> is linked to <math>d</math>-spacing with the following relation:</p> $1/d^2 = M_{hkl} = \alpha_1 h^2 + \alpha_2 k^2 + \alpha_3 l^2 + \alpha_4 kl + \alpha_5 hl + \alpha_6 hk$ <p>with <math>\alpha_i</math> reciprocal lattice parameters.</p> <p>The variance of <math>M_{hkl}</math> is written by :</p> $\sigma^2(M_{hkl}) = \sum_{HKL} S_{HKL} h^H k^K l^L \text{ with } S_{HKL} \text{ defined for } H + K + L = 4$ <p>Table from Peter W. Stephens publication:</p>		
Restrictions on anisotropic strain parameters for the seven crystal systems		
Those $S_{HKL}$ not listed in the last column must be zero		
Crystal system	Restrictions on metric parameters	Anisotropic strain parameters
<b>Cubic</b>	$A = B = C, D = E = F = 0$	$S_{400} = S_{040} = S_{004}, S_{220} = S_{202} = S_{022}$
<b>Tetragonal</b>	$A = B, D = E = F = 0$	$S_{400} = S_{040}, S_{202} = S_{022}, S_{004}, S_{220}$
<b>Orthorhombic</b>	$D = E = F = 0$	$S_{400}, S_{040}, S_{004}, S_{220}, S_{202}, S_{022}$
<b>Monoclinic</b>	$D = F = 0$	$S_{400}, S_{301}, S_{220}, S_{202}, S_{121}, S_{103}, S_{040}, S_{022}, S_{004}$
<b>Trigonal (R3 etc.)</b>	$A = B = C, D = E = F$	<b>Rhombohedral indices:</b> $S_{400} = S_{040} = S_{004}, S_{220} = S_{202} = S_{022}$ $S_{211} = S_{121} = S_{112}$ $S_{310} = S_{130} = S_{301} = S_{103} = S_{031} = S_{013}$
		<b>Hexagonal indices:</b> $S_{400} = S_{040} = S_{310}/2 = S_{130}/2 = S_{220}/3,$ $S_{202} = S_{022} = S_{112}, S_{004}$ $S_{301}/2 = -S_{031}/2 = S_{211}/3 = -S_{121}/3$
<b>Hexagonal, trigonal (P3 etc.)</b>	$A = B = F, D = E = 0$	$S_{400} = S_{040} = S_{310}/2 = S_{130}/2 = S_{220}/3,$ $S_{202} = S_{022} = S_{112}, S_{004}$
<b>Triclinic</b>		All 15 $S_{HKL}$ allowed
<p>In Jana2006, these symmetry restriction are automatically calculated</p>		

Start **“Edit profile”**

In page **“Profile”** select **“Tensor method”** and press **“Refine all”** (Step 1)

(During refinement, Jana will automatically apply restrictions to refine only St400, St220, St103, St022, St121, St040, St301, St202, St004.)

OK; Yes

Run **“Refine”** (On singularity warnings, select **“Skip warnings”**)

## Notes

*The refinement converges with*

*Structure factors  $R(\text{obs}) \approx 3.4$ ,  $wR(\text{obs}) \approx 5.1$ ,  $R(\text{all}) \approx 3.4$ ,  $wR(\text{all}) \approx 5.08$*

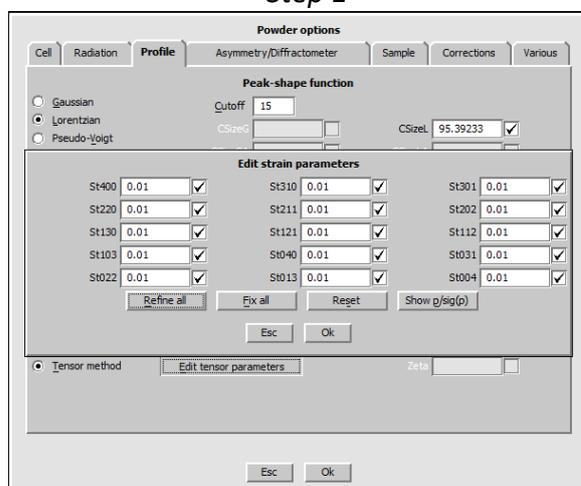
*Profile factors  $\text{GOF} \approx 3.4$ ,  $R_p \approx 10.3$ ,  $wR_p \approx 14.0$*

Run **“Edit Profile”**

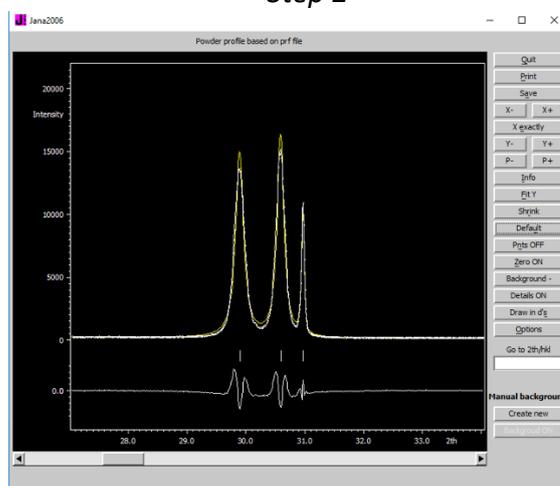
Run **“Profile viewer”**

Press **“Default”** and examine peaks between **27 and 33 degrees** (Step 2)

### Step 1



### Step 2



Right click on **“Refine”**

In page **“Various”**, **“Fixed commands”**:

**Delete “fixed all \*”**

**Fix positions of oxygen atoms (“fixed xyz O\*”)**

Fix ADP parameters for all atoms (**“fixed u \*”**)

OK; OK; **“Yes + Start”**

Right click **“Refine”**

In page **“Various”**, **“Fixed commands”**, **“delete fixed xyz O\***

OK; OK; **“Yes +start”**

Right click **“Refine”**

In page **“Various”**, **“Fixed commands”**, **delete “fixed u \*”**

OK; OK; **“Yes +start”**

(Now we are refining all structure parameters)

(Warning about negative ADP for Mn1)

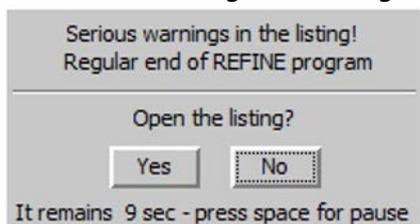
## Notes

The refinement converges with

Structure factors  $R(\text{obs}) \approx 3.5$ ,  $wR(\text{obs}) \approx 4.9$ ,  $R(\text{all}) \approx 3.5$ ,  $wR(\text{all}) \approx 4.9$

Profile factors  $\text{GOF} \approx 3.4$ ,  $R_p \approx 10.4$ ,  $wR_p \approx 14.1$

There are warnings about negative ADP for Mn1:



Actually, this compound is not exactly  $\text{MnWO}_4$  but  $\text{Cu}_{0.3}\text{Mn}_{0.7}\text{WO}_4$ , as follows from chemical analysis. In the next part, we will create a mixed site for these two elements. However, Cu and Mn are very close in the periodic table and refinement of their partial site occupancies would not be possible. Thus the composition will be fixed to that determined by chemical analysis.

## 4. Split atomic position

File → Structure → Save as → **CuMnWO4**

OK; **“YES”** (You want to continue with the new structure)

Start **“EditM50”**

In page **“Composition”**, **“Formula – list of atomic types”**, type **Mn O4 W Cu**

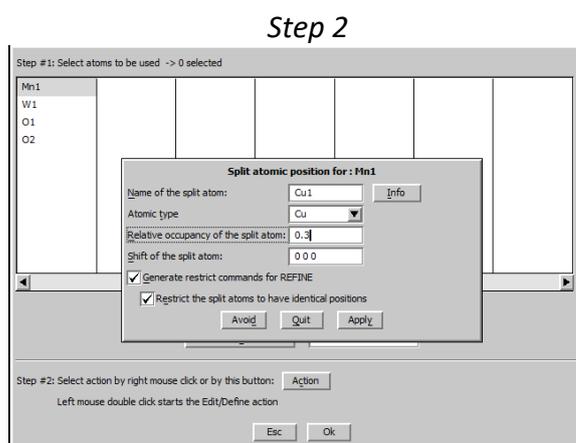
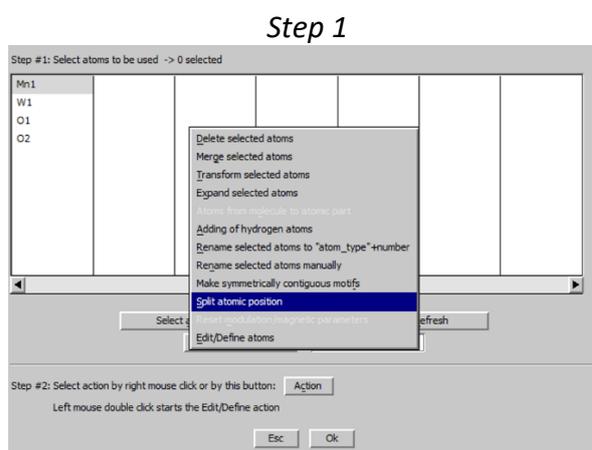
OK; YES

**“Edit Atoms”** → Right click on **Mn1**

**“Split atomic position”** (Step 1)

Change **“Atomic Type”** for **Cu**; **“Name of the split atom”**: **Cu1**; **“Relative occupancy of the split atom”**: **0.3** (Step 2)

**“Apply”**; OK



## Run "Refine"

In case of oscillations, press "Parameters" and decrease "Damping factor" to 0.5

### Notes

The refinement converges with

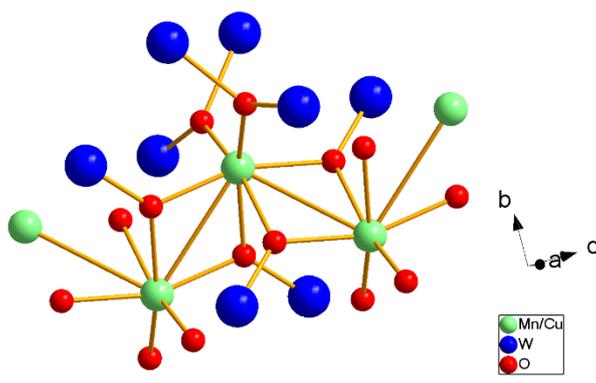
Structure factors  $R(\text{obs}) \approx 3.1$ ,  $wR(\text{obs}) \approx 4.1$ ,  $R(\text{all}) \approx 3.1$ ,  $wR(\text{all}) \approx 4.1$

Profile factors  $\text{GOF} \approx 2.8$ ,  $R_p \approx 8.9$ ,  $wR_p \approx 11.6$

### [On the screen: window of Diamond]

Start "Build -> Get molecules" or use  on the bottom toolbar

Rotate the molecule ( and  on the bottom toolbar) to get an optimal view.



Quit Diamond (without saving changes)

Right click on "Dist"

Uncheck d(max) derived from atomic radii and typical distances

Change value to **d(max)** from 2.5 to **3** (step 4)

Press "Define coefficients for bond valences"

Select 1<sup>st</sup> atom type **Mn**, 2<sup>nd</sup> atom type **O**

Press From file -> Mn<sup>2+</sup> O<sup>2-</sup> coefficients **1.74 0.417** OK; Add

Select 1<sup>st</sup> atom type **Cu**, 2<sup>nd</sup> atom type **O**

Press From file -> Cu<sup>2+</sup> O<sup>2-</sup> coefficients **1.649 0.37** OK; Add

Select 1<sup>st</sup> atom type **W**, 2<sup>nd</sup> atom type **O**

Press From file -> W<sup>6+</sup> O<sup>2-</sup> coefficients **1.909 0.339** OK; Add

OK; (Step 5)

### Step 4

### Step 5

- OK; Yes + start
- Yes to open the listing
- Go to list of distances (Step 6)
- Go to list of bond valence sums (Step 7)

### Step 6

```

Jana2006 - Dist
Find Find next Go to Print PgTop Open in editor Close
*****
* List of distances *
*****
Full coordination of atoms will be printed
The results will be printed in columns without symmetry codes
Distances will be calculated from d(min)= 0.000 to d(max)= 3.000
*****
* atom Mn1 *
Mn1.....0.0000
O1.....2.106(7)
O2.....2.252(7)
O1.....2.106(7)
O2.....2.252(7)
O1.....2.106(7)
O2.....2.058(7)
O2.....2.058(7)
O2.....2.058(7)
*****
* atom Cu1 *
Cu1.....0.0000
O1.....2.106(7)
O2.....2.252(7)
O1.....2.106(7)
O2.....2.252(7)
O1.....2.106(7)
O2.....2.058(7)
O2.....2.058(7)
O2.....2.058(7)
*****
* atom W1 *
W1.....1.838(7)
O1.....2.721(10)
O2.....2.836(9)
O1.....2.819(10)
O2.....2.994(10)
O1.....2.885(9)
O2.....2.780(9)
O2.....2.835(9)
O2.....2.865(10)
O2.....2.865(10)
*****
* atom O1 *
O1.....2.106(7)
Cu1.....2.106(7)
W1.....1.858(7)
W1.....2.168(7)
O1.....2.790(9)
O1.....2.439(9)
*****
Calculating of distances, angles, torsion angles and best planes
structure :

```

### Step 7

```

Jana2006 - Dist
Find Find next Go to Print PgTop Open in editor Close
Calculating of distances, angles, torsion angles and best planes
structure :
*****
* List of bond valence sums *
*****
Bond valence sum for : Mn1 2.349(16)
Bond valence sum for : Cu1 1.635(13)
Bond valence sum for : W1 5.72(5)
Bond valence sum for : O1 2.01(3)
Bond valence sum for : O2 1.92(2)

```

### Notes

The Mn-O and Cu-O distances are generally between 1.7 Å and 2.5 Å and for that of W-O between 1.17 Å and 2.34 Å  
 The bond valence sums for Cu Mn and O are close to 2 and close to 6 for W.  
 This corresponds with valencies expected for this structure.

Check the final profile fit in Profile viewer

In “Edit profile”, page “Profile”, look at the resulting crystallite size:  $664\text{ nm}$

In “Edit profile”, page “Profile”, press “Edit tensor parameters” and look at the resulting strain parameters. Press “Show p/sig(p)” to see their significance in terms of sigma.

## Notes

St400	7.1*su	St310	fixed	St301	38*su
St220	61.1*su	St211	fixed	St202	36.2*su
St130	fixed	St121	6.7*su	St112	fixed
St103	22.1*su	St040	7.2*su	St031	fixed
St022	8.5*su	St013	fixed	St004	7.5*su

*The largest value corresponds to the expected strain direction because of stretching of the structure along the  $1\ 1\ 0$  direction during the transition from monoclinic to triclinic phase. However, some other strain parameters are also fairly above the 3 sigma limit, and this is the reason why the classical uniaxial method fails.*

## References

Journal of Applied Crystallography **32**, 281–289 (1999).

# Example 3.1: AD3

Revised: 4 March 2019

Data	Topic	Level
X-ray single crystal data	structure of a pseudo-merohedric twin	Basic

## Tasks

Solving structure with pseudo-merohedric twinning and unequal twin volume fractions

- Finding twinning matrix using Symmetry wizard
- Creating publication CIF.

## Initial data

### Data

Single crystal data measured with Oxford Diffraction four-circle diffractometer

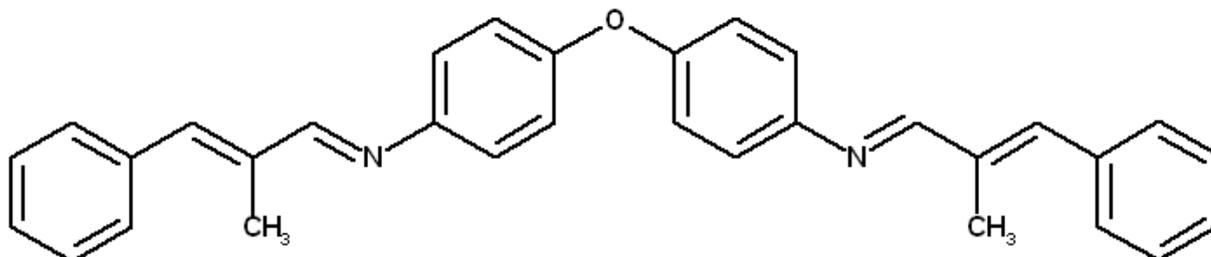
### Input files:

AD3.hkl, AD3\_red.sum

### Additional information:

Frame scaling, absorption correction: done by the diffractometer software

Chemical formula: Bis[N-(2-benzylidenepropylidene)phenyl]ether



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# Instructions

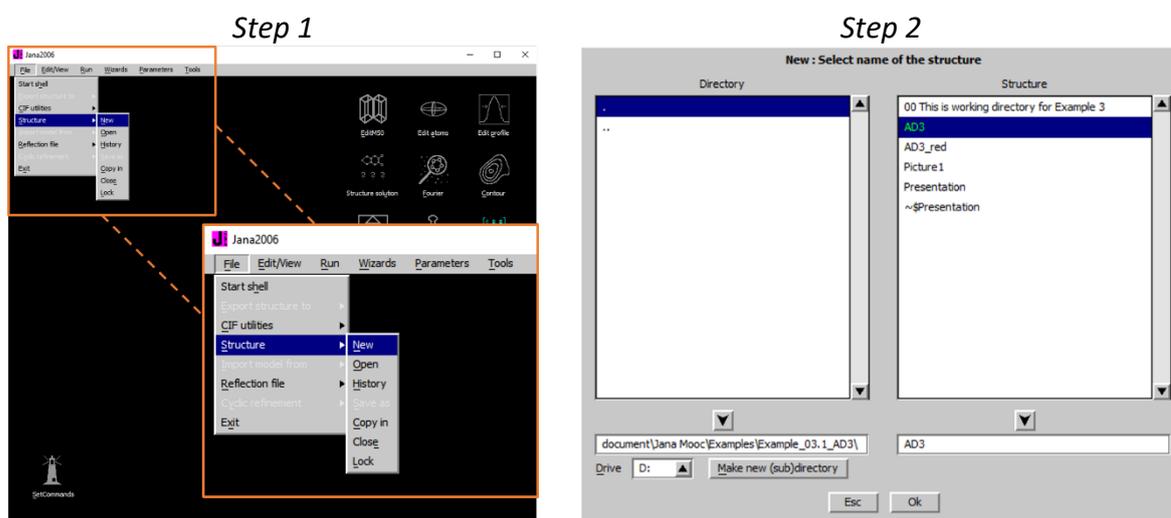
## III. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager (*Step1*)

Left pane: locate directory with input files; Right pane: double-click AD3 (*Step2*)

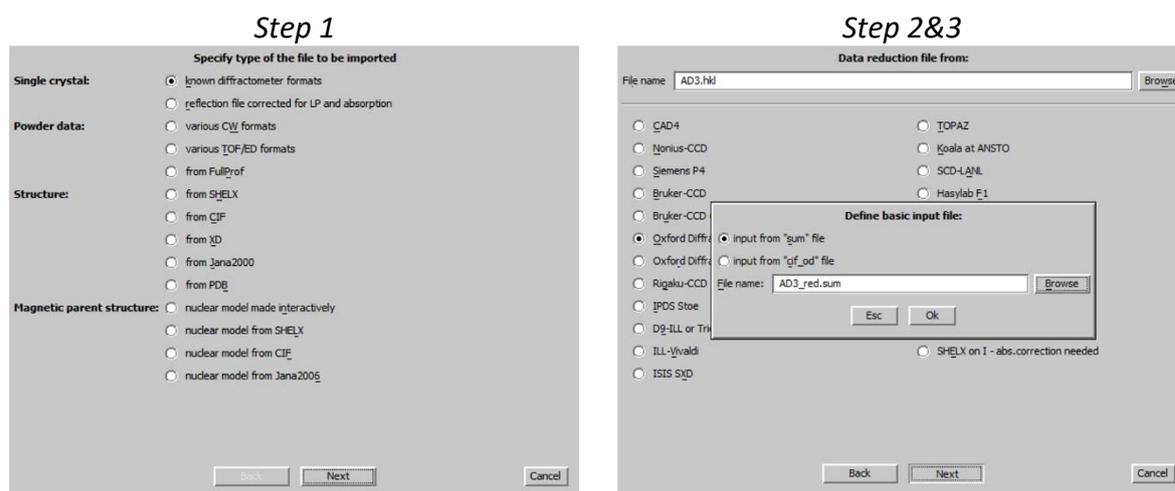


### 2. Import wizard

Select “Known diffractometer formats”; NEXT (*Step1*)

Select “Oxford Diffraction → CCD”; NEXT (*Step2*)

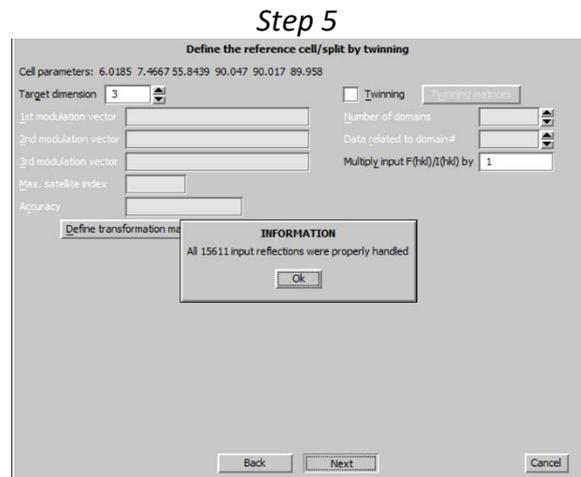
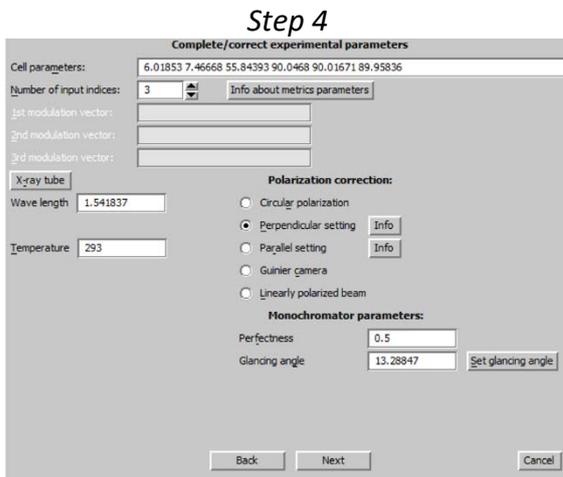
Select “Input from “sum” file”; OK (*Step3*)



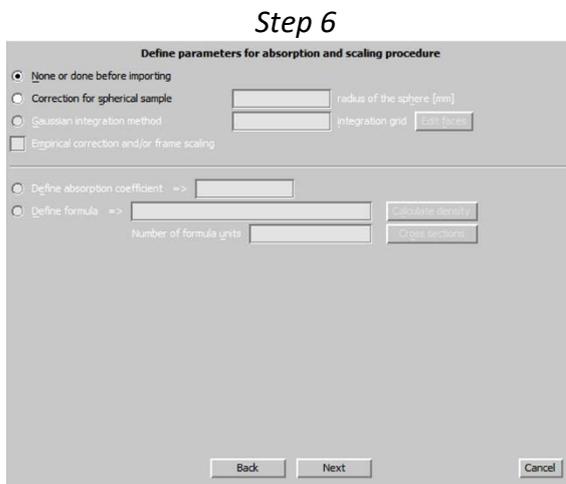
Leave all settings unchanged; NEXT (*Step4*)

Leave all settings unchanged; NEXT; OK; (*Step5*)

The program reads 15611 reflections from hkl file

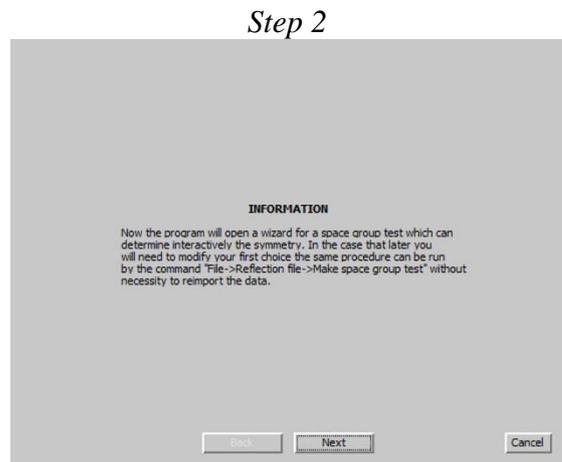
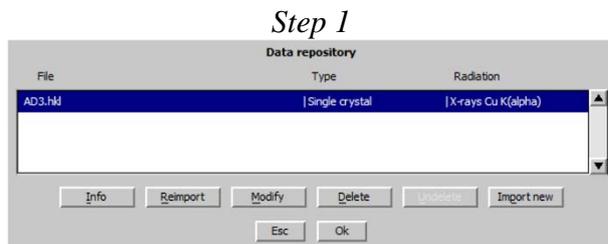


For absorption correction, select “None or done before importing”; NEXT (Step6)  
FINISH (Step7)



### 3. Data Repository

OK; YES to accept the data set (Step1)  
Next; (Step2)



## IV. Symmetry and data merging

### 1. Symmetry wizard

[On the screen: "Tolerances for crystal system recognition".]

Select "Introduce twin laws in case of subgroups"

Leave all other settings default; NEXT (Step 1)

[On the screen: Select Laue symmetry]

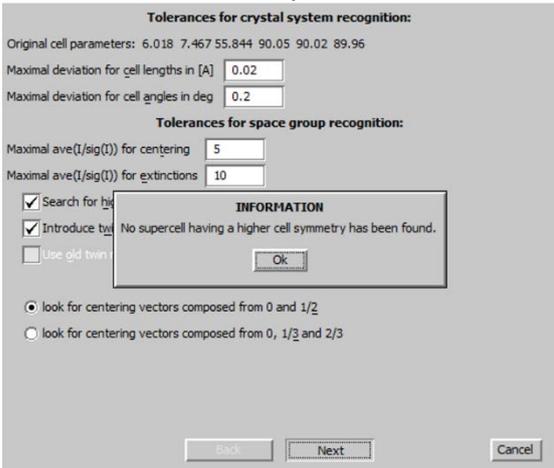
Select Monoclinic – setting "c"; NEXT (Step 2)

**Notes**

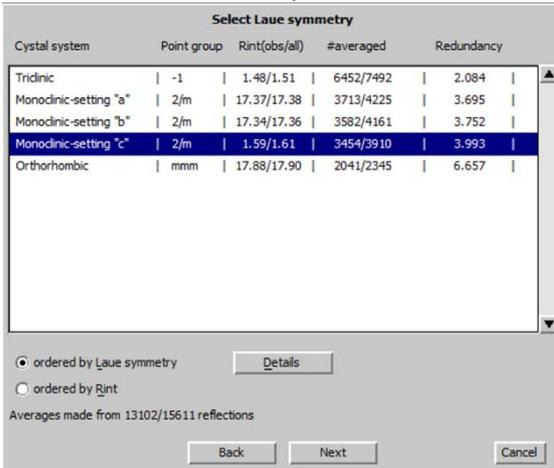
The highest Laue symmetry consistent with cell parameters is orthorhombic. It has rather high  $R_{int}$  (~17%) which indicates that orthorhombic symmetry is violated. Typical reason for such violation is presence of twinning where the structure of twins has lower symmetry and the twin domain fractions are not equal.

The selected Laue symmetry is monoclinic. In the previous step, we have activated an option "Introduce twin laws in case of subgroups". This means that the symmetry operation generating the orthorhombic symmetry from the selected monoclinic symmetry will be used as the twinning operation and considered in the merging process.

#### Step 1



#### Step 2



Crystal system	Point group	Rint(obs/all)	#averaged	Redundancy
Triclinic	-1	1.48/1.51	6452/7492	2.084
Monoclinic-setting "a"	2/m	17.37/17.38	3713/4225	3.695
Monoclinic-setting "b"	2/m	17.34/17.36	3582/4161	3.752
Monoclinic-setting "c"	2/m	1.59/1.61	3454/3910	3.993
Orthorhombic	mmm	17.88/17.90	2041/2345	6.657

Select primitive unit cell; NEXT (Step 3)

[On the screen: Select space group]

Using the criteria described in the first example select P21/n, (Step4)

### Step 3

Select cell centering

Centering	obs/all	ave(I/sig(I))
<input checked="" type="radio"/> P	0/0	0.000/0.000
<input type="radio"/> A	6526/7811	37.641/31.643
<input type="radio"/> B	5745/7825	26.467/19.737
<input type="radio"/> C	6531/7812	37.053/31.175
<input type="radio"/> I	6606/7818	36.164/30.748
n.a. R-obverse	5755/6944	37.705/31.452
n.a. R-reverse	5755/6944	37.705/31.452
<input type="radio"/> F	9401/11724	34.023/27.514

Warning: The cell centering need not be one you expect from collection as the program first transform the cell to the reduced form.  
Moreover after your selection the program makes another transformation whenever the centering is not the standard one.

Back Next Cancel

### Step 4

Select space group

Space group	obs/all	ave(I/sig(I))	FOM
P21/n	46/170	6.025/2.272	0.40433
P2/n	21/94	5.666/1.950	0.50411
Pn	21/94	5.666/1.950	0.50411
P2/m	0/0	0.000/0.000	1.00000
Pm	0/0	0.000/0.000	1.00000
P2	0/0	0.000/0.000	1.00000
P21/m	25/76	6.327/2.670	1.27704
P21	25/76	6.327/2.670	1.27704

Details

Back Next Cancel

Press "Details" to verify it is really acceptable; NEXT (Step 5)

### Notes

The 46 reflections violating the extinction rules have mostly low I/p. Some additional spots in the diffraction pattern from e.g. a small crystal attached at the surface of the measured sample might cause the violations.

Select "Accept twinning matrices induced by the space group test"

Select "Accept the space group in the standard setting"; FINISH (Step 6)

### Step 5

Jana2006

End Find next Go to Print PgUp Open in editor Close

List of strongest reflections contradicting the space group P21/n structure :

Original cell parameters: 6.018 7.467 55.844 90.05 90.02 89.96  
Transformation matrix: 0.000 0.000 -1.000  
1.000 0.000 0.000  
0.000 -1.000 0.000  
Actual cell parameters: 7.467 55.844 6.018 90.00 90.04 90.00  
Centrosymmetric space group: P21/n  
List of centering vectors:  
0.000000 0.000000 0.000000  
Symmetry operators:  
x y z  
-x+1/2 -y+1/2 z+1/2  
-x -y z  
x+1/2 -y+1/2 z+1/2

\* List of strongest reflections contradicting the space group P21/n \*

h	k	l	I	sig(I)	I/sig(I)
0	45	0	200.4	12.4	16.2
0	48	0	223.2	14.9	18.0
0	47	0	129.8	13.6	9.6
0	47	0	138.7	16.3	9.1
3	0	2	202.0	23.6	8.6
3	0	2	160.8	20.2	8.0
4	0	1	189.7	23.9	7.9
0	21	0	153.0	19.3	7.9
3	0	4	77.3	9.8	7.9
0	21	0	146.8	19.1	7.7
4	0	1	123.0	30.4	7.3
3	0	0	86.0	13.3	7.2
1	0	-2	136.6	19.0	7.1
3	0	-2	226.6	31.9	7.1
3	0	1	70.6	10.0	7.0
0	21	0	120.6	17.7	6.8
0	48	0	61.2	9.1	6.7
4	0	-1	164.6	24.7	6.7
0	49	0	73.9	11.4	6.5
0	23	0	101.4	18.7	6.6
0	23	0	104.1	16.7	6.2
0	11	0	74.8	12.2	6.1
0	23	0	111.6	10.6	6.0

### Step 6

Final step of the space group test

accept the space group in the standard setting:  
Space group: P21/n  
Cell parameters: 7.4667 55.8439 6.0185 90 90.042 90  
Transformation matrix: a' = 0.000\*a +1.000\*b +0.000\*c  
b' = 0.000\*a +0.000\*b -1.000\*c  
c' = -1.000\*a +0.000\*b +0.000\*c

accept the space group transformed into the original cell:  
Space group: P21/n  
Cell parameters: 6.0185 7.4667 55.8439 90 90 89.958

discard the changes

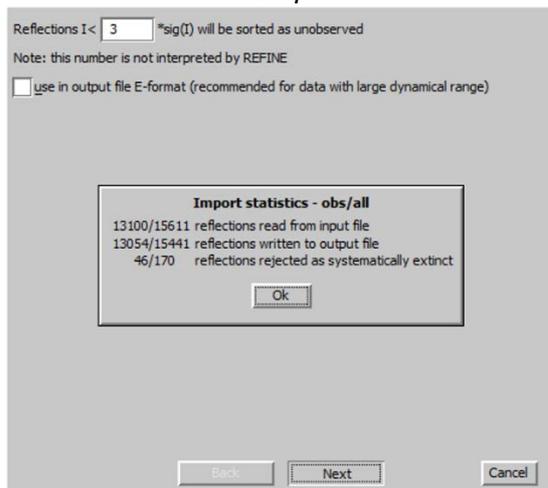
Accept twinning matrices induced by the space group test

Back Finish Cancel

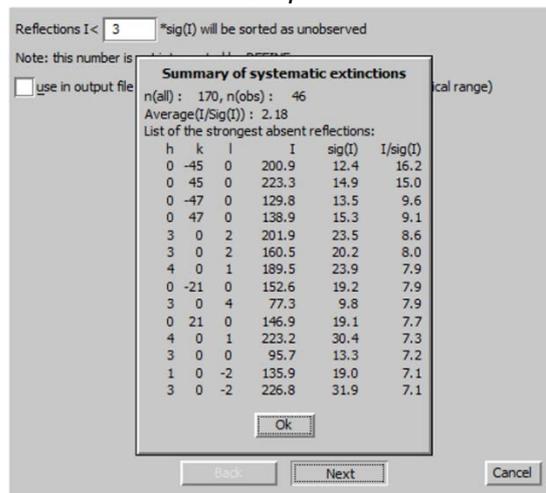
## 2. Creating refinement reflection file

NEXT to confirm threshold 3sigma; OK; OK (Step1)

### Step 1



### Step 1b

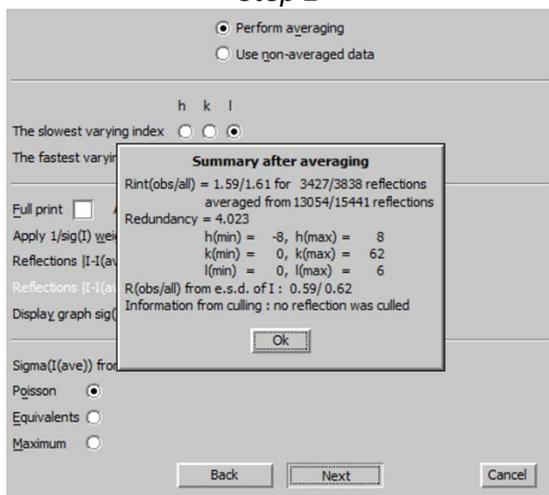


[On the screen: settings for merging of reflections]

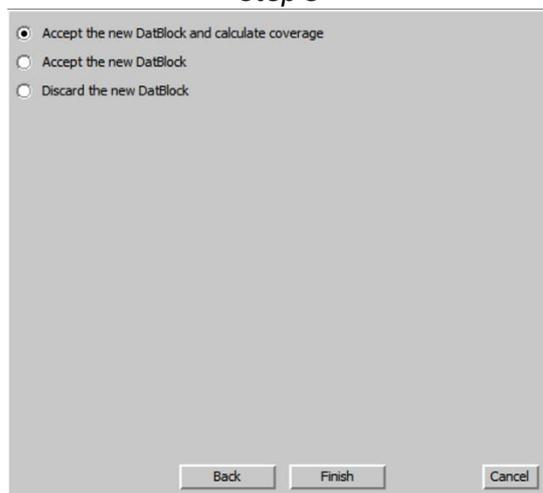
Leave all settings default; NEXT (Step 2)

Accept the new DatBlock and calculate coverage; FINISH (Step3)

### Step 2



### Step 3



## V. Structure solution

### 3. Structure solution wizard

[On the screen: window of Structure solution]

In "Formula" textbox type list of chemical elements for AD3: C N O H

Select "Superflip", "Peaks from Jana2006"; "Repeat Superflip: Number of runs" and 15 for number of runs; limit Maxcycles to 1000; leave other settings default

Press "Run Solution" (Step 1)

## Step 1

**Structure solution**

use SJR: 2011  
 use Superflip

Formula: C N O H  
Formula units: 4  
Actual space group: P2<sub>1</sub>/n

allow manual editing of the command file before start  
 use previously prepared input file for Superflip  
 use old solution and reinterpret it  
 Repeat Superflip: Until the convergence detected  
 Repeat Superflip: Number of runs => 15  
 Use local normalization  
 Use a specific random seed  
 Define explicitly delta value

Iteration scheme:  CF  
 LDE  
 AAR

Starting model:  Random phases  
 Patterson superposition map

Biso: 0  
Maxcycles: 1000

For peak search use:  EDMA - fixed composition  
 EDMA - fixed number of atoms  
 EDMA - peak interpretation by Jana2006  
 Peaks from Jana2006

[On the screen: listing of Superflip]

### Notes

With this setting Superflip repeats calculation 15 times (from different randomly generated set of phases) and returns the result with the best fit between the electron density map and the user-defined symmetry. Because of twinning the fit of symmetry generators is worse and it may happen that Superflip suggests P2<sub>1</sub> instead of P2<sub>1</sub>/n - please ignore this fact, "n" is confirmed by systematic extinctions. With this structure, the results of Superflip are significantly better when "Biso" is set to 3 in the charge flipping options; however, this would be an empirical step useless for other structures.

[Close listing of Superflip](#)

[Press "Draw structure" to see result of charge flipping \(Step 2\)](#)

### Notes

It may happen that Diamond shows two molecules instead of one. This is because twinning also biases the bond lengths, some distances are too long and some atoms are not properly assigned. To see the complete molecules, change the bonding limits in Diamond through Build → Connectivity

## Step 2

**Structure solution**

use SIR 2014 Formula: CNOH  
 use Superflip Formula units: 4 Calculate density  
 use Shelxt Actual space group: P21/n Change the space group

---

allow manual editing of the command file before start  
 use previously prepared input file for Superflip  
 use old solution and reinterpret it Biso: 0  
 Repeat Superflip: Until the convergence detected Maxcycles: 1000  
 Repeat Superflip: Number of runs => 15  
 Use local normalization  
 Use a specific random seed  
 Define explicitly delta value

Iteration scheme:  CF For peak search use:  EDMA - fixed composition  
 LDE  EDMA - fixed number of atoms  
 AAR  EDMA - peak interpretation by Jana2006

Starting model:  Random phases  Peaks from Jana2006  
 Patterson superposition map  Peaks from Jana2006 but first run Fourier

Quit Diamond without saving changes

In case of doubts repeat structure solution and plotting

Finally press "Accept last solution" to close the structure solution wizard

## 4. Verification of the structure solution

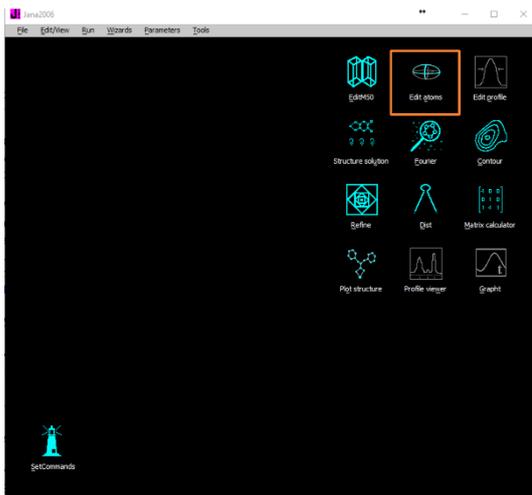
Start "Edit atoms" (Step 1)

[On the screen: list of atoms]

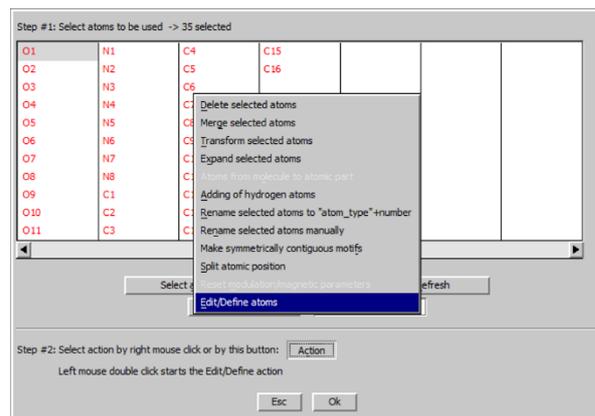
Press "Select all"

Start "Action → Edit/define" (Step 2)

### Step 1



### Step 2



Double-click "Type" textbox

## Notes

Double-click unlocks the yellow textboxes. They are locked for security reasons because the selected atoms have different parameters (here chemical types).

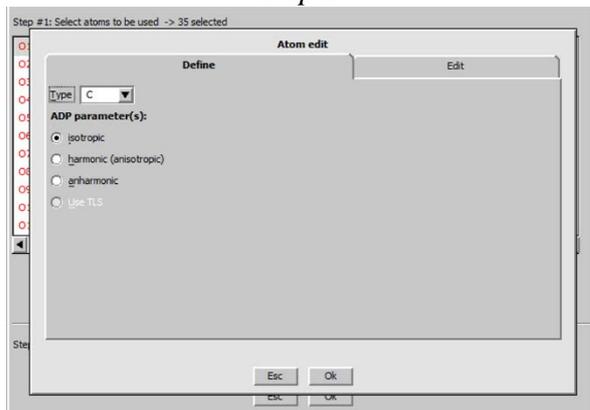
Select Carbon, OK (Step3)

[On the screen: list of atoms.]

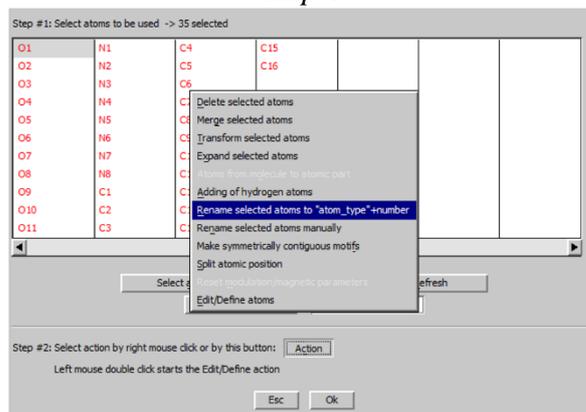
The labels are still the original ones but the chemical type of all atoms is carbon

Start "Action → Rename selected atoms to atom type + number" (Step4)

Step 3



Step 4



Press "Select all"

Start "Action → Make symmetrically contiguous motifs" (Step5)

OK; YES to save changes

## Notes

These steps help to get a reasonable plot in Diamond (next step) even with biased distances and improper chemical types

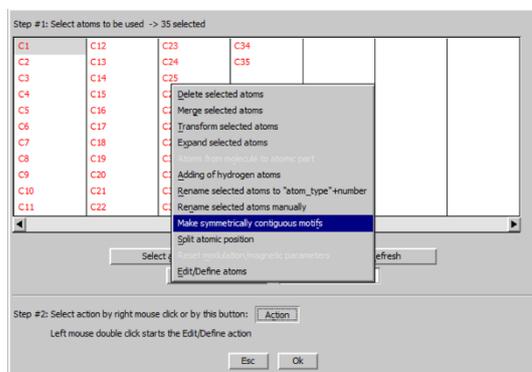
Start "Plot structure" (Step6)

Press "Draw+continue"

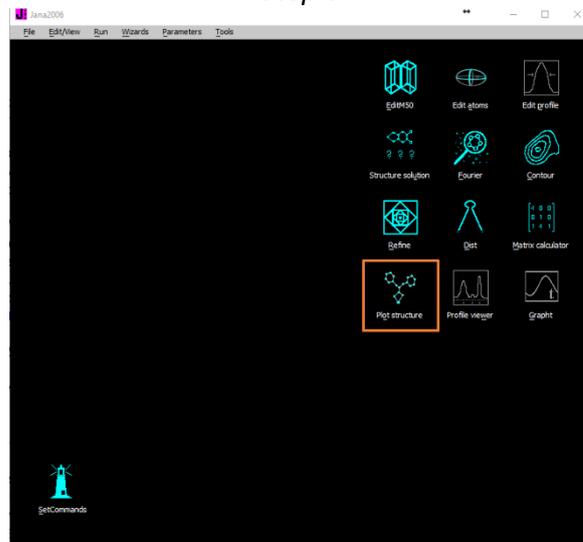
## Notes

In this mode Jana will launch Diamond but it will not wait for its end

Step 5



Step 6



[On the screen: window of Diamond]

Start "Build → Molecules → Get molecules → OK" **or** use  on the bottom toolbar  
Rotate the molecule ( and  on the bottom toolbar) to get an optimal view  
Draw rectangle to select all atoms of the molecule or press Ctrl-A  
Right-click on one of the selected atoms, choose "Add  Atom labels"

[On the screen: dialogue of Diamond for atom labeling]

For "Content" select: "Atom symbol"

Define relative position of labels 0.3,0.3,10

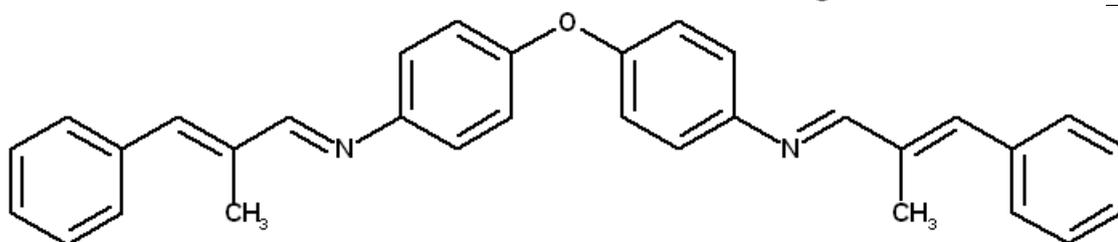
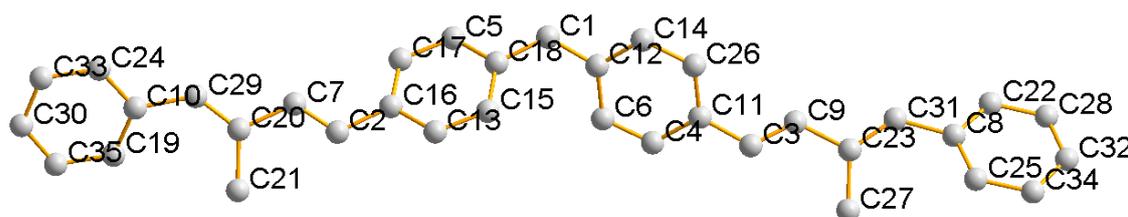
Define text size ~0.8Å; OK

Rotate the molecule to similar orientation like has the chemical scheme

[On the screen: plot of the molecule with atom labels]

#### Notes

*The results may be slightly different for each run of Superflip. This is because Superflip starts from random phases and the resulting electron density map differs for each run. In our case, chemical types of some atoms need to be corrected.*



Compare the plot with the chemical scheme **and note labels of atoms**, which must be oxygen or nitrogen.

#### Notes

*In our example, C2 and C3 should be nitrogen and C1 should be oxygen.*

Quit Diamond

## 5. Assignment of correct chemical types

[On the screen: basic Jana window]

Start "Edit atoms"

[On the screen: list of atoms]

Select the atom which should be oxygen (C1 in our example)

Editing of one atom can be also started by right mouse button or by double-click  
 Start "Action → Edit/define" and choose chemical type "O"; OK  
 Press "Refresh"  
 Hold Ctrl and select atoms which should be nitrogen (C2,C3 in our example)  
 Start "Action → Edit/define" and choose chemical type "N"; OK  
 [On the screen: list of atoms, labels are still the original ones but chemical types are correct]  
 Press "Select All"  
 Press "Action" or right-click on one of the selected atoms  
 Choose "Rename selected atoms to atom\_type + number"  
 [On the screen: list of atoms with labels corresponding to chemical types]

## Notes

You should see one oxygen, two nitrogens and carbons. If not press ESC and start again 😊

OK; YES to save the changes  
 Check chemical types with Diamond

## VI. Refinements and model improvement

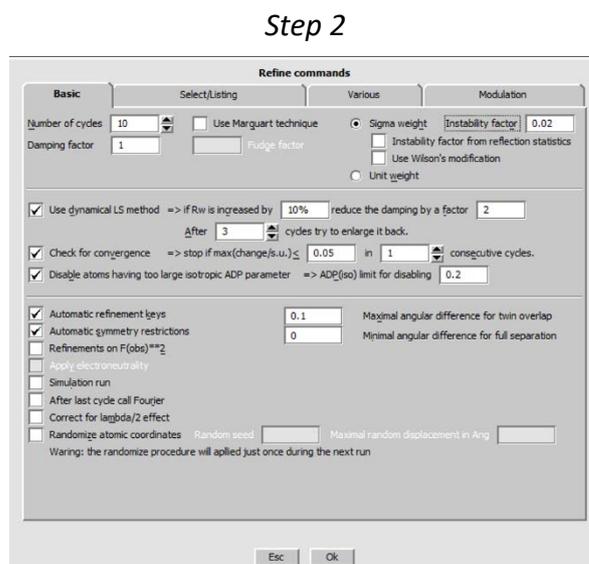
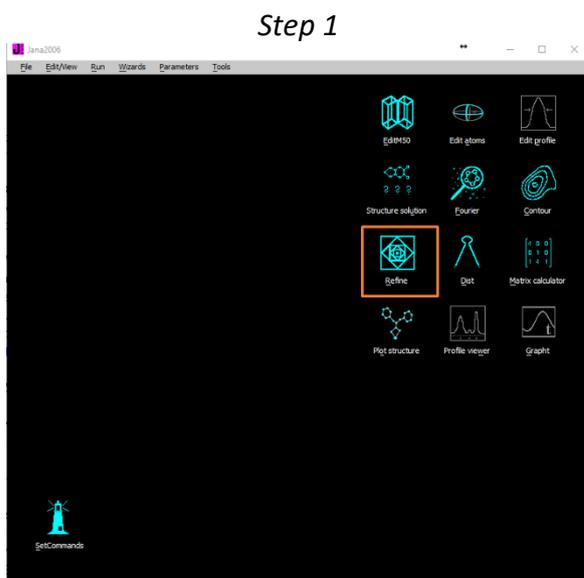
### 1. Refinement

[On the screen: basic window of Jana]  
 Right-click the icon of Refine. (Step1)  
 [On the screen: refinement options]  
 Define 100 of cycles, Damping factor 1 and Instability factor 0.02; OK (Step2)

## Notes

This instability factor slightly lowers goodness of fit, which makes happy editors used for SHELX. However, we cannot change this number arbitrarily because values below 0.01 or above 0.02 are usually in contradiction with the instrument characteristics.

Choose "YES+START"  
 Refinement converges with R value about 16%, GOF about 8, 141 refined parameters



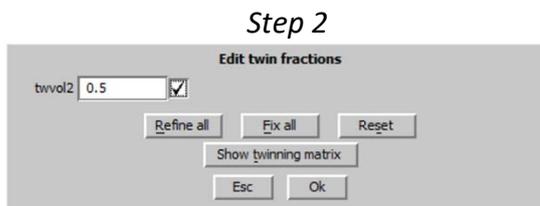
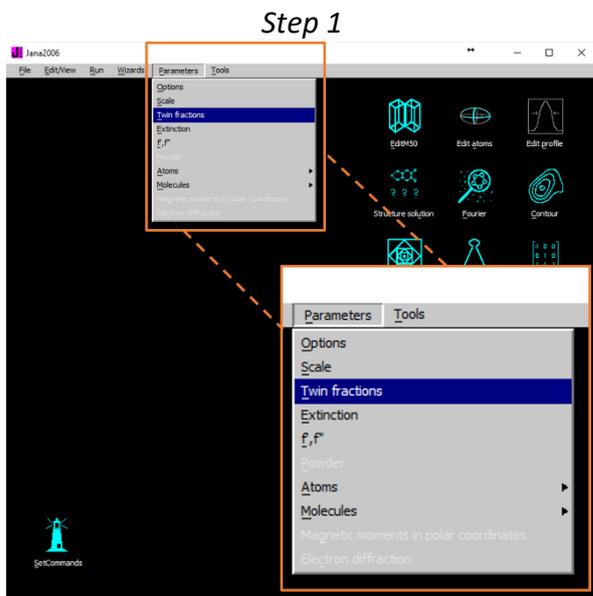
## 2. Twin volume fraction

Start “parameters → Twin fractions” (Step1)

### Notes

The volume fraction of the twin domain introduced by the Symmetry wizard is 0.5 and twinning matrix relating the monoclinic and orthorhombic symmetry is  $(1\ 0\ 0\ | 0\ 1\ 0\ | 0\ 0\ -1)$ .

Activate refinement of the twin fraction (Step2)



Repeat refinement

Refinement converges with R value about 11%, GOF about 7

Twin volume fraction drops to 0.29.

Start “Edit atoms”

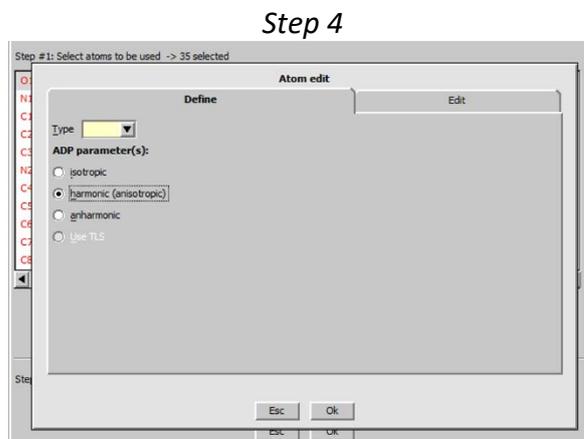
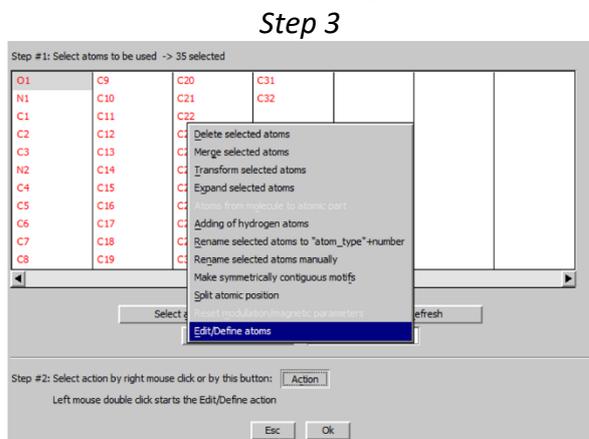
[On the screen: list of atoms]

Press “Select all” and “Action → Edit/define” (Step3)

Choose “harmonic” for ADP parameters. (Step4)

This defines anisotropic temperature parameters for all atoms.

OK, OK, YES to save changes



Double-click the icon Refine.

Refinement converges with R value about 9%, GOF about 6, 317 refined parameters.

### 3. Adding of hydrogen atoms & Final refinement

[On the screen: basic window of Jana]

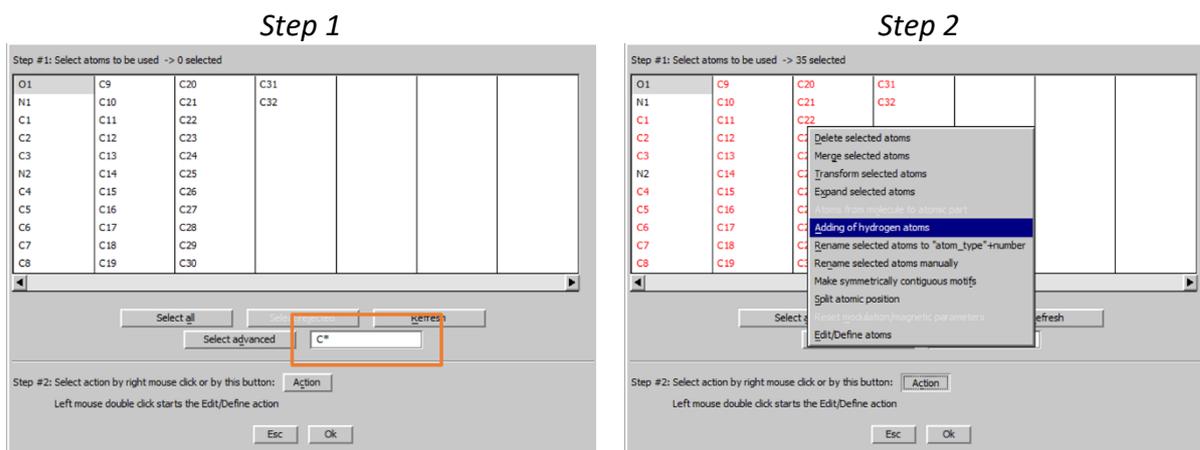
Start "Edit atoms"

In the textbox type "C\*"; TAB. (Step1)

#### Notes

This will select atoms starting with C, i.e. carbons

Start "Action → Adding of hydrogen atoms" (Step2)



[On the screen: Adding of hydrogen atoms dialogue]

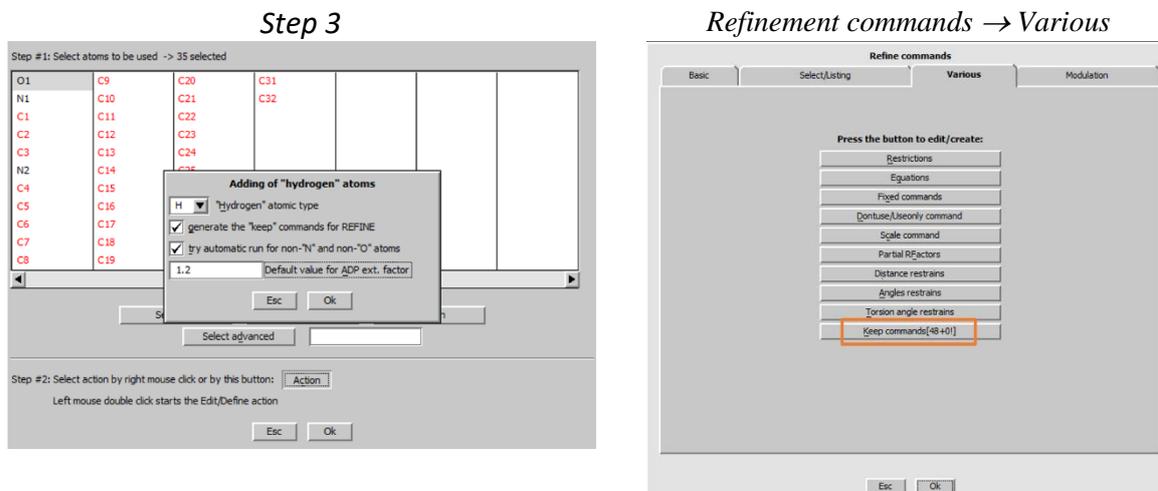
Leave all settings default; OK (Step3)

[On the screen: list of atoms with new hydrogens]

#### Notes

Total number of atoms should be 63 (can be verified using "Select All")

The hydrogens are kept in ideal geometry by commands which can be viewed or edited in "Refinement commands → Various → Keep commands".



OK to close “Edit atoms”; Yes to save changes  
“Plot structure” to check results of automatic hydrogen assignment  
Make refinement of the final structure

#### Notes

Oscillation may occur during the refinement. In such case do not break refinement, press Parameters, change Damping factor to 0.5 and close the dialogue. Refinement will continue with damping.  
Refinement converges with R value 3.7%, GOF 2.7, 317 refined parameters.

## VII. Creating CIF file

#### Notes

The information for the CIF file is cumulated in the file M70 during the data processing as well as solution and refinement steps. For creating a publication CIF, repetition of the basic steps is recommended in order to refresh the information in M70. In our case, we have started from the \*.sum file so M70 does not contain any information about the experiment

Start “File → Reflection file → Create refinement reflection file”

#### Notes

In our case this step is not necessary because it has been already done

Repeat refinement

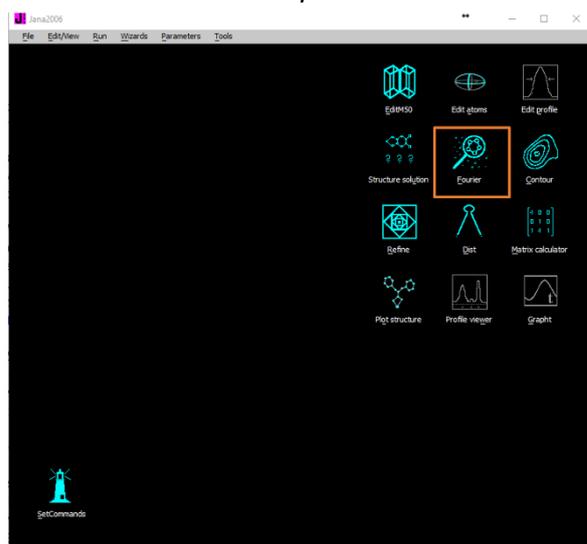
#### Notes

In our case this step is not necessary because it has been already done

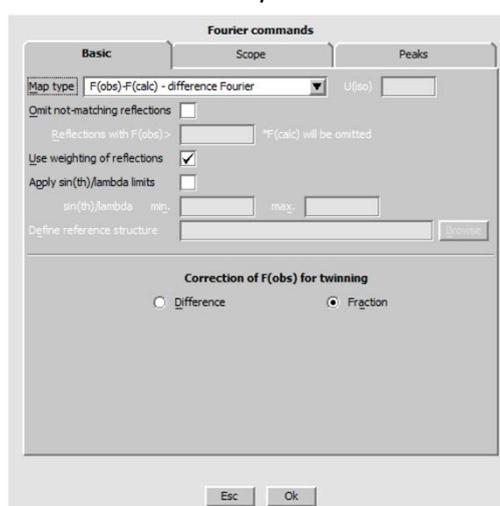
Right-click Fourier; (Step1)

Select “F(obs)-F(calc) - difference Fourier”; make sure that “Weighting of reflections” is checked and “Apply sin(th)/lambda limits” unchecked; (Step2)

Step 1



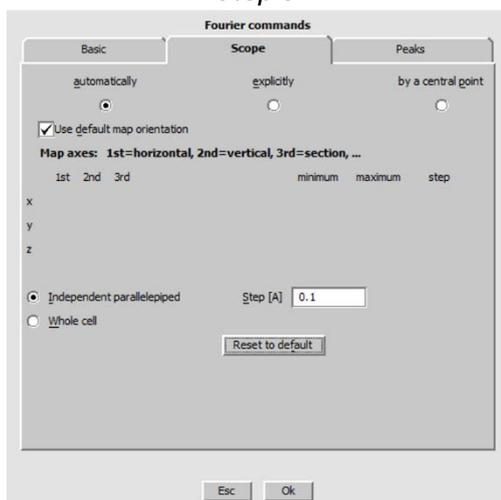
Step 2



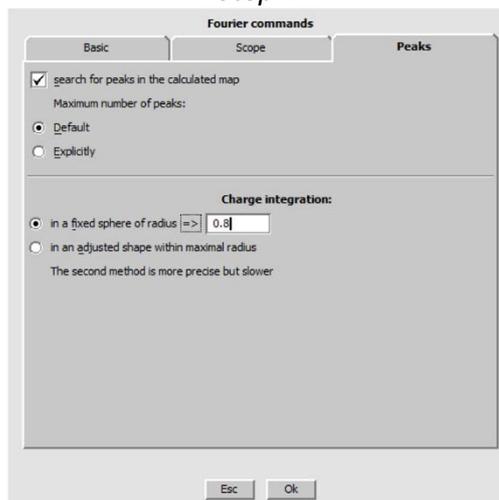
In the page “Scope” press “Reset to default”; (Step3)

In the page “Peaks” choose “in a fixed sphere of radius 0.8” (Step4)

### Step 3



### Step 4

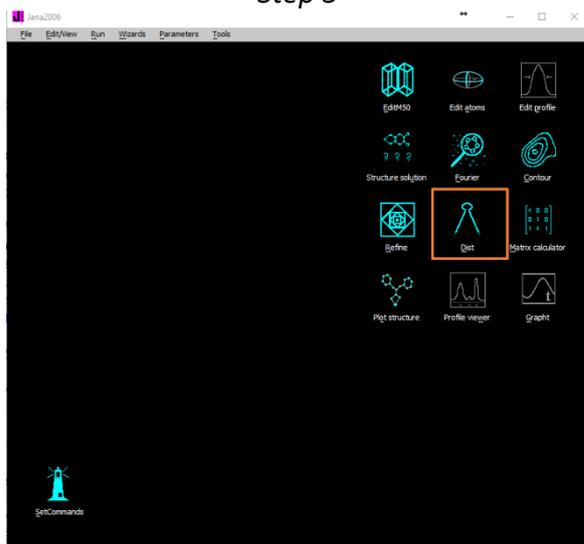


OK; YES+START; NO to include new atoms; NO to see the listing

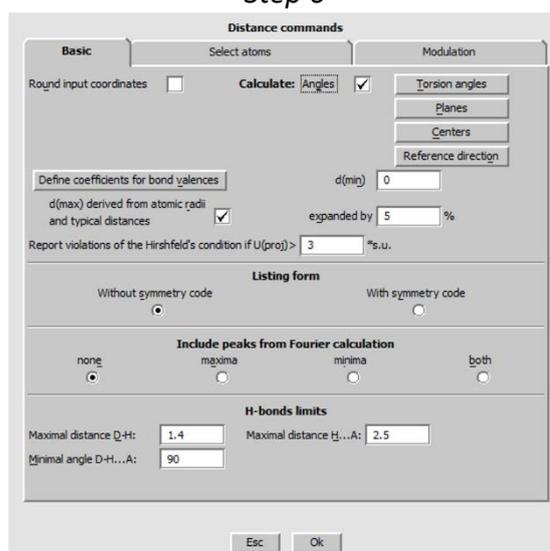
Right-click Dist icon (Step 5)

Select "d(max) derived from atomic radii and typical distances and adjust "expanded by" value" when needed; check "Calculate angles"; in needed, adjust limits for H-bonds; (Step 6)

### Step 5



### Step 6

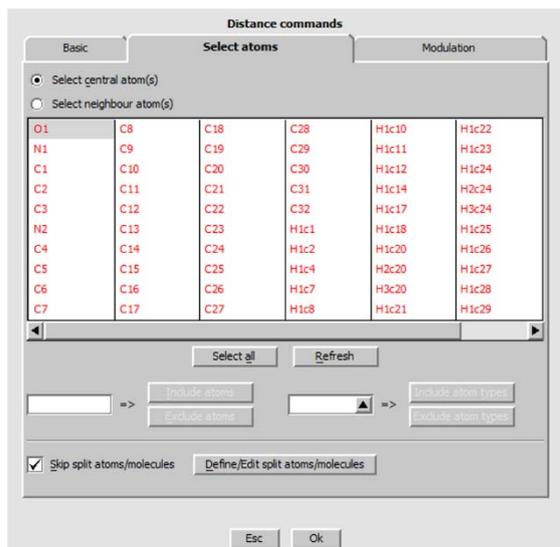


In the page "Select atoms" check central atoms and neighbor atoms – usually we want to have all atoms in both roles; (Step 7)

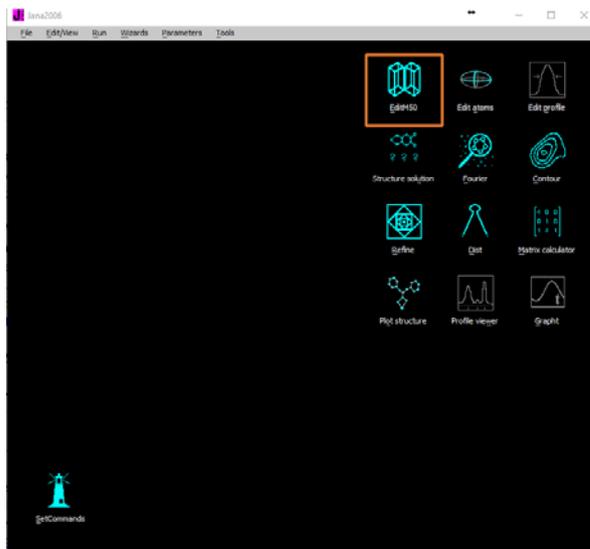
OK; YES+START; Close;

Start EditM50; (Step 8)

### Step 7



### Step 8

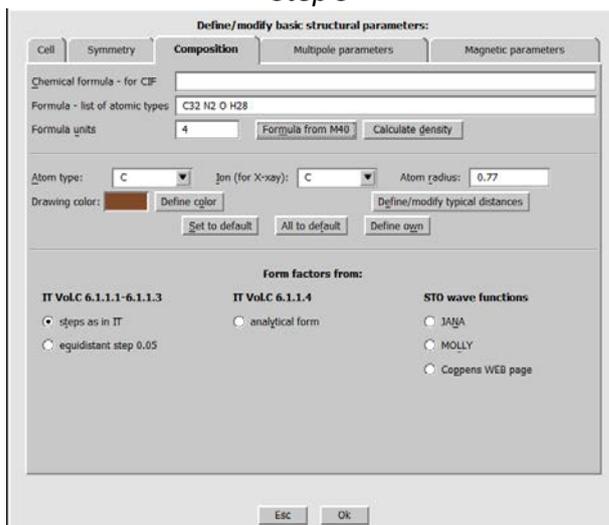


Go to page Composition; enter 4 for “Formula units”, press “Formula from M40” (Step9)  
OK; YES for updating the formula.

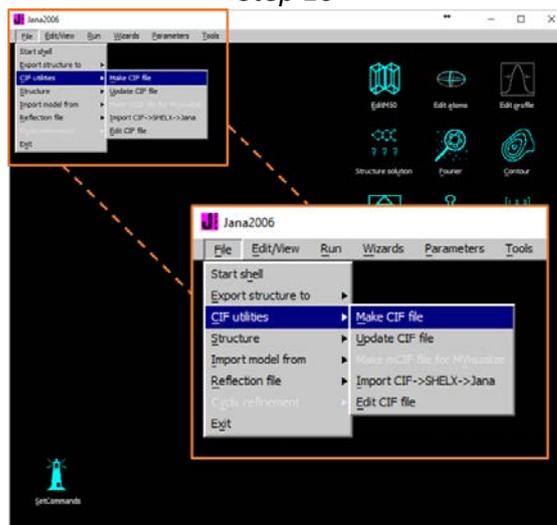
OK; YES to rewrite M50

Start “File → CIF utilities → Make CIF file” (Step10)

### Step 9



### Step 10



### Notes

When formula to be listed in CIF differs of the formula generated from the structure model, it can be defined in the “Chemical formula – for CIF” textbox

### References



# Example 3.2: PyNinit

Revised: 07 March 2018

Data	Topic	Level
X-ray single crystal data	structure with pseudo-merohedric 3-fold twinning	Advance

## Tasks

Solving simple structure with non-merohedric twinning using Jana2006

- Handling twin overlaps in Jana2006.

## Initial data

### Data

Single crystal data measured with Oxford Diffraction four-circle diffractometer

### Input files:

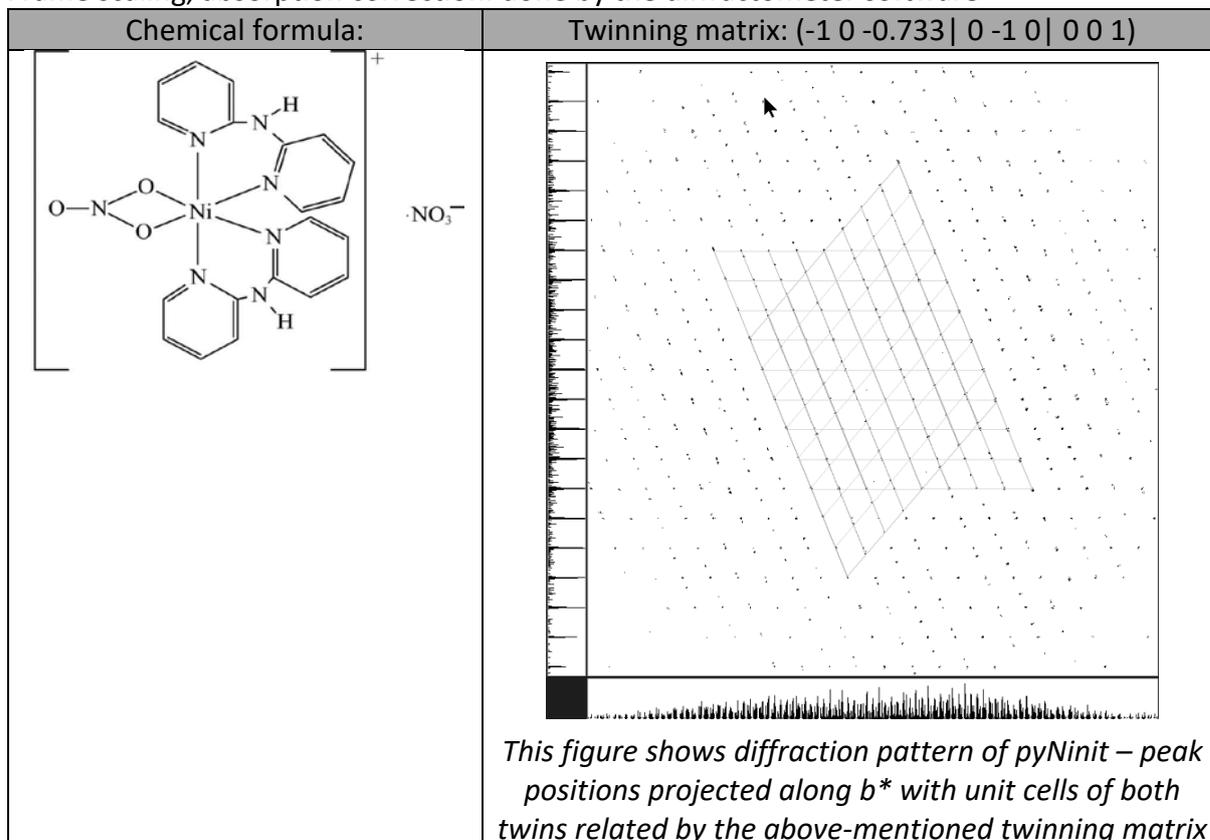
1<sup>st</sup> twin domain: pyNinit\_twin1.hkl, pyNinit\_twin1\_red.sum

2<sup>nd</sup> twin domain: pyNinit\_twin2.hkl, pyNinit\_twin2\_red.sum

hklf5: pyNinit\_twin1\_hklf5.hkl

### Additional information:

Frame scaling, absorption correction: done by the diffractometer software



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# Instructions

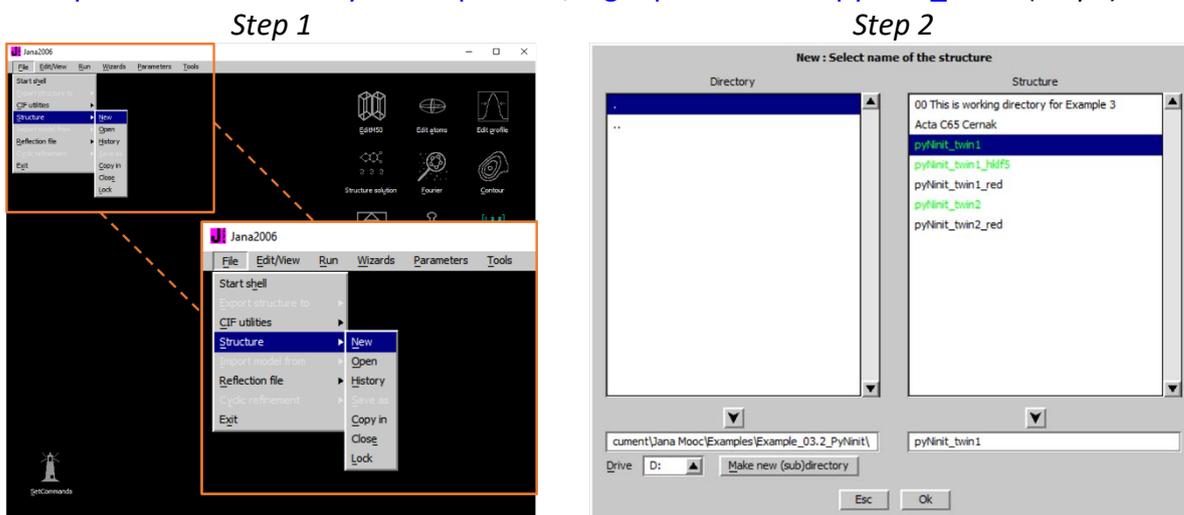
## I. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager (*Step1*)

Left pane: locate directory with input files; Right pane: double-pyNinit\_twin1 (*Step2*)

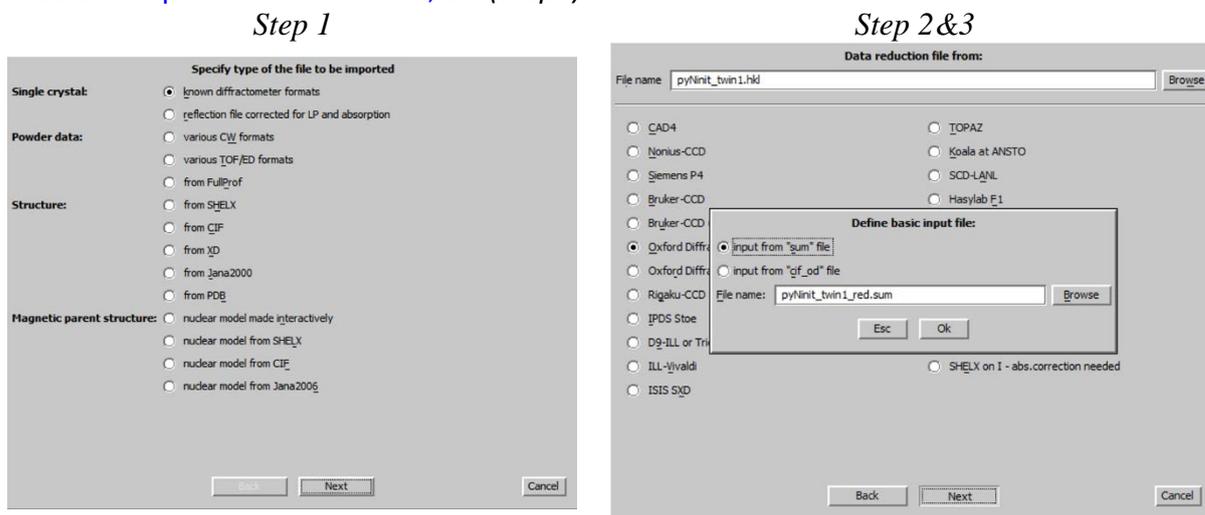


### 2. Import wizard (for the 1<sup>st</sup> twin domain)

Select “Known diffractometer formats”; NEXT (*Step1*)

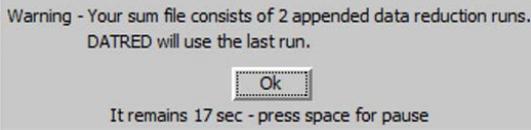
Select “Oxford Diffraction → CCD”; NEXT (*Step2*)

Select “Input from “sum” file”; OK (*Step3*)



Warning; (*Step 4*)

### Step 4



### Notes

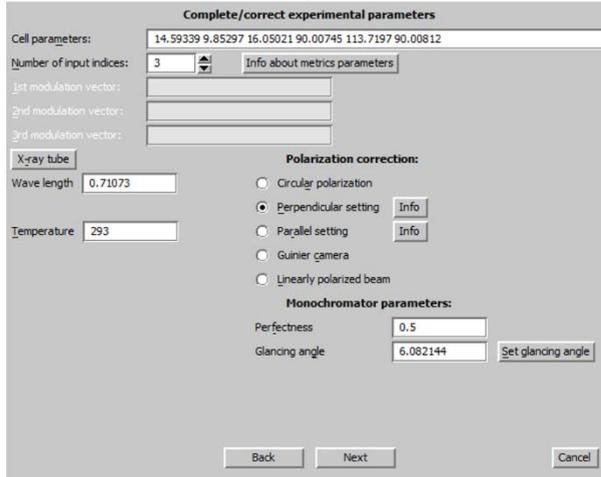
Old input files (sum) cumulated information from subsequent data reductions.

Leave all settings unchanged; NEXT (Step5)

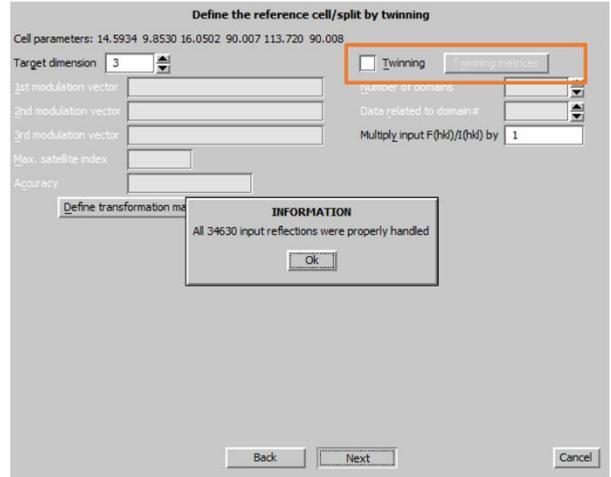
Leave all settings unchanged (leave Twinning checkbox clear); NEXT; OK; (Step6)

The program reads 34630 reflections from hkl file

### Step 5



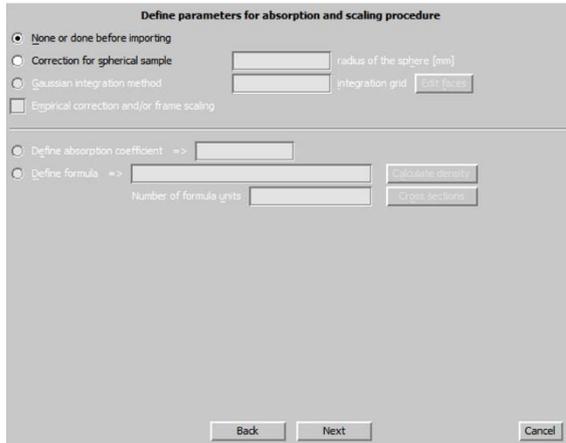
### Step 6



For absorption correction select "None or done before importing"; NEXT (Step7)

FINISH (Step8)

### Step 7



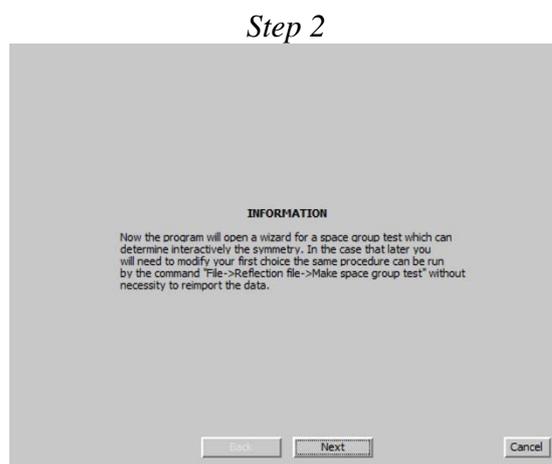
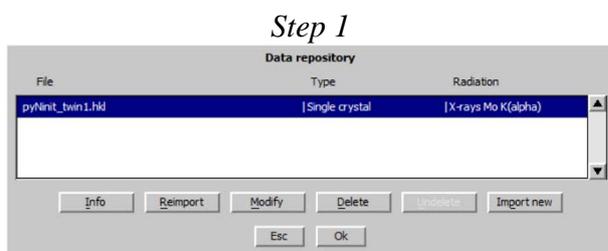
### Step 8



## 3. Data Repository

OK; YES to accept the data set (Step1)

Nest; (Step2)



## II. Symmetry and data merging

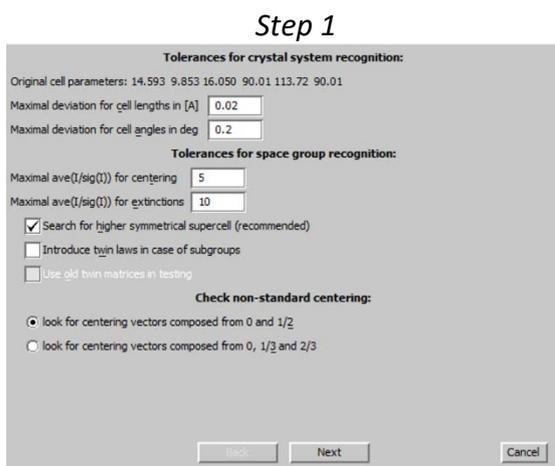
### 1. Symmetry wizard

[On the screen: "Tolerances for crystal system recognition".]

Leave all other settings default; NEXT (Step1)

[On the screen: Select Laue symmetry]

Select continue with the basic cell; NEXT (Step2)

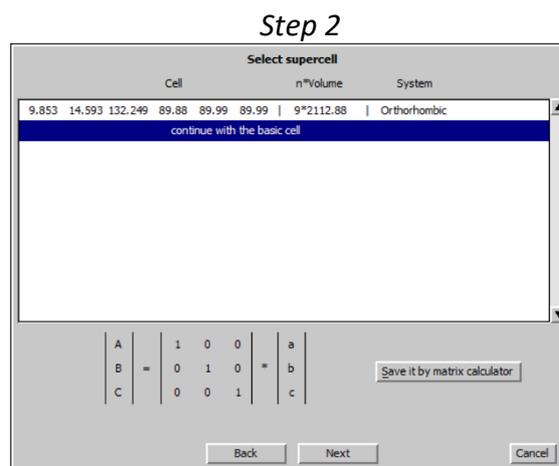


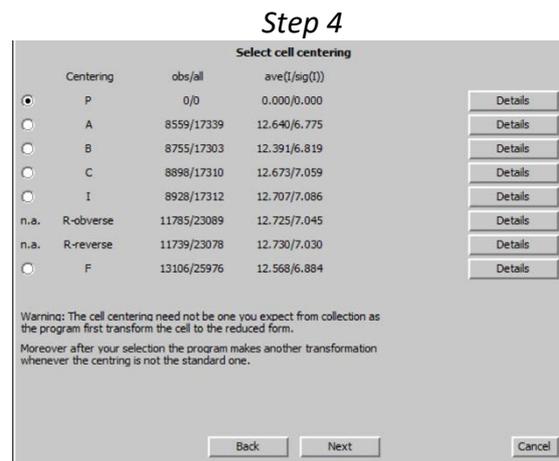
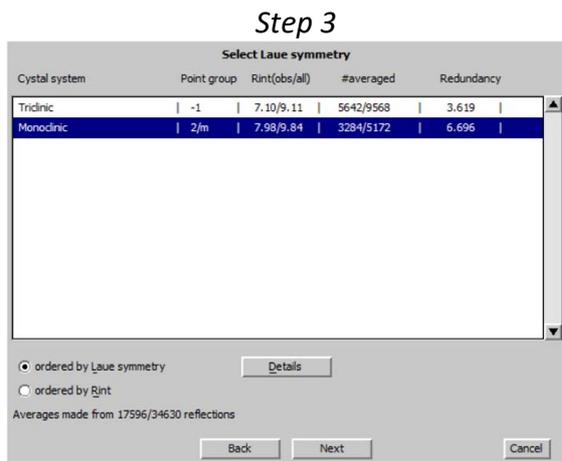
[On the screen: Select Laue symmetry]

Select Monoclinic; NEXT (Step3)

[On the screen: Select cell centering]

Select primitive unit cell; NEXT (Step4)





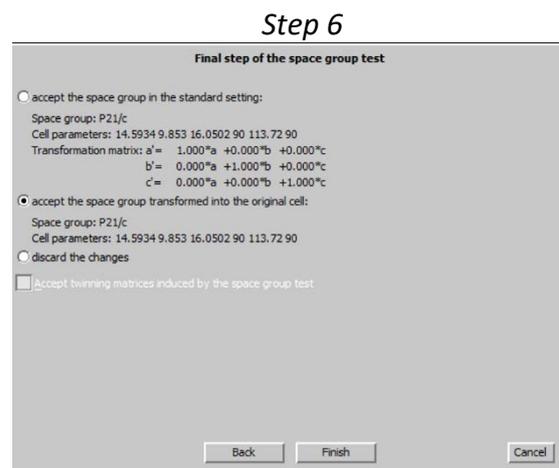
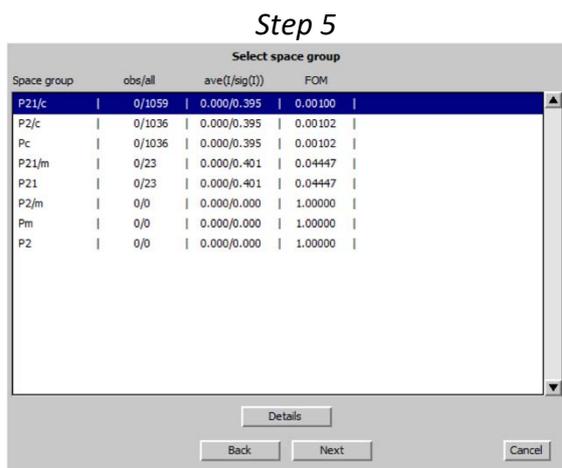
[On the screen: Select space group]

Using the criteria described in the first example Select  $P2_1/c$ ; NEXT (Step5)

[On the screen: Final step of the space group test]

Accept the space group transformed into the original cell; FINISH (Step6)

Follow the wizard for creation of the refinement reflection file



### III. Structure solution

“Run → Structure solution”

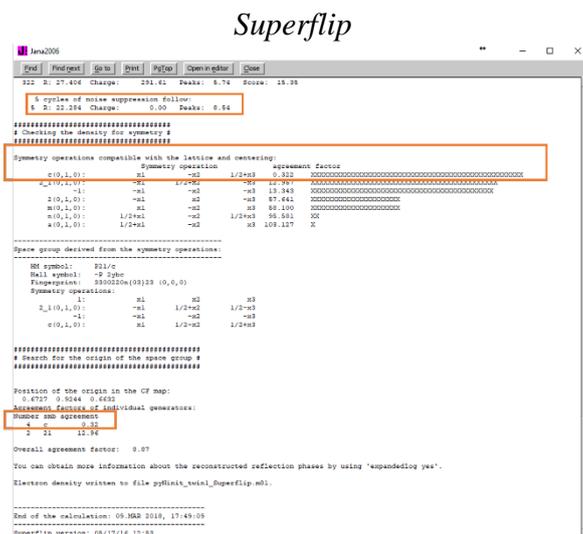
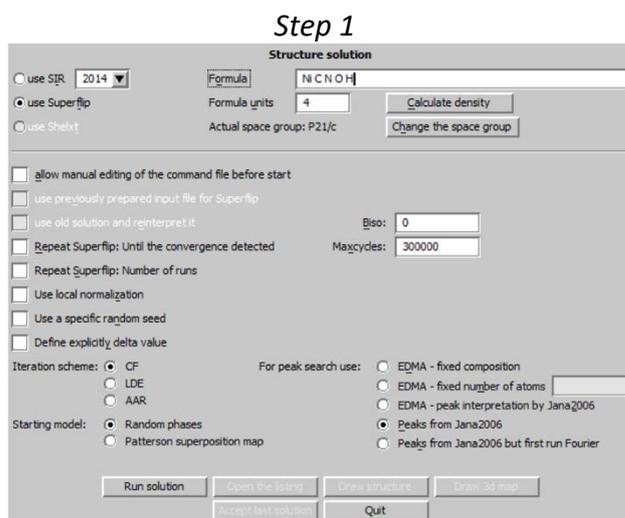
[On the screen: window of Structure solution]

In “Formula” textbox check list of chemical elements for PyNinit: Ni C N O H

Select “Superflip”, “Peaks from Jana2006”; leave other settings default; “Run solution”

#### Notes

Superflip converges (after noise suppression) with R value  $\approx 23\%$ .  
Fit of symmetry elements is very good for c, slightly worse for  $2_1$



Press CLOSE to leave the listing  
 Press “Draw structure”  
 Press “Accept last solution”

## IV. Refinements and model improvement

### 1. Refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine. (Step1)

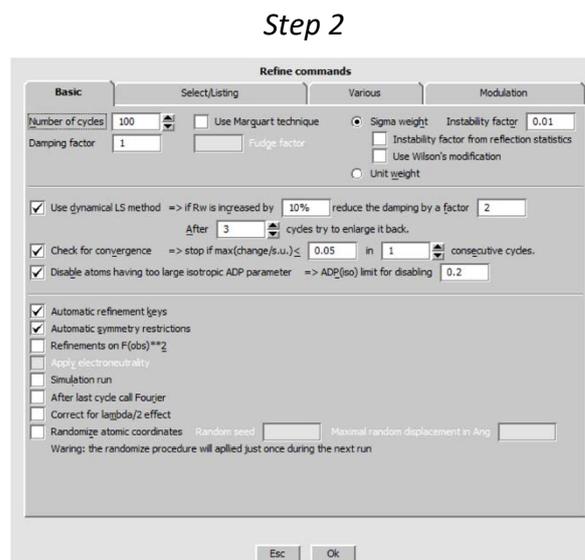
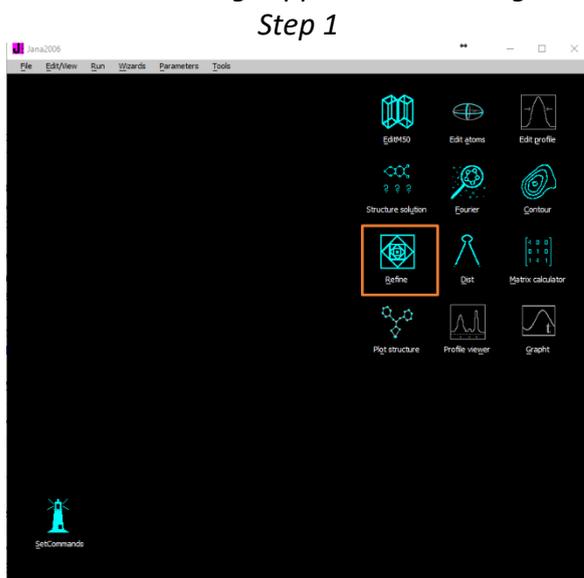
[On the screen: refinement options]

Define 100 of cycles, (Step2)

Choose “YES+START”

Refinement converges with R value about 19%, GOF about 10, 145 refined parameters

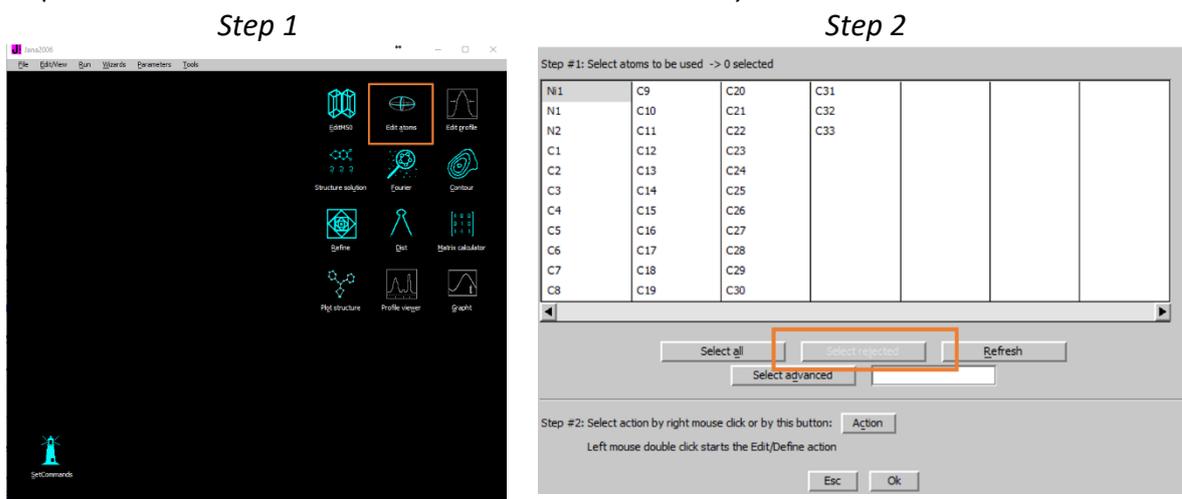
Serious warnings appear in the listing.



### 2. Assignment of the correct chemical types

Use “Edit atoms” (Step1)

And “Select rejected” to delete atoms which may be automatically rejected during the refinement because of too large Uiso (Step2)  
 (The button is disabled when there are no such atoms)



Using “Plot structure” identify the incorrectly assigned chemical types by comparison of the plot with the chemical scheme

Using “Edit atoms” (Step1)

Correct the chemical types, delete wrong atoms, “rename atoms according to chemical type” and “create symmetrically contiguous motifs” (Step3)

Repeat refinement

Run difference Fourier and complete the possibly missing atoms (Step3)

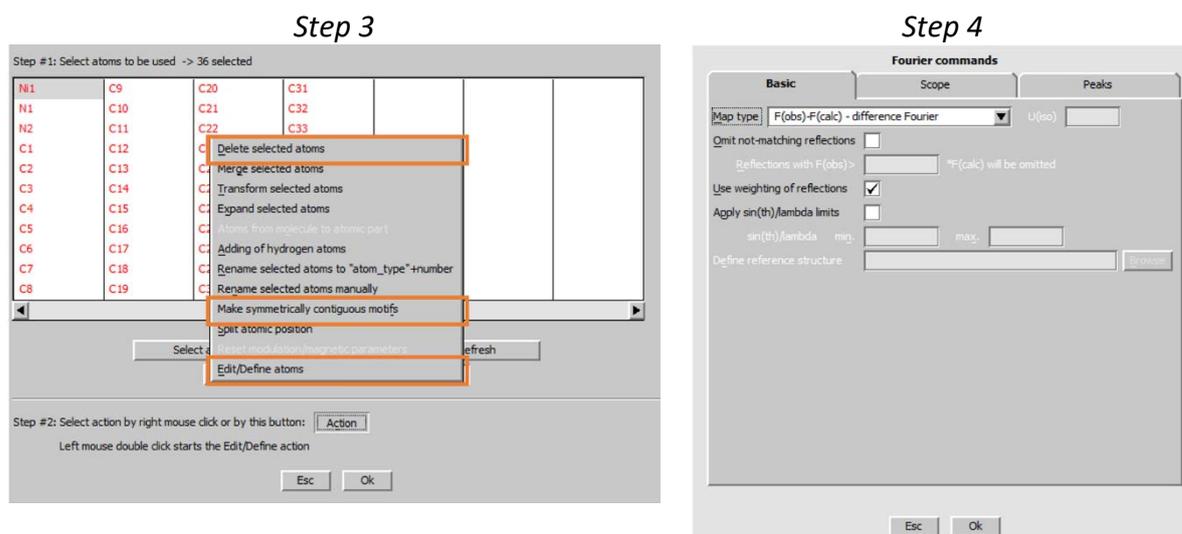
Repeat refinement

Refinement converges with R value about 17%.

Using “Edit atoms” set harmonic ADP for all atoms

Refinement converges with R value about 17%.

Serious warnings appear in the listing due to non-positive definite ADP of some atoms



### 3. Adding hydrogen atoms

Using "Edit atoms" add hydrogens to carbon and nitrogen atoms (Step1)

#### Notes

For nitrogen atoms skip cases when Ni is listed as a neighbor (this is the nitrogen coordinated to Ni) and skip also cases when nitrogen has three oxygen atoms as neighbors (this is NO<sub>3</sub> group).

*Check the hydrogen atoms by plotting. The geometry is slightly distorted due to unresolved twinning which may confuse the automatic procedure for adding hydrogens.*

*Finally, the structure model should have 53 atoms*

#### Step 1

Step #1: Select atoms to be used -> 2 selected

Ni1	C3	C10	C19	H1C11		
O1	C4	N7	C20	H1C12		
O2	C5	C11	H1C1	H1C13		
O3	N4	C12	H1C2	H1C14		

Adding "hydrogen" atoms for "N3"

Tetrahedral    0.87    H dist.    1.2    ADP ext. factor

Trigonal    2    Neighbor(s)    Hydrogen(s)

Apical    C20    1st    H1N3    1st

C16    2nd

Avoid->Go to next    Quit    Apply->Go to next

Step #2: Select action by right mouse click or by this button: Action

Left mouse double click starts the Edit/Define action

Esc    OK

#### Repeat refinement

#### Notes

*Refinement converges with R value around 16.6% and GOF 8.5, 316 parameters*  
*Several non-positive definite ADPs are indicated in the List of serious warnings in the refinement listing*

### 4. Add a twinning matrix

In "EditM50" check "Twinning" (Step1)

And define twinning matrix (-1 0 -0.733 | 0 -1 0 | 0 0 1); OK; Yes; OK; Yes (Step2)

#### Notes

*The twinning matrix is known from the diffractometer software and represents a rotation by 180° around c. The program offers re-creation of the refinement reflection file because twinning may change rules for merging of symmetrically equivalent reflections. In this case, it is not necessary.*

## Step 1

Define/modify basic structural parameters:

Cell Symmetry Composition Multipole parameters Magnetic parameters

Structure

Cell parameters 14.5934 9.853 16.0502 90 113.7197 90

E.s.d.'s 0 0 0 0 0

Twinning  #twin domains 2 Matrices

Dimension = 3

Esc Ok

## Step 2

Define/modify basic structural parameters:

Cell Symmetry Composition Multipole parameters Magnetic parameters

Structure

Cell parameters

E.s.d.'s

Twinning

Dimension 3

2nd twinning matrix

h' = -1 h+ 0 k+ -0.733

k' = 0 h+ -1 k+ 0

l' = 0 h+ 0 k+ 1

Two-fold axis in direction (0 0 1)

Select alternative representative of the coset

Round to closest integers Round to closest rationals

Matrix calculator

Rotation axis 0 0 1

in direct base  Proper rotation

in reciprocal base  Improper rotation

Rotation angle:

0 deg  120 deg  270 deg

60 deg  180 deg  300 deg

90 deg  240 deg  explicitly

Esc Ok

Esc Ok

“Do You want to re-create refinement reflection file just now”? No

In “Parameters → Twin fractions” check refinement of “twvol2”

Repeat refinement

Refinement converges with R value around 15% and GOF 8 for 317 parameters

Open listing of Refine (Edit/View → View of Refine → Go to → List of serious warnings)

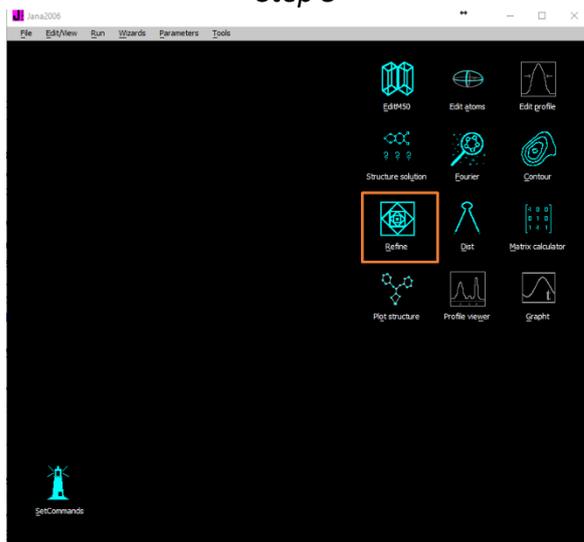
ADP tensors are still not positive definite for some atoms.

### Notes

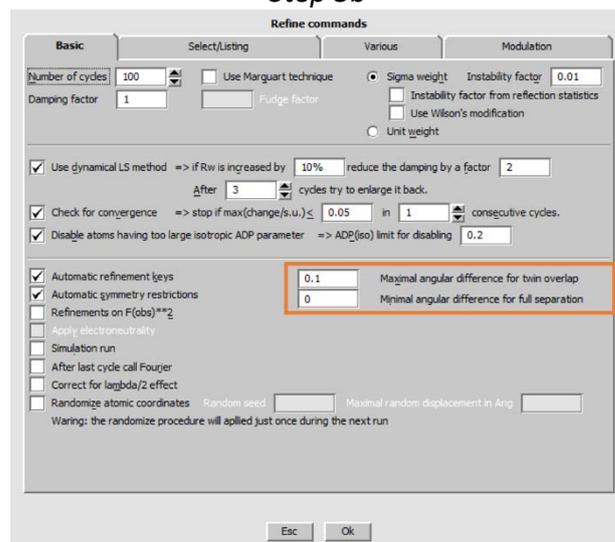
*This twin has a diffraction pattern where some reflections are partially overlapped. In refinement options there are two limits available for treating partial overlaps. The reflections with difference in theta smaller than “Maximal angular difference for twin overlap” are treated as fully overlapped; the reflections with theta difference larger than “Minimal angular difference for full separation” are treated as fully separated; the reflections between the limits are discarded. The limits should be adjusted carefully not to discard too many reflections.*

In Refinement command options change values of “Maximal angular difference for twin overlap” (L1 in the table) and “Minimal angular difference for full separation” (L2 in the table) and watch their impact on R factors, number of excluded reflections and ADP tensors. Find an optimal combination. (Step3)

### Step 3



### Step 3b



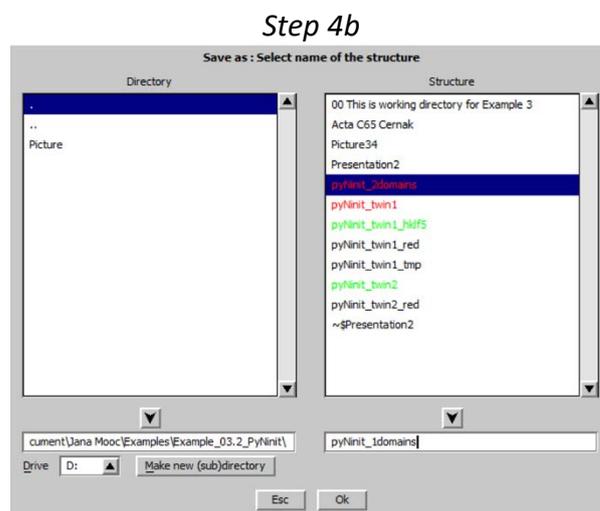
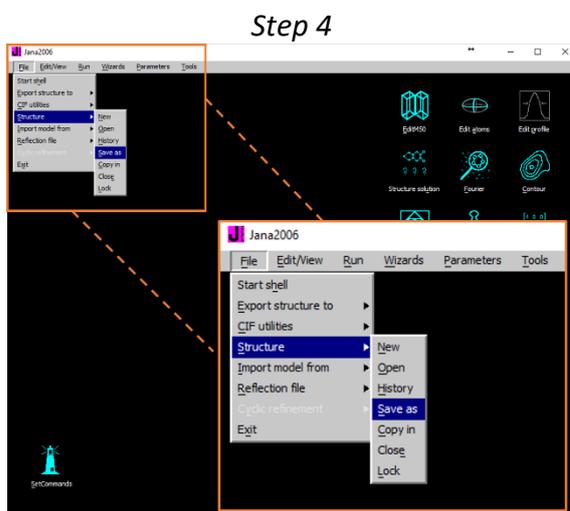
### Notes

(This table is calculated for refinement on  $F$  and instability factor 0.01)

L1	L2	R <sub>obs</sub>	GOF	discarded
0	0	15.3	8.2	0
0.1	0	12.8	7.4	0
0.2	0	7.4	3.6	0
0.3	0	7.1	3.5	0
0.4	0	9.8	5.5	0
0.35	0	9.6	5.4	0
0.31	0	9.3	5.3	0
0.3	0.4	6.9	3.6	778
0.3	0.5	7.4	3.8	1264
0.3	0.6	7.9	4.1	1916
0.2	0.3	6.2	3.0	415
0.2	0.4	5.7	3.0	1193
0.15	0.3	5.3	2.4	709
0.1	0.3	4.8	1.9	1120
0.1	0.4	3.9	1.4	1898

With maximal angular difference for twin overlap 0.1 and minimal angular difference for full separation 0.4, refinement converges with R value 3.9% and GOF 1.4, all ADP tensors are positive definite, the fraction of the second twin domain refines as 0.468(2) (see "Parameters → Twin fractions").

Using "Structure → Save as", create a backup copy, for instance pyNinit\_1domain (Step4)  
 "Do you want to continue with the new structure?"; No

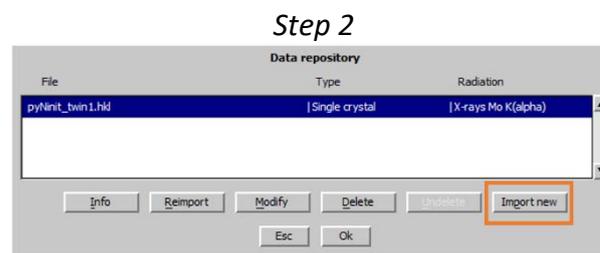
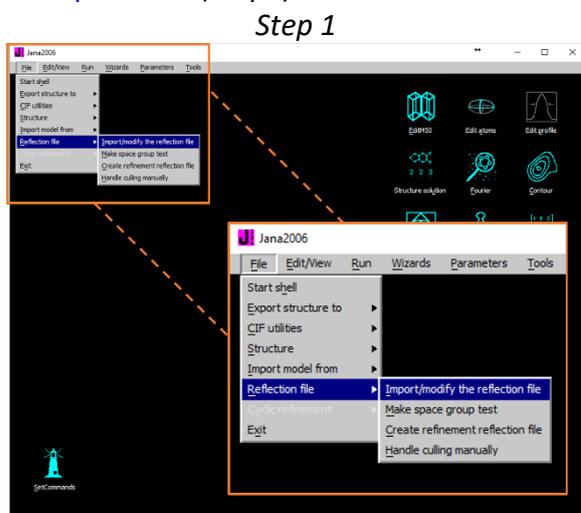


## 5. Add data of the second domain

### Notes

Usually (and also in this case) the first twin domain + twinning matrix is sufficient for the refinement. If data of the second domain are good, we can add it as another data set to get better refinement of the twin fraction.

“File → Reflection file → Import/modify the reflection file”; (Step1)  
 Import new (Step2)



Known diffractometer formats; Oxford Diffraction-CCD  
 Browse for PyNinit\_twin2.hkl  
 Select “Input from “sum” file”; OK ; OK  
 Leave all settings unchanged; NEXT

[On the screen: Relationship to the reference cell/split by twinning]

### Notes

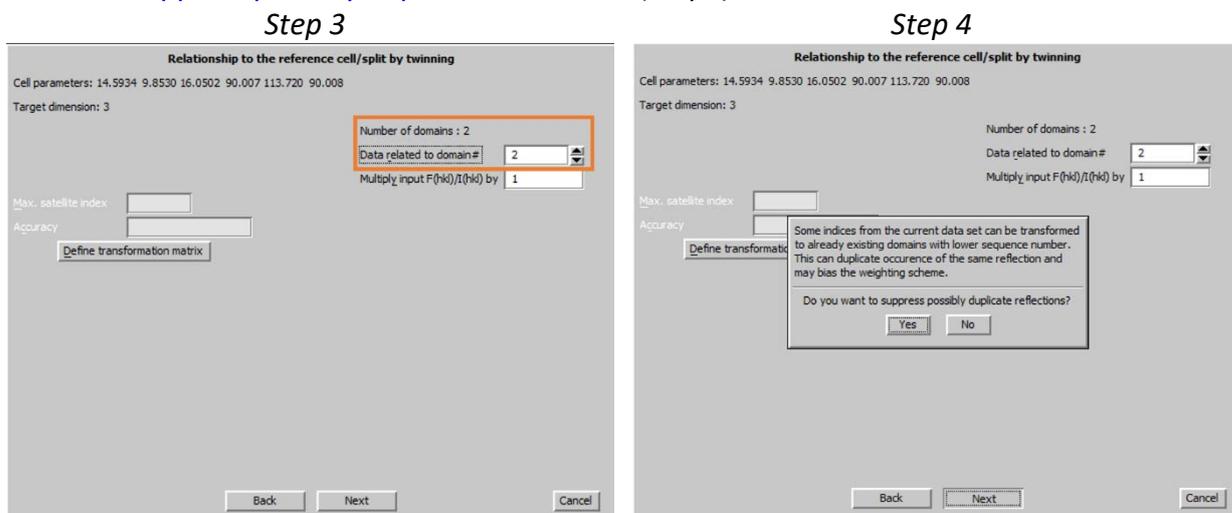
Here we have to define that reflections of the second domain were indexed according to orientation matrix of the second domain.

**Data related to domain #2; NEXT; Accept cell parameters (Step3)**

[On the screen: Information about difference in cell parameters]

Select "Continue with the old reference cell parameters"

**YES** to suppress possibly duplicate reflections (Step4)



### Notes

Data processing of each twin was done on the same experimental frames. Therefore, overlapped reflections are processed twice with the same result. Merging of dublicately processed reflections would lead to very low sigma and unrealistic high weight in the refinement.

For absorption correction select "None or done before importing"; NEXT

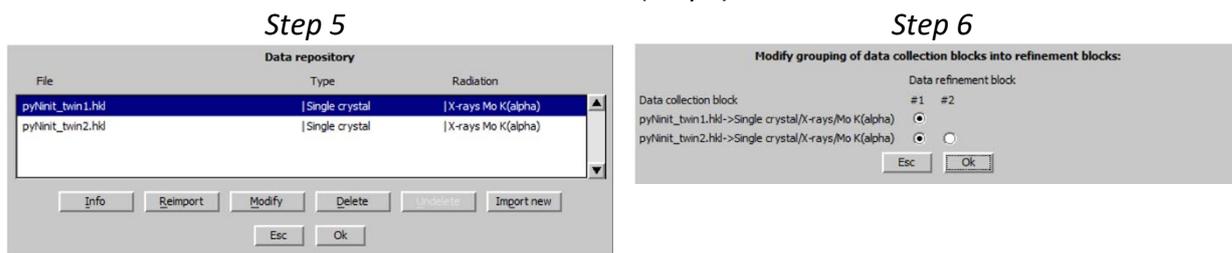
**FINISH**

[On the screen: Data repository]

Each line in data repository window corresponds to one data set.

OK; YES to accept the data set; (Step5)

Set Data collection block #1 for both datasets (Step6)

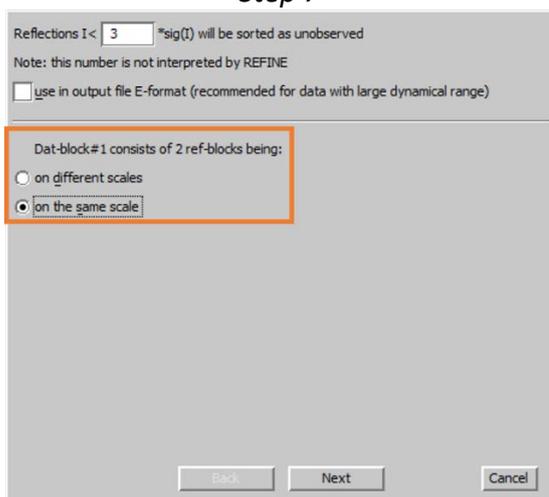


### Notes

In this step the program offers sorting of the data sets to data blocks. Each data block has an independent scale factor. In our case, both twin domains come from the same measurement and they should be used as one data block.

Select "**on the same scale**" for both data sets

## Step 7



Follow the wizard for creation of the refinement reflection file;  
Refine

### Notes

*Refinement converges with R 4.1%, GOF 1.36, 3800 excluded reflections, fraction of the second domain is 0.4641(6) (the number with s.u. is printed in the refinement listing).*

Create a backup copy, e.g., pyNinit\_2domains (File → Structure → Save as)

“Do you want to continue with the new structure?”; No

## 6. Are both domains really on the same scale?

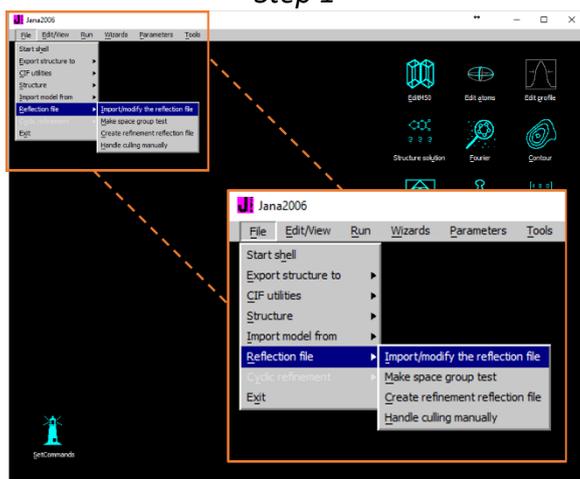
### Notes

*It may be unclear whether both data sets are on the same scale. Different scales would bias refinement of the volume fraction.*

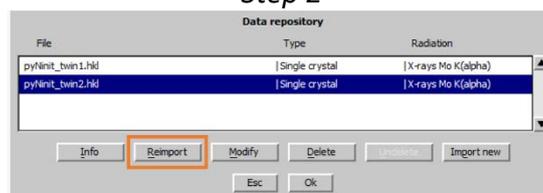
“File → Reflection file → Import/modify the reflection file” (Step1)

In Data repository highlight pyNinit\_twin2.hkl and use “Reimport” (Step2)

### Step 1



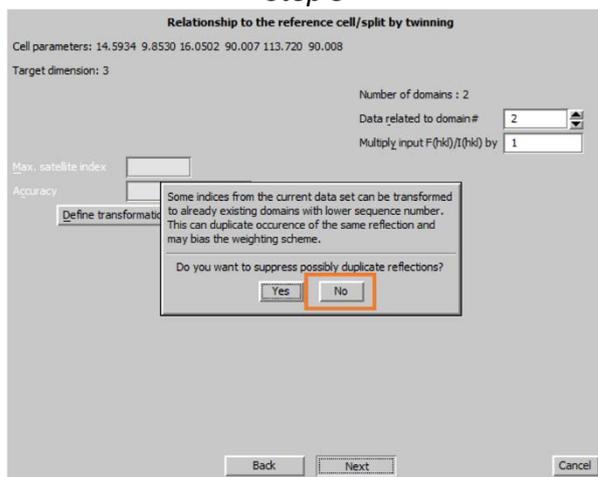
### Step 2



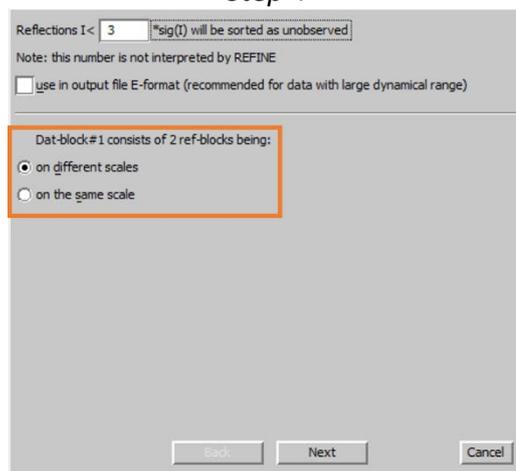
Follow the import wizard as previously, but do NOT suppress possibly duplicate reflections  
Duplicate reflections will be used to find the common scale (Step3)

Follow the steps the wizard for creation of the refinement reflection file; select “on different scales” for both data sets (Step4)

### Step 3

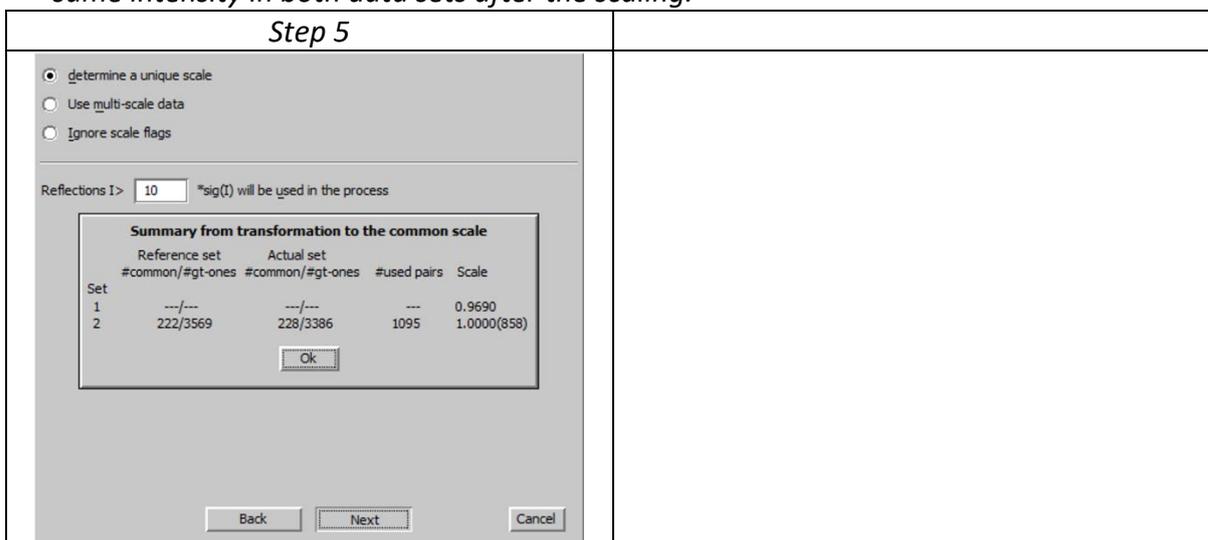


### Step 4



In the next step, Jana will determine the unique scale based on the duplicate reflections (Step5)

The scale is calculated from 4334 pairs of equivalent reflections, which should have the same intensity in both data sets after the scaling.



### Refine

#### Notes

Refinement converges with  $R$  about 4.1%,  $GOF$  1.39, 3800 excluded reflections, fraction of the second twin domain is 0.4716(6). However, in this refinement we have unrealistic weight of the duplicate reflections because they were entered two times with the same sigma.

## 7. Use of HKLF5

## Notes

The diffractometer software should better detect overlaps of diffraction spots than the simple criterion in Jana2006. HKLF5 file produced by diffractometer software contains flags saying which reflections are overlapped. Jana2006 can work with HKLF5 if twinning is activated (twinning matrix can be arbitrary).

“File → Reflection file → Import/modify the reflection file”; Delete both datasets;  
Import new

[On the screen: Specify type of the file to be imported]

Choose “reflection file corrected for LP and absorption”, NEXT (Step1)

Select “SHELX hklf5”

Browse for pyNinit\_twin\_hklf5.hkl; NEXT (Step2)

### Step 1

Specify type of the file to be imported

Single crystal:

- known diffractometer formats
- reflection file corrected for LP and absorption

Powder data:

- various CW formats
- various TOF/ED formats

Buttons: Back, Next, Cancel

### Step 2

Single crystal data from:

File name: pyNinit\_twin1\_hklf5.hkl [Browse]

Single crystal data from:

- SHELX on F
- SHELX on I
- SHELX HKLF5
- IPDS STOE
- CCD Bruker
- From CIF file
- From Grindex file
- From FullProf file
- From XD file
- From DABEX
- Jana2006-M90
- General file on F
- General file on I

Input format: [ ]

Buttons: Back, Next, Cancel

Leave all settings unchanged; NEXT

Leave all settings unchanged; do not select “HKLF5 file by Jana tools”; (Step5)

NEXT;

OK to confirm information about 68907 imported reflections

### Step 3

Relationship to the reference cell/split by twinning

Cell parameters: 14.5934 9.8530 16.0502 90.007 113.720 90.008

Target dimension: 3

Number of domains: 2

Data related to domain# [ ]

Multiply input  $F(hk)I(hk)$  by 1

HKLF5 file by Jana tools

Max. satellite index [ ]

Accuracy [ ]

Define transformation matrix [ ]

Buttons: Back, Next, Cancel

FINISH

OK; YES to close and save Data repository

Follow the wizard for averaging of reflections and creation of the refinement reflection file

Jana2006 merges only fully separated reflections from both domains

## Refine

### Notes

*Refinement converges with R 5.4%, GOF 1.6, fraction of the second domain is 0.4728(5). The R value is slightly larger than previously but we are using all reflections. Results based on this refinement should be considered the most reliable.*

*The following table summarizes refinement of the twin volume fraction*

	twvol2
First twin domain, L1 = 0.1, L2 = 0.4	0.468(2)
Both domains, L1 = 0.1, L2 = 0.4	0.4644(6)
Both domains, L1 = 0.1, L2 = 0.4, scaling	0.4716(6)
HKLF5	0.4728(5)

## References

---



# Example 3.3.1: CsLiSO<sub>4</sub>

Revised: 02 December 2018

Data	Topic	Level
X-ray single crystal data	structure with pseudo-merohedric 3-fold twinning	Advanced

## Tasks

---

Solving a structure with pseudo-merohedric 3-fold twinning using Jana2006 software

- Finding twinning matrix from group → subgroup transformation.
- Transformation to four times larger reciprocal cell.

## Initial data

---

### Data

Single crystal data measured with Oxford Diffraction four-circle diffractometer

### Input files:

CsLiSO4.hkl, CsLiSO4\_red.sum

### Additional information:

Frame scaling, absorption correction: done by the diffractometer software

Chemical formula: **CsLiSO<sub>4</sub>**

## Contents

---

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# Instructions

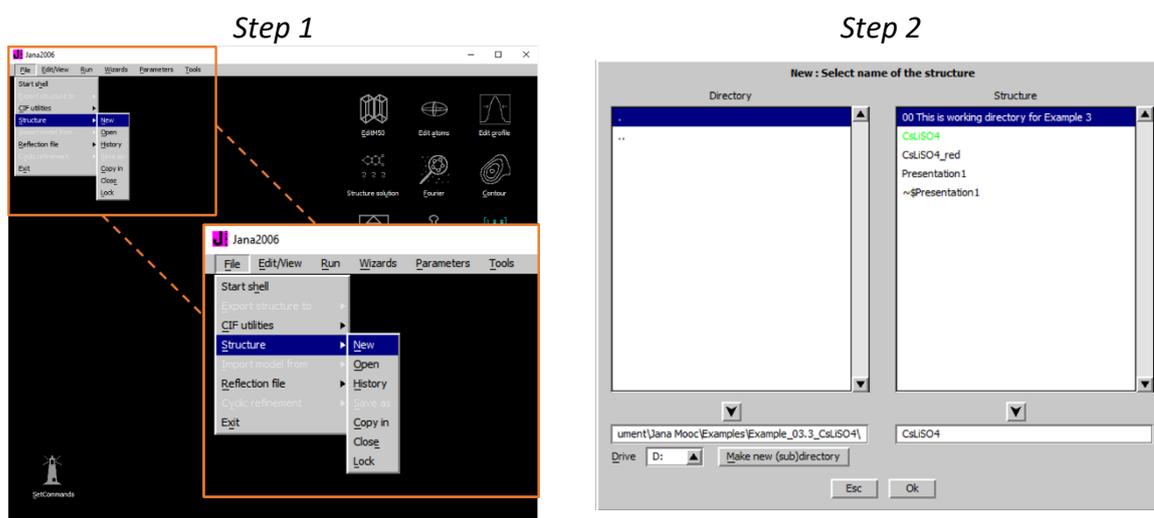
## I. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager (*Step1*)

Left pane: locate directory with input files; Right pane: double-click CsLiSO4 (*Step2*)

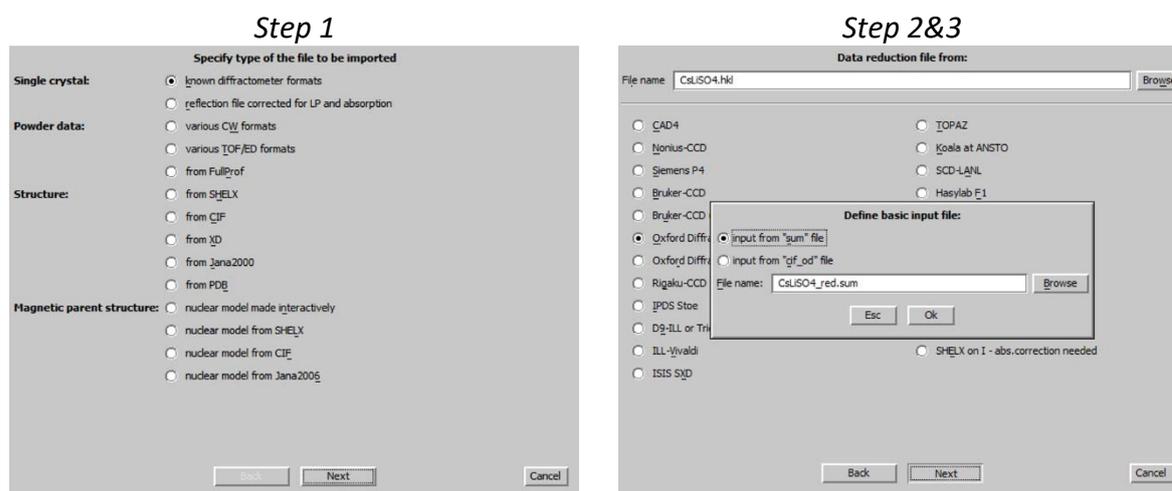


### 2. Import wizard

Select “Known diffractometer formats”; NEXT (*Step1*)

Select “Oxford Diffraction → CCD”; NEXT (*Step2*)

Select “Input from “sum” file”; OK (*Step3*)



Warning; (*Step 4*)

Leave all settings unchanged; NEXT (*Step5*)

Leave all settings unchanged (leave Twinning checkbox clear); NEXT; OK; (*Step6*)

The program reads 15611 reflections from hkl file

### Step 5

**Complete/correct experimental parameters**

Cell parameters: 10.89451 10.88937 8.80485 90.00104 90.02358 119.9455

Number of input indices: 3

1st modulation vector:

2nd modulation vector:

3rd modulation vector:

X-ray tube

Wave length: 0.71073

Temperature: 293

**Polarization correction:**

Circular polarization

Perpendicular setting

Parallel setting

Guinier camera

Linearly polarized beam

**Monochromator parameters:**

Perfection: 0.5

Glancing angle: 6.082144

### Step 6

**Define the reference cell/split by twinning**

Cell parameters: 10.8945 10.8894 8.8048 90.001 90.024 119.946

Target dimension: 3

Twinning

1st modulation vector:

2nd modulation vector:

3rd modulation vector:

Max. satellite index:

Accuracy:

Data related to domain #:

Multiply input F(hkl)/I(hkl) by: 1

**INFORMATION**

All 11132 input reflections were properly handled

For absorption correction select "None or done before importing"; NEXT (Step7)  
FINISH (Step8)

### Step 7

**Define parameters for absorption and scaling procedure**

None or done before importing

Correction for spherical sample  radius of the sphere [mm]

Gaussian integration method  integration grid

Empirical correction and/or frame scaling

Define absorption coefficient =>

Define formula =>

Number of formula units:

### Step 8

**INFORMATION**

The import wizard is complete. As a next step you can import another file or modify the previously imported ones.

## 3. Data Repository

OK; YES to accept the data set (Step1)  
Next; (Step2)

### Step 1

**Data repository**

File	Type	Radiation
CaLSO4.hkl	Single crystal	X-rays Mo K(alpha)

### Step 2

**INFORMATION**

Now the program will open a wizard for a space group test which can determine interactively the symmetry. In the case that later you will need to modify your first choice the same procedure can be run by the command "File->Reflection file->Make space group test" without necessity to reimport the data.

## II. Symmetry and data merging

### 1. Symmetry wizard

[On the screen: "Tolerances for crystal system recognition".]

Leave all other settings default; NEXT (Step 1)

[On the screen: Select Laue symmetry] (Step 2)

**Step 1**

**Tolerances for crystal system recognition:**

Original cell parameters: 10.894 10.889 8.805 90.00 90.02 119.95

Maximal deviation for cell lengths in [Å]

Maximal deviation for cell angles in deg

**Tolerances for space group recognition:**

Maximal ave(I/sig(I)) for centering

Maximal ave(I/sig(I)) for extinctions

Search for higher symmetry

Introduce twin laws

Use old twin laws

look for centering vectors composed from 0 and 1/2

look for centering vectors composed from 0, 1/3 and 2/3

**INFORMATION**

No supercell having a higher cell symmetry has been found.

**Step 2**

**Select Laue symmetry**

Crystal system	Point group	Rint(obs/all)	#averaged	Redundancy
Triclinic	-1	5.68/5.74	2752/3790	2.937
Monoclinic-setting "c"	2/m	6.31/6.37	1493/2026	5.495
Orthorhombic-setting "a,2b-a"	mmm	13.80/13.85	849/1097	10.148
Orthorhombic-setting "b,-2a-b"	mmm	10.93/10.98	844/1097	10.148
Orthorhombic-setting "-a-b,a+b"	mmm	7.41/7.47	848/1097	10.148
Trigonal	-3	14.35/14.40	1012/1270	8.765
Trigonal	-31m	14.46/14.50	559/698	15.948
Trigonal	-3m1	14.46/14.51	618/740	15.043
Hexagonal	6/m	14.46/14.51	543/682	16.323
Hexagonal	6/mmm	14.51/14.56	344/425	26.193

ordered by Laue symmetry  ordered by Rint

Averages made from 7493/11132 reflections

### Notes

We can see that hexagonal symmetry is slightly violated, because corresponding  $R_{int}$  is about 14%. On the other hand, an orthorhombic symmetry with setting "-a-b,a+b" has  $R_{int}$  comparable with the triclinic symmetry, given much higher redundancy of equivalent reflections.

For exactly hexagonal cell parameters, merohedric twinning is highly probable. Another indication of twinning is the fact that the three equivalent orthorhombic settings have quite different  $R_{int}$ . It might be caused by merging reflections belonging to different unequally populated twin domains.

In the next step, we will repeat test of Laue symmetry but this time considering twinning. That means for any subgroup of 6/mmm the program will generate corresponding pseudo-merohedric twinning matrices and it will merge reflections using only the symmetry elements present in a twinned structure for general case of not equally populated twin domains.

Press BACK

Check „Introduce twin laws in case of subgroups“ ;NEXT (Step 3)

### Step 3

**Tolerances for crystal system recognition:**  
 Original cell parameters: 10.894 10.889 8.805 90.00 90.02 119.95  
 Maximal deviation for cell lengths in [Å]   
 Maximal deviation for cell angles in deg

**Tolerances for space group recognition:**  
 Maximal ave(I/sig(I)) for centering   
 Maximal ave(I/sig(I)) for extinctions

Search for higher symmetry  
 Introduce twin  
 Use standard twin

**INFORMATION**  
 No supercell having a higher cell symmetry has been found.

look for centering vectors composed from 0 and 1/2  
 look for centering vectors composed from 0, 1/3 and 2/3

Back Next Cancel

### Step 4

**Select Laue symmetry**

Crystal system	Point group	Rint(obs/all)	#averaged	Redundancy
Triclinic	-1	5.68/5.74	2752/3790	2.937
Monoclinic-setting "c"	2/m	6.31/6.37	1493/2026	5.495
Orthorhombic-setting "a,2b-a"	mmm	6.31/6.37	1493/2026	5.495
Orthorhombic-setting "b,-2a-b"	mmm	6.31/6.37	1493/2026	5.495
Orthorhombic-setting "-a-b,a+b"	mmm	6.31/6.37	1493/2026	5.495
Trigonal	-3	14.35/14.40	1012/1270	8.765
Trigonal	-31m	14.46/14.50	559/698	15.948
Trigonal	-3m1	14.46/14.51	618/740	15.043
Hexagonal	6/m	14.46/14.51	543/682	16.323
Hexagonal	6/mmm	14.51/14.56	344/425	26.193

ordered by Laue symmetry  
 ordered by Rint

Averages made from 7493/11132 reflections

Details Back Next Cancel

This time, the three orthorhombic cases give the same internal R factor.  
 Select the highlighted orthorhombic Laue symmetry; NEXT (Step 4)

### Notes

The three orthorhombic cases correspond to the three twin domains. The selected one gave us in the previous test the lowest  $R_{int}$ . This means that this domain is more populated than the others are.

Select C centering; NEXT (Step 5)

### Notes

Hexagonal unit cell transformed to an orthorhombic one should be C centered. There is also some non-standard X centering, which we will investigate later on.

[On the screen: Select space group]  
 Select Ccce space group; NEXT (Step 6)

### Step 5

**Select cell centering**

Centering	obs/all	ave(I/sig(I))
<input type="radio"/> P	0/0	0.000/0.000
<input type="radio"/> A	823/1405	26.669/16.090
<input type="radio"/> B	823/1405	26.669/16.090
<input checked="" type="radio"/> C	0/0	0.000/0.000
<input type="radio"/> I	4521/5580	51.128/41.615
n.a. R-obverse	3343/4955	51.598/35.155
n.a. R-reverse	3357/4962	51.951/35.488
<input type="radio"/> F	823/1405	26.669/16.090
<input type="radio"/> X (1/2,0,0), ...	0/0	0.000/0.000

### Step 6

**Select space group**

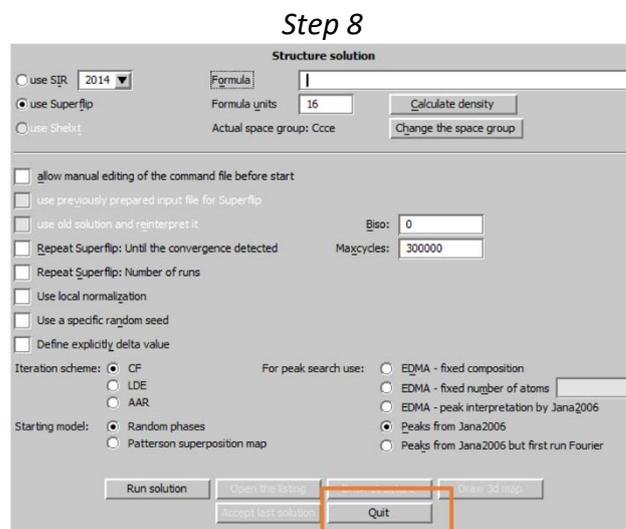
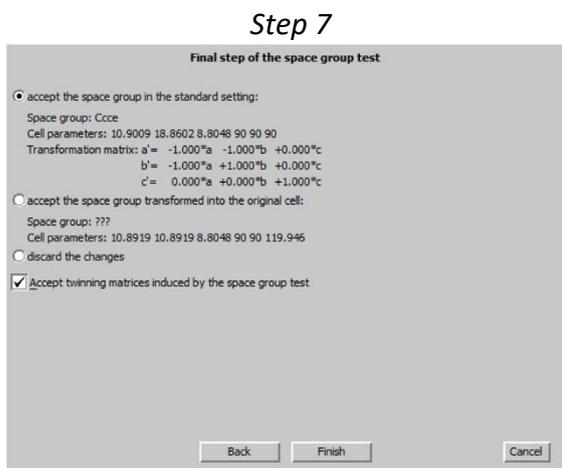
Space group	obs/all	ave(I/sig(I))	FOM
Ccce	1/13	4.308/1.108	0.17532
Cccn	1/13	4.308/1.108	0.17532
Ccme	1/13	4.308/1.108	0.17532
Cmce	1/13	4.308/1.108	0.17532
Ccmm	1/13	4.308/1.108	0.17532
Cmcm	1/13	4.308/1.108	0.17532
C2ce	1/13	4.308/1.108	0.17532
Cc2e	1/13	4.308/1.108	0.17532
C2cm	1/13	4.308/1.108	0.17532
Cc2m	1/13	4.308/1.108	0.17532
Ccc2	1/13	4.308/1.108	0.17532
Ccm21	1/13	4.308/1.108	0.17532
Cmc21	1/13	4.308/1.108	0.17532
C2221	1/13	4.308/1.108	0.17532
Cmme	0/0	0.000/0.000	1.00000

Details Back Next Cancel

### Notes

There are several possibilities for selecting space group and at this stage it is unclear which is the correct one.

Accept the space group in the standard setting; *FINISH* (Step 7)  
 Follow wizard for creation of the refinement reflection file  
 QUIT the wizard for structure solution without solving the structure (Step 8)



## 2. Space group test results

[On the screen: basic window of Jana]

Check new cell parameters and symmetry with EditM50 (Step 1)

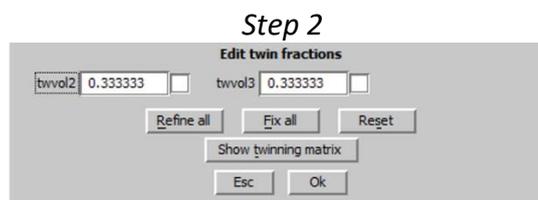
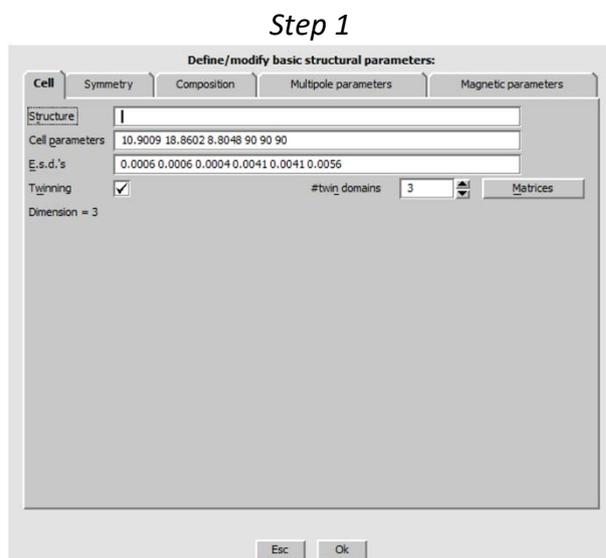
Cell parameters 10.8919 18.8653 8.8048 90 90 90

Space group Ccce

ESC

[On the screen: basic window of Jana]

Start "Parameters → Twin fractions" (Step 2)

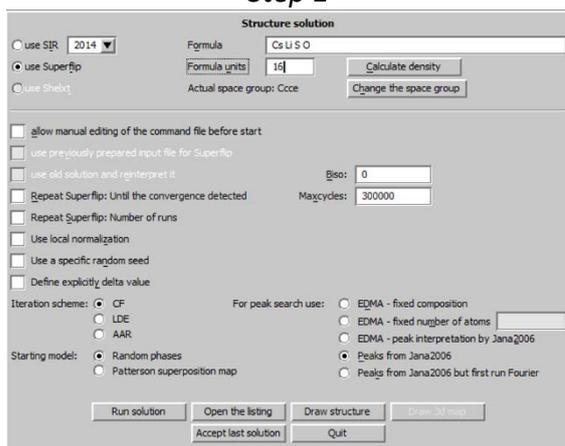


### Notes

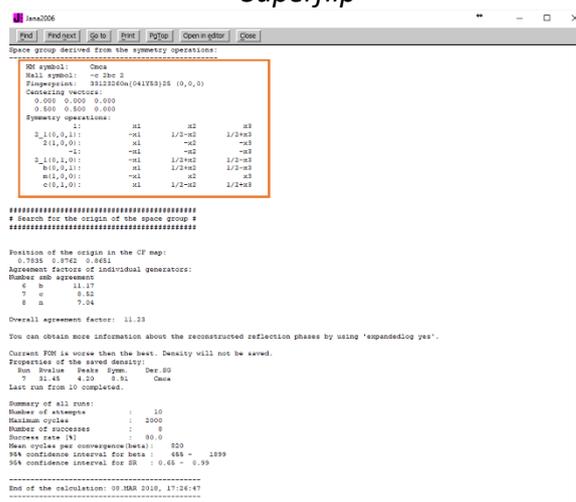
The initial volume fractions are equal but we already know they must be different; otherwise,  $R_{int}$  for hexagonal Laue symmetry would be lower.



## Step 1



## Superflip



Press **Change the space group**; (*Step 2*)

For Space group type **Cmcm**; (*Step 3*)

OK, YES to rewrite M50 file

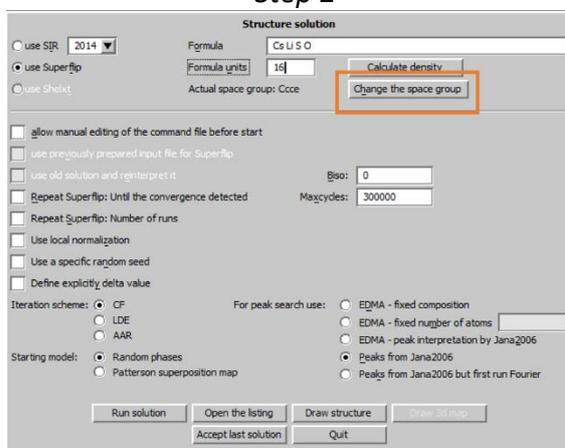
Follow steps of the wizard for creation of the refinement reflection file until the program returns to the Structure solution wizard

[On the screen: window of Structure solution]

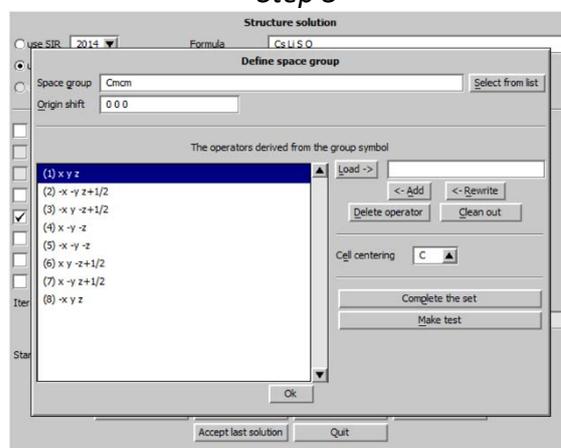
Press **“Run solution”**

Repeat it several times until Superflip confirms Cmcm. In some runs, Superflip might suggest different symmetry, which is indication of some structure solution troubles.

## Step 2



## Step 3



Press **“Draw structure”**; Select **“Draw+Continue”**;

[On the screen: window of Diamond]

Start **“Build → Get molecules”** or use  on the bottom toolbar

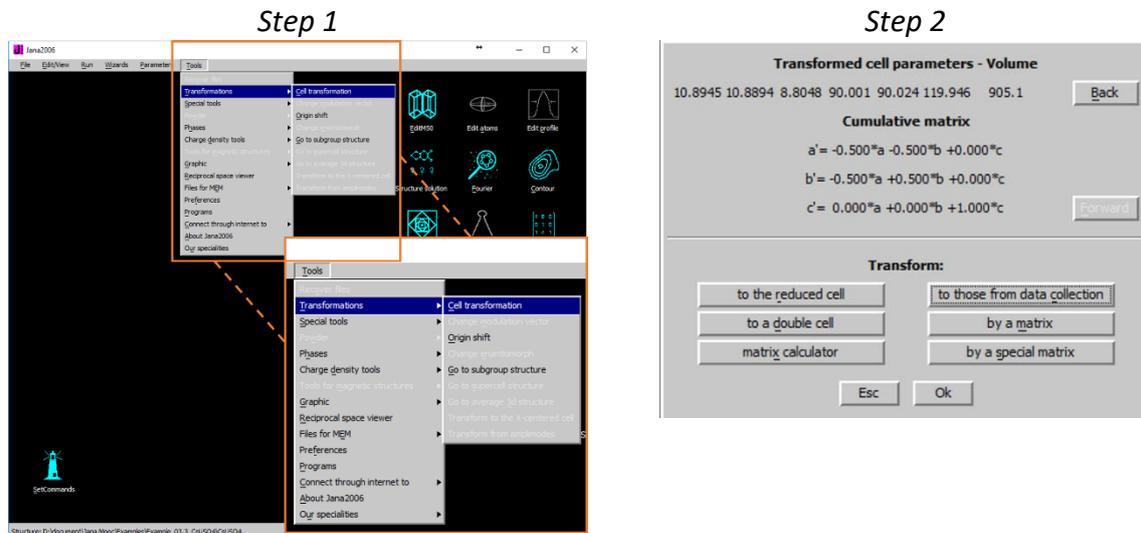
The solution looks unreasonable and other attempts to solve the structure (direct methods, SHELXT, use of different symmetry etc.) would fail as well.

Quit Diamond

Quit the Structure solution wizard (YES to discard the last solution)

#### 4. Application of X centering

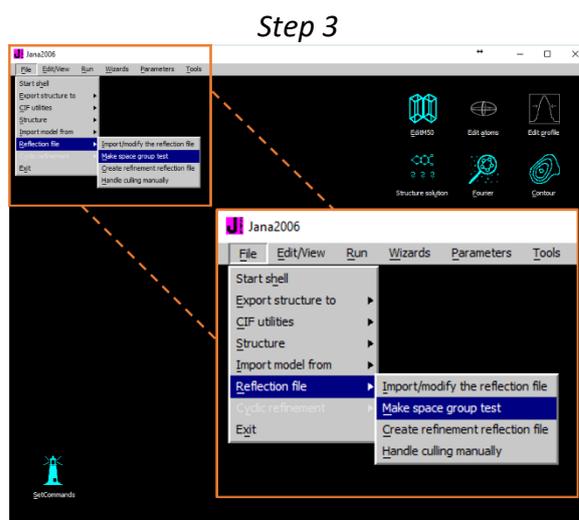
“Tools → Transformation → Cell transformation” (Step 1)  
Press “to those from data collection”; OK (Step 2)



Select “rewrite the old structure”; OK  
Follow steps of the wizard for creation of the refinement reflection file

**Notes**  
We are now back at the original hexagonal unit cell. In EditM50, you can see there is no standard symbol for the transformed symmetry operation. However, we will check for the symmetry again.

“File → Reflection file → Make space group test” (Step 3)  
This manually starts the Symmetry wizard.  
[On the screen: Tolerances for crystal system recognition]  
Check „Introduce twin laws in case of subgroups”  
NEXT; OK “



Select the highlighted orthorhombic Laue symmetry (like before); NEXT

[On the screen: Select cell centering] (Step 4)

This time, we will accept X centering instead of C centering

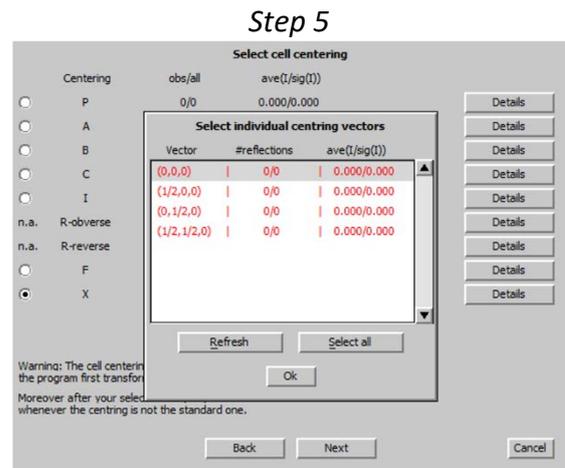
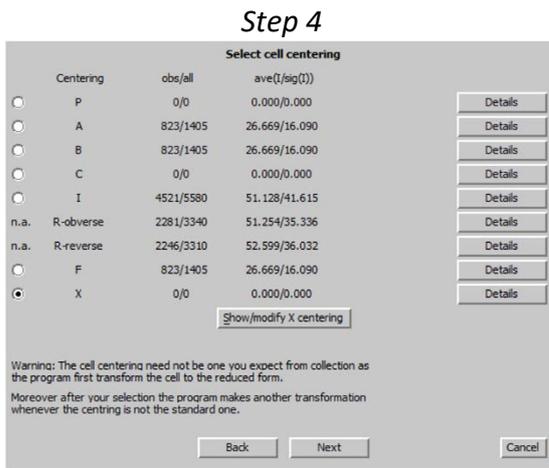
Press "Show/modify X centering" to see the individual centering vectors (Step 5)

**Notes**

We can see the centering vector ( $\frac{1}{2} \frac{1}{2} 0$ ) corresponding to the C centering but also additional vectors ( $\frac{1}{2} 0 0$ ) and ( $0 \frac{1}{2} 0$ ) suggesting that a and b unit cell parameters could be halved.

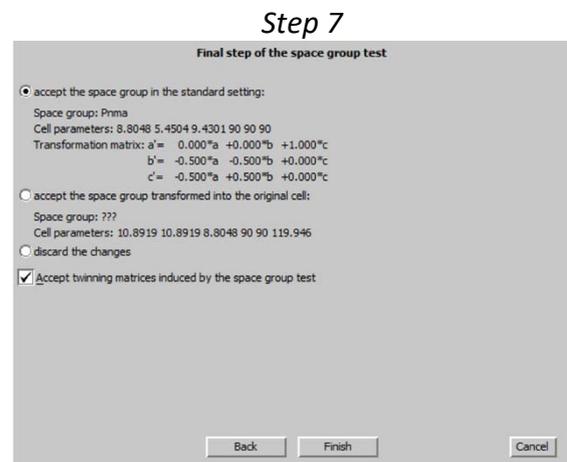
OK;

Select X centering; NEXT



Select space group Pmcn; NEXT (Step 6)

Accept space group in the standard setting; FINISH (Step 7)



NO we don't want to repeat the test

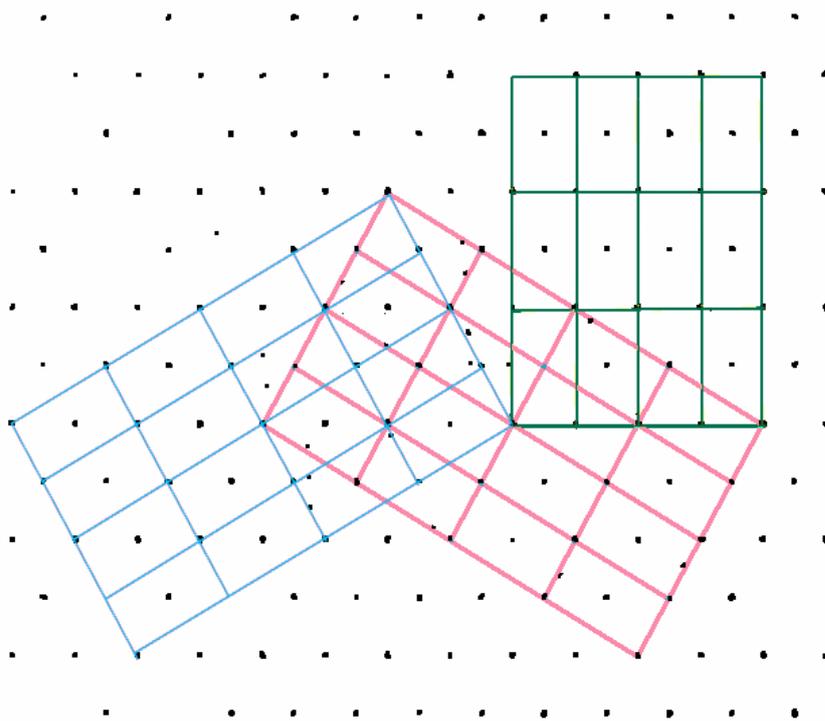
YES to create refinement reflection file

Follow steps of the wizard for creation of the refinement reflection file

## Notes

83 observed reflections will be discarded due to the selected space group. This is probably caused by spurious peaks, which are present in the diffraction pattern

The transformation suggested at the final step of the space group test produces an orthorhombic unit cell with four times smaller volume compared with the previously tested orthorhombic unit cell. Such unit cell alone could not index all diffraction spots, but combined with a three-fold twinning it can. The indexing of the hexagonal diffraction pattern with a three-fold twin of this small orthorhombic unit cell is indicated in the next figure.



### III. Structure solution

“Run → Structure solution”

[On the screen: window of Structure solution]

In “Formula” textbox check list of chemical elements for CsLiSO<sub>4</sub>: Cs Li S O

Select “Superflip”, “Peaks from Jana2006”; leave other settings default; “Run solution”

## Notes

Superflip converges (after noise suppression) with R value 22%. The suggested space group by Superflip is *Imma* but for twins such prediction is unreliable. On the other hand, Superflip confirms the symmetry elements of the current space group symmetry *Pnma*.

Press CLOSE to leave the listing

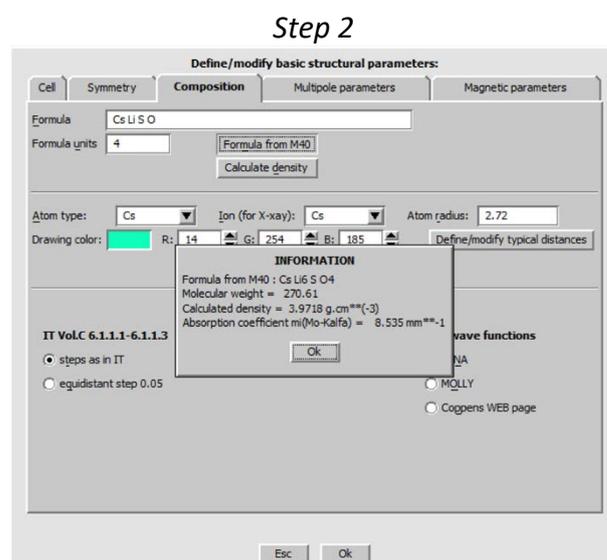
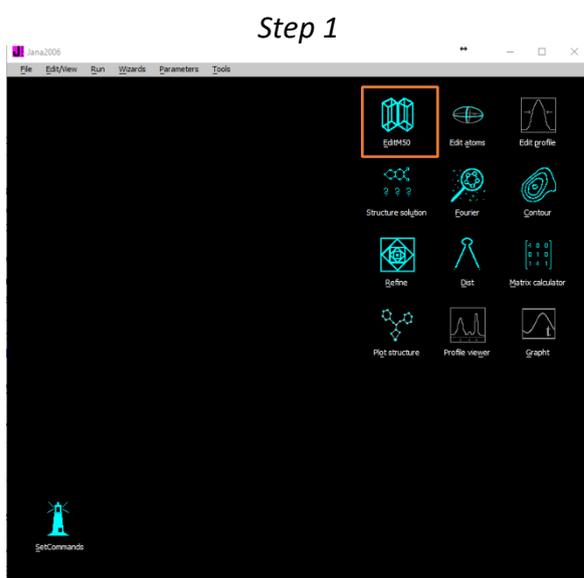
Press “Draw structure”

Press “Accept last solution”

Start EditM50; (Step 1)

Go to page Composition; change Formula units to 4; press Formula from M40; (Step2)

OK; Yes; OK



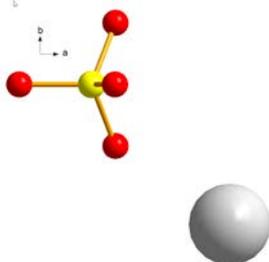
### Notes

*In most cases, the formula should be Cs Li<sub>n</sub> S O<sub>4</sub>, where “n” can be zero, 1 or more. This means all heavy atoms except Li have been properly interpreted. If not, repeat the structure solution.*

Start “Edit atoms”; delete all Li atoms  
 “Plot structure”

### Notes

*Diamond should show SO<sub>4</sub> tetrahedron and Cs. For this plot, all bonds to Cs will need to be disabled through “Build – Connectivity”*



## IV. Refinements and model improvement

### 1. Refinement

*[On the screen: basic window of Jana]*

Right-click the icon of Refine. (Step1)

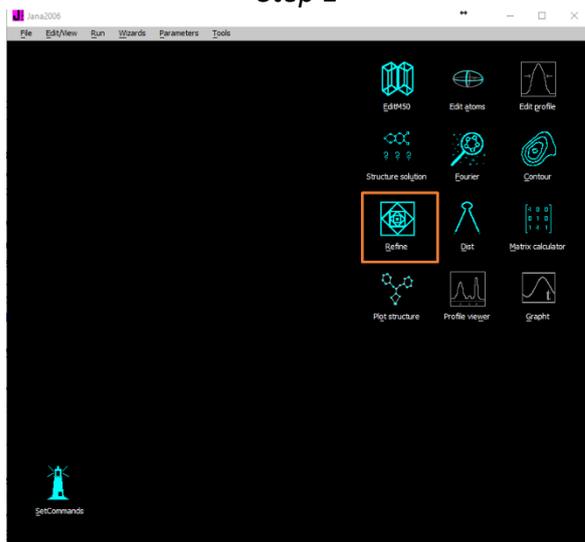
*[On the screen: refinement options]*

Define 100 of cycles, (Step2)

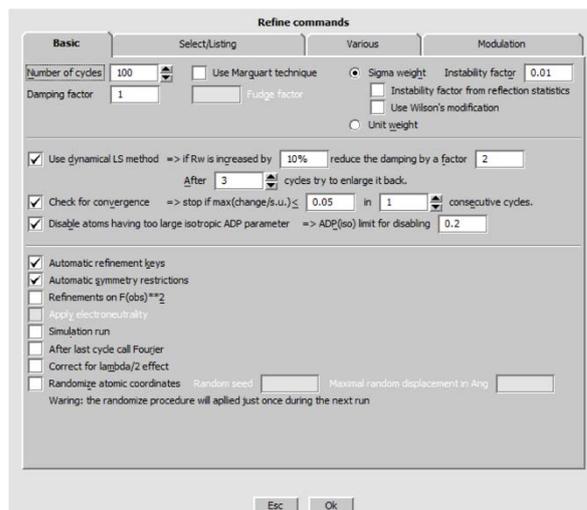
Choose “YES+START”

*Refinement converges with R value about 9%, GOF about 9, 17 refined parameters*

## Step 1



## Step 2

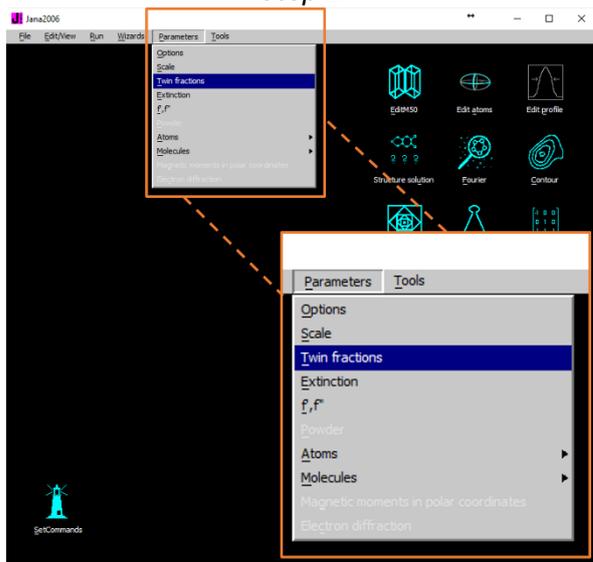


## 2. Twin volume fraction

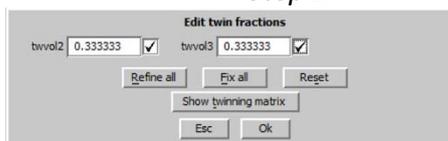
Start “parameters → Twin fractions” (Step 1)

Activate refinement of both twin fractions (Step 2)

### Step 1



### Step 2



### Repeat refinement

Refinement converges with R value about 5%, GOF about 5

Twin volume fraction drops to 0.26 (twvol2) and 0.30 (twvol3).

### Start “Edit atoms”

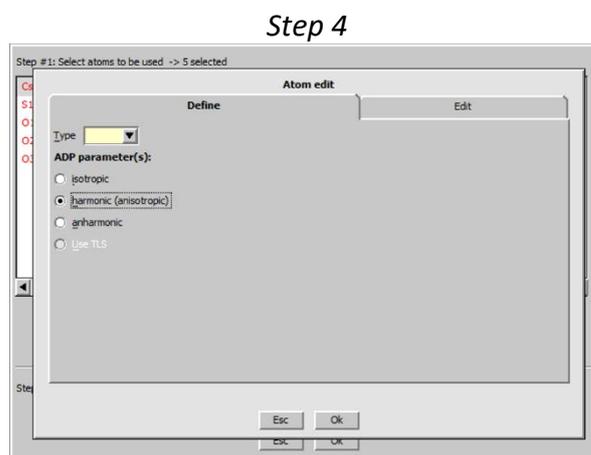
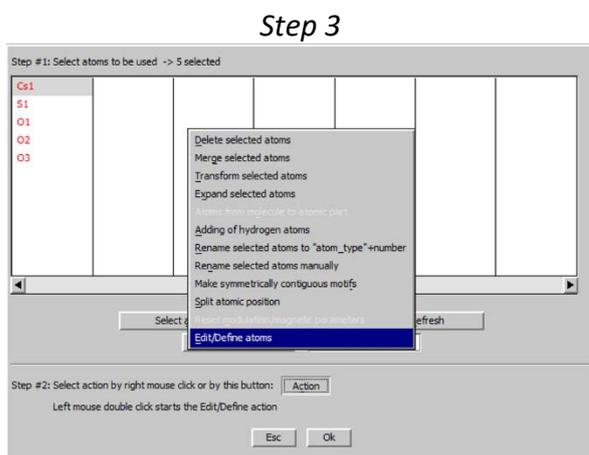
[On the screen: list of atoms]

Press “Select all” and “Action → Edit/define” (Step3)

Choose “harmonic” for ADP parameters. (Step4)

This defines anisotropic temperature parameters for all atoms.

OK, OK, YES to save changes



Run Refine.

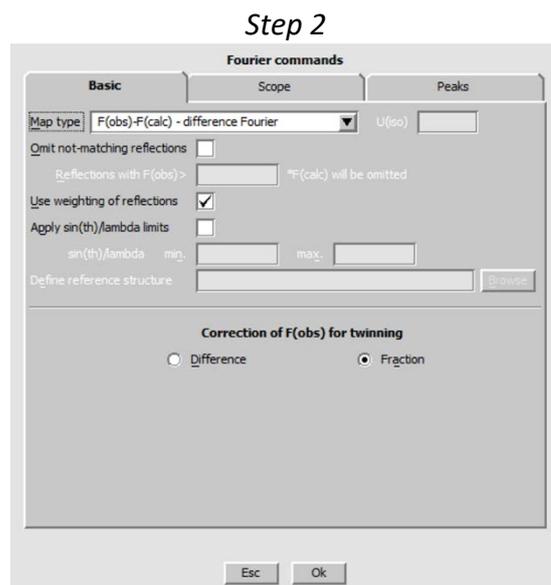
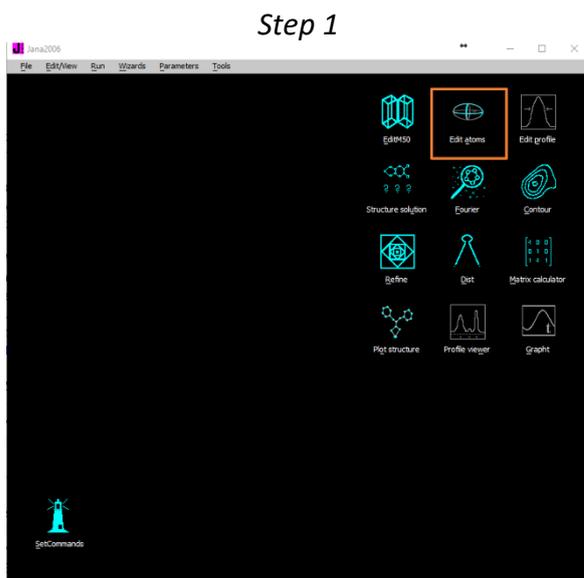
Refinement converges with R value about 4.4%, GOF about 4.4, 36 refined parameters.

### 3. Find remaining atoms using Fourier

[On the screen: basic window of Jana]

Right-click Fourier (Step1)

Select "Map type" = "F(obs)-F(calc) – difference Fourier" (Step2)

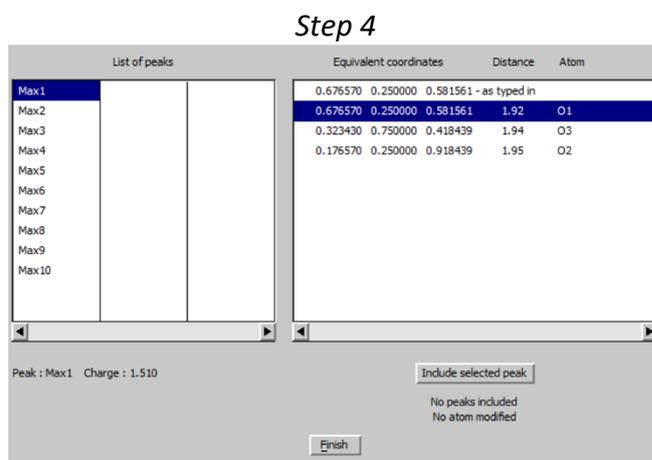
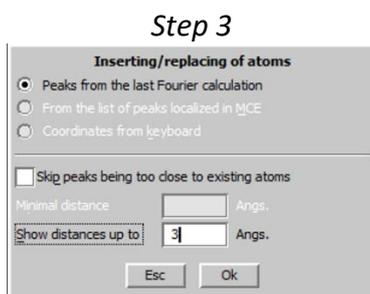


OK; YES+START; YES to include new atoms

[On the screen: Inserting/replacing of atoms]

OK(Step3)

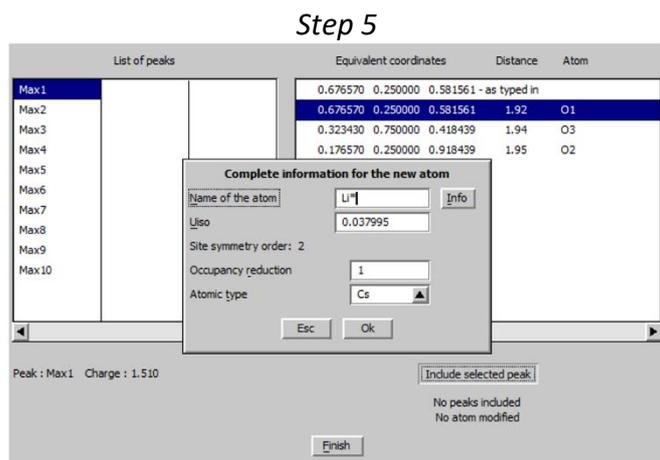
[On the screen: List of peaks] (Step4)



## Notes

*The strongest difference peak (Max1) has reasonable Li-O distances to oxygen atoms. We can add it as Lithium in the first highlighted symmetry position.*

Press “Include selected peak”  
 For “Name of atom” type Li\*;  
 TAB; OK; FINISH; YES to include the new atom.



Run refinement  
*Refinement converges with GOF ~ 3 and R(obs) ~ 2.7% for 39 parameters*

## 4. Extinction correction

[On the screen: basic window of Jana2006]  
 Open listing of Refine (by “Edit/View → View of Refine”)  
 Press “Go to” and select “Statistics Fo, sin(th)/lambda after refinement” (Step1)

## Step 1

Statistics as a function of sin(th)/lambda and structure factors

sin(th)/lambda	limits	0.300350	0.381961	0.435144	0.480711	0.517336	0.560540	0.589865	0.627326
number +		79	75	73	79	73	45	47	59
-		55	57	60	51	61	87	85	72
together		134	132	133	130	134	132	132	131
av. wd F		43.2964	4.5169	2.5122	4.9112	2.8146	2.5069	3.1005	3.4326
numerator +		122.8	106.8	76.4	95.1	87.9	42.0	38.7	70.7
-		-460.2	-88.2	-49.7	-72.0	-41.3	-65.4	-90.2	-67.4
together		582.7	195.0	126.2	167.2	129.1	107.4	128.9	138.0
denominator		11943.5	9489.3	7549.7	7568.8	6031.1	5790.1	5338.9	5343.9
R factor		4.88	2.05	1.67	2.21	2.14	1.85	2.42	2.58

struct. factors	limits	10.2	14.8	25.7	45.3	59.6	75.6	107.6	347.2	unobs
number +		65	57	66	72	62	56	78	70	88
-		63	76	66	60	70	77	54	62	89
together		132	133	132	132	132	133	132	132	177
av. wd F		3.6193	26.2395	2.7545	3.9384	5.4538	4.2044	4.2956	16.9612	0.5491
numerator +		52.3	48.5	37.8	48.9	67.2	67.8	130.8	186.8	106.3
-		-39.2	-49.3	-48.4	-44.0	-75.6	-90.4	-65.2	-522.3	-76.9
together		91.5	97.8	86.3	92.8	142.8	158.1	196.0	709.1	183.2
denominator		1078.9	1643.7	2578.2	4642.9	6959.6	8947.2	11755.0	21448.9	904.7
R factor		8.48	5.95	3.35	2.00	2.05	1.77	1.67	3.31	20.25

final check	number +	sin(th)/lambda	structure factors
	530	530	530
	528	528	528
	1058	1058	1058
	640.1	640.1	640.1
	-934.4	-934.4	-934.4
	1574.5	1574.5	1574.5
	59054.4	59054.4	59054.4
	R-factor	2.67	2.67

### Notes

The Statistics show that the strongest low-angle reflections are systematically weaker. This is an indication that extinction correction is needed.

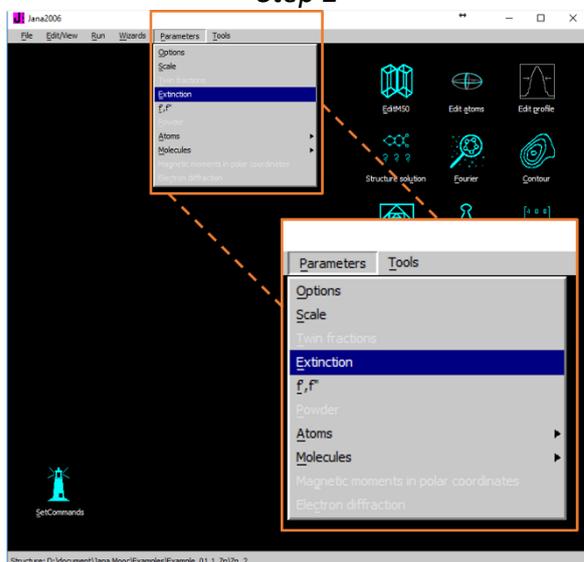
Close the refinement listing

“Parameters → Extinction” (Step2)

Select “Isotropic-Becker&Coppens” “Type 1” “Gaussian”; OK (Step3)

Refinement of extinction coefficient is enabled by default

### Step 2



### Step 3

**Extinction model:**

None  Type 1  Gaussian

Isotropic - Becker & Coppens  Type 2  Lorentzian

Anisotropic - Becker & Coppens  Mixed

SHELX model

Radius [cm]  used only if tbar not present on M90 file

---

**Extinction parameters:**

Giso

Refine all Fix all Reset

Esc Ok

[On the screen: basic window of Jana2006]

Run Refine

Refinement converges with GOF ~ 2.7 and R(obs) ~ 2.2% for 40 parameters

Start “Edit atoms”; change ADP of Lithium to harmonic

Refinement converges with GOF ~ 2.6 and R(obs) ~ 2.2% for 43 parameters

Right-click Refine; go to the page Basic  
Check “Instability factor from reflection statistics” (Step4)

#### Step 4

Refine commands

Basic Select,Listing Various Modulation

Number of cycles 100  Use Marguaret technique  Sigma weight Instability factor   
Damping factor 1  Fudge factor  Instability factor from reflection statistics   
 Use Wilson's modification  
 Unit weight

Use dynamical LS method => if R<sub>w</sub> is increased by 10% reduce the damping by a factor 2  
After 3 cycles try to enlarge it back.

Check for convergence => stop if max(change/s.u.) ≤ 0.05 in 1 consecutive cycles.

Disable atoms having too large isotropic ADP parameter => ADP(iso) limit for disabling 0.2

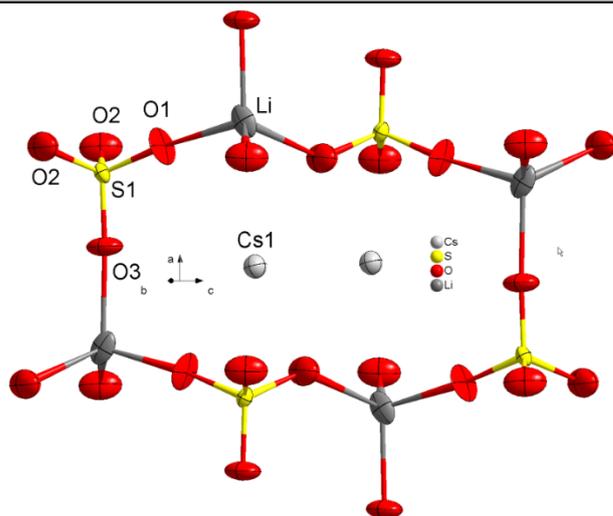
Automatic refinement keys 0.1 Maximal angular difference for twin overlap  
 Automatic symmetry restrictions 0 Minimal angular difference for full separation

Refinements on F(obs)\*\*2  
 Apply electroneutrality  
 Simulation run  
 After last cycle call Fourier  
 Correct for lambda/2 effect  
 Randomize atomic coordinates Random seed  Maximal random displacement in Ang   
Warning: the randomize procedure will applied just once during the next run

Esc Ok

OK; YES+START

#### Notes



*The final structure*

*Refinement converges with R value around 2.3% and GOF 1.4, for 43 parameters  
In this case, the instability factor from reflection statistics seems to be reasonable because the structure of a three-fold twin is fully solved and data are not expected to contain more information.*

#### References

# Example: kamotoite-(Y)

Revised: 9 March 2019

## Complex structure with pseudo-merohedric twinning and unequal twin volume fractions

---

Single crystal data measured with Rigaku SuperNova four-circle diffractometer (kappa geometry) with Atlas S2 CCD detector.

Input files: kamotoite\_abs.hkl, kamotoite\_abs.cif\_od

Frame scaling, absorption correction: done with software of diffractometer

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left panel: locate directory with input files

Right panel: double-click kamotoite

### 2. Import Wizard

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction → CCD”; NEXT

Select “Input from “cif\_od” file”; OK

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

For absorption correction select “None or done before importing”; NEXT FINISH

### 3. Data Repository

The line in data repository window corresponds to one data set.

OK; YES to accept the data set

### 4. Symmetry Wizard, twinning

[On the screen: “Tolerances for crystal system recognition”.]

Leave all settings default; NEXT; OK

Leave with „Continue with basic cell“, press „Next“

[On the screen: Select Laue symmetry]

Select monoclinic

NEXT Select  $P$ -centered unit cell; NEXT

[On the screen: Select space group]

Select the space group  $P2_1/n$ ; NEXT

(Differences between  $P2/n$  and  $P2_1/n$  support the existence of the  $2_1$  symmetry) NEXT

Select „Accept the space group transformed into original cell “; FINISH

## 5. Creating refinement reflection file

NEXT to confirm threshold  $3\sigma$

[On the screen: settings for merging of reflections]

Leave all settings default; NEXT

Accept the new DataBlock and calculate coverage; FINISH

## 6. Structure Solution Wizard

[On the screen: window of Structure solution]

Select „use SHELXT“

In “Formula” text box type list of chemical elements for kamotoite: Y U O

Notice: Kamotoite-(Y) contains also C as a fundamental element in the structure, nevertheless, such light atom would make the solution overnoisy – instead of O atoms you would get C atoms. It is simpler to introduce C atoms into the refinement later and assign them to the corresponding correct sites.

Leave all other fields empty

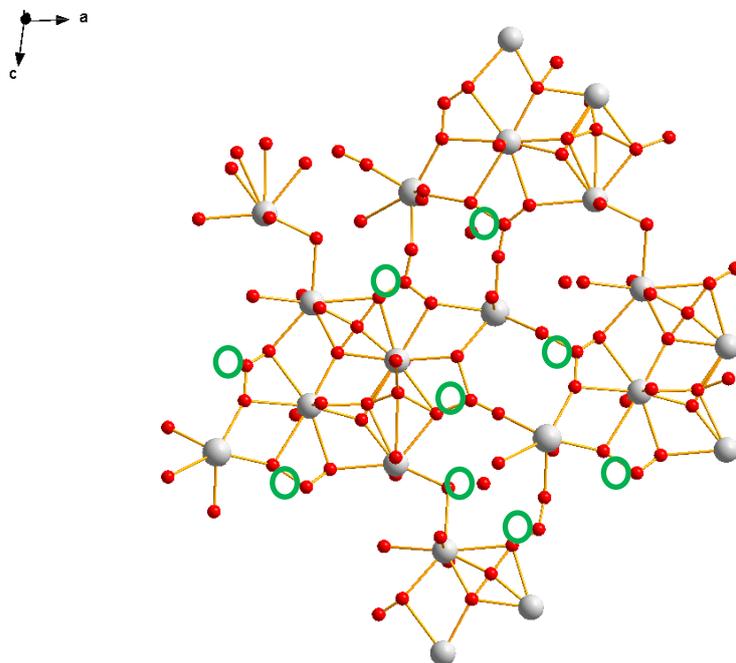
Press „Run solution“

[On the screen: output of SHELXT]

SHELXT converged and provided us a list of possible solutions.

Among them the first and suggested is our choice =>  $P2_1/n$  (despite of higher R value)

Press “Draw structure” to see result of SHELXT



You can see that some O atoms have been assigned to false Fourier peaks, and some of the O atoms actually correspond to C atom instead (marked by circles).

Quit Diamond without saving changes

In case of doubts repeat structure solution and plotting

Finally press “Accept last solution” to close the structure solution wizard

## 7. Refinement [On the screen: basic window of Jana]

Right-click the icon of Refine.

[On the screen: refinement options]

Define 100 of cycles, damping factor 0.5, Instability factor 0.01; Refinement on  $F(\text{obs})^{**2}$ , OK; Choose "YES+START"

Refinement converges with  $R$  value about 17%, GOF about 5, 161 refined parameters

During refinement, number of refined parameters decreases because some atoms get too high  $U_{\text{iso}}$  are automatically rejected. This feature can be controlled on the Basic page of Refine commands.

## 8. Editing of atoms

[On the screen: basic Jana window]

Start "Edit atoms"

Press „Select rejected“, Press „Action“ or right-click at one of the selected [highlighted in red color] atom; Choose „Delete selected atoms“, choose „Yes to all“.

Press „Select all“, right-click, choose „Rename selected atoms to atom\_type“+number.

Select U1 to U4 atoms [with shift or one each another], double-click and switch to the harmonic approach to the ADP parameters [ADP will be refined anisotropically] – by double clicking on the corresponding field. OK; OK; YES to save changes

## 9. Refinement [On the screen: basic window of Jana]

Start refinement double-clicking „Refine“

You can see that  $R$  values drop down to ~12% (GOF ~4)

## 10. Assignment of correct chemical types

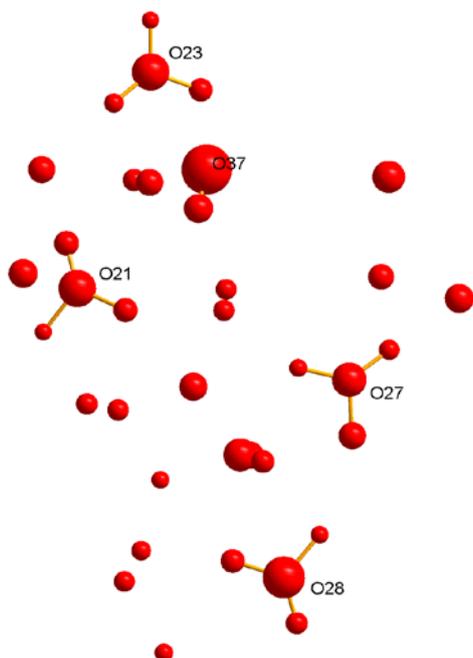
Start "EditM50"; switch to the page Composition

[On the screen: Composition]

Add in the row „Formula – list of atomic types“: C, Dy [at the end after O; C is essential, while Dy is minor]; OK, OK

Start Diamond double-clicking "Plot structure"

The best way to deal with is to add only oxygen atoms (by clicking  or starting Build → „Add atoms“). Then click  or start Build → Connectivity, and select O-O pairs only. Click „Fill coordination spheres directly“ ; and click „Model“  to plot ellipsoids. Inspect the molecular fragment you get by rotation to view it approx. along **b**. Now you can read out which O atoms are in fact C atoms: they have three bonds to neighboring oxygen atoms, and large  $U_{\text{iso}}$ . Notice their labelling to be changed later, or rename them in Jana immediately. Some other oxygen atoms with large  $U_{\text{iso}}$  might still be false Fourier peaks.



Start "Edit atoms"

Select the atoms which should be carbons (O21, O23, O27, O28 in our example)

Start "Action → Edit/define" and choose chemical type "C"; OK

Press "Select all", right-click „Rename selected atoms to atom\_type"+number.

*We can proceed with refinement of ADP of Y atoms using harmonic description.*

select Y1 and Y2, turn on the harmonic (anisotropic) ADPs; OK, OK, Yes.

### **11. Refinement** [On the screen: basic window of Jana]

Start refinement double-clicking „Refine“

*You can see that refinement converged to slightly lower R values than previous, ~11%, however, on the last screen that appeared after the last-cycle, the warnings appeared. You can find them at the end of the listing*

Press „Open the listing“

Press „Go to“ → „List of serious warnings“

*You can see that serious warnings concern harmonic ADPs of the Y atoms, which turned out to reach the physically unreasonable values. We have to inspect them in a greater detail.*

### **12. Inspection of the ADPs and site-scattering refinement**

Start "Edit atoms"

Select Y1 and Y2 atoms; double-click, choose „Edit“, allow refinement of the occupation factors (labelled „ai“); OK, OK, Yes.

Start the refinement

*You can see that ai especially for Y2 is changing significantly. Refinement converged to ~10.5% with GOF ~3.75.*

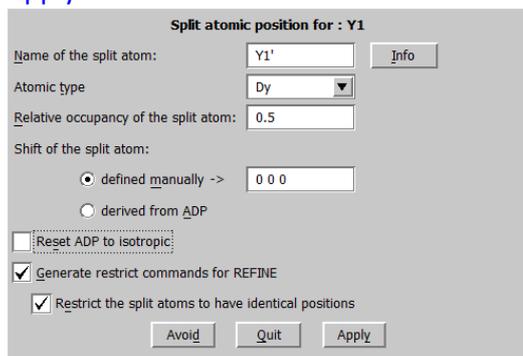
*We have to check how the refined values of the Y atoms look like. You can do that in this case right in the panel for editing atoms. You can see that ai for both Y atoms has risen up, which means that there is a heavier atom substituting for Y at both atom sites. From the results of*

the electron-microprobe analysis we are quite sure that it goes about Dy. Therefore we can introduce it to the refinement and treat both Y sites as a mix sites. First you have to rest values of site-occupancies for both sites.

Start "Edit atoms"

in Edit window, Y1, press „Show/reset site occupancy“, press Yes. Do the same for Y2. Press OK.

Right-click on Y1, choose „Split atomic positions“, choose „Atomic type“ as Dy, click onto „defined manually“ („shift of the split atom“), leave „0,0,0“, untick „reset ADP to isotropic“, Apply



Repeat the same procedure also with Y2.

Check, if the refinement of occupation factors for all involved atoms is allowed  
OK, Yes

Start the refinement

Refinement converged to 10.6% and there are no serious warnings after the last cycle.

### 13. Completing oxygen atoms

Plot the structure with „ellipsoids“ for all atoms

Note oxygen atoms with large Uiso and unreasonable geometry and delete them using Edit atoms

Refine the structure

Right-click on „Fourier“

Select from „Map type“ „Fobs-Fcalc difference Fourier“, leave all settings default, OK, Yes+Start

Start procedure for including new atoms

Tick „Skip peaks being too close to existing atoms“, fill in the minimal distance 1 Å. OK

[The window with list of peaks appeared]

Click on the maximum Max1

The bottom left part shows the charge of this maximum (about five). The right pane shows distances of Max1 to atoms of the structure. The distance to Y1/Y1' is about 2.5 Å so this maximum correspond to one of missing oxygen atoms

Press „Include selected peak“, fill in the „name of the atom“ „O\*“.

Repeat the procedure with rest of the peaks you want to include.

There should be four missing oxygen atoms. In case of smaller number, it is possible that some of these atoms were either included in the initial structure model or will be found in the next step.

Press „Finish“, Yes

Start refinement

Run a difference Fourier again to localize all resting atoms; include the maximum with  $\sim 2.8 \text{ \AA}$  to one of existing oxygen atoms (without any shorter distances).

#### Start the refinement

Refinement converged to  $R \sim 9.2\%$  ( $GOF \sim 3.06$ ), 217 refined parameters

It is important to see 217 as number of refined parameters. In case of lower number, some oxygen atoms are missing (each of them adds 4 parameters)

You can check the structure in Diamond, and see that it looks quite complete.

#### Run a difference Fourier

Start "Edit  $\rightarrow$  View of Fourier" to open Fourier listing

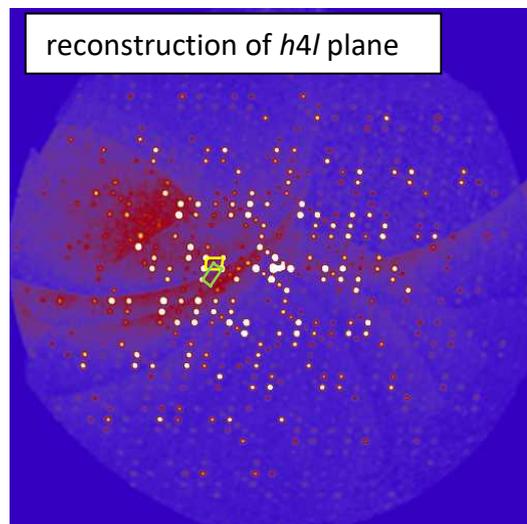
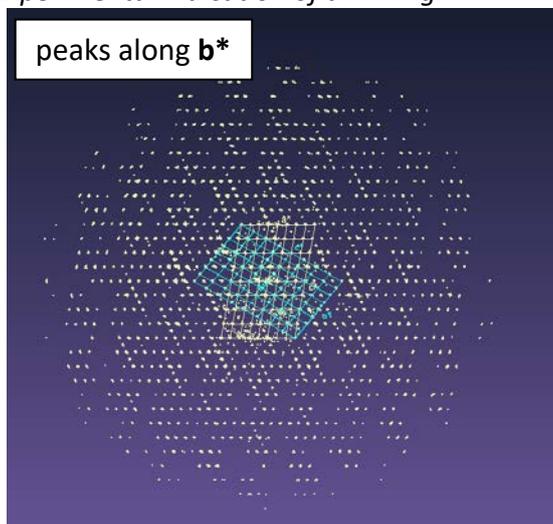
In the listing, use the Go to button to see the list of positive peaks

Although there are no additional reasonable peaks in the difference Fourier, nevertheless, there is a lot of resting electron density with the maximal difference Fourier density peak corresponding to  $12.18 \text{ e\AA}^{-3}$ , which is a rather high value. With the complete structure model, we are still missing something. The high final  $R$  values (as a consequence) is due to twinning present in the crystal analyzed.

### 14. Identification and introduction of twinning

The fact the sample is a twin is evident from the diffraction experiment. Here we are going to show how to find the twinning matrix directly from the supercell data we have been using in previous steps.

Experimental indication of twinning:



Start File  $\rightarrow$  Structure  $\rightarrow$  Save As

Save the structure under the new name, kamotoite\_abs\_twin, and continue with the new structure

Go to „Tools“  $\rightarrow$  „Special tools“  $\rightarrow$  „Search for reticular twinning“

[On the screen: Look for reticular twinning]

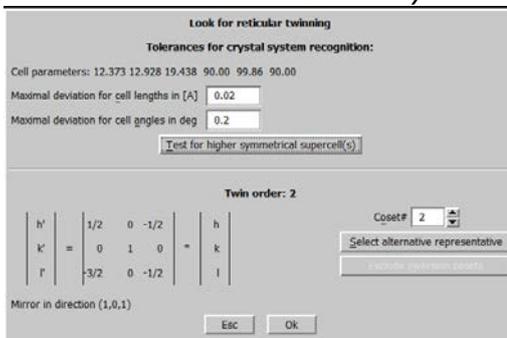
Keep the default settings, press „Test for higher symmetrical supercell(s)“

[On the screen: Select supercell]

Choose orthorhombic, n\*Volume = 4\*3063.51

Click OK

You can see that the twin actually is the mirror in (101) and corresponding twinning matrix.



Proceed with OK, Yes, and re-create refinement reflection file, which will change due to presence of twinning. OK.

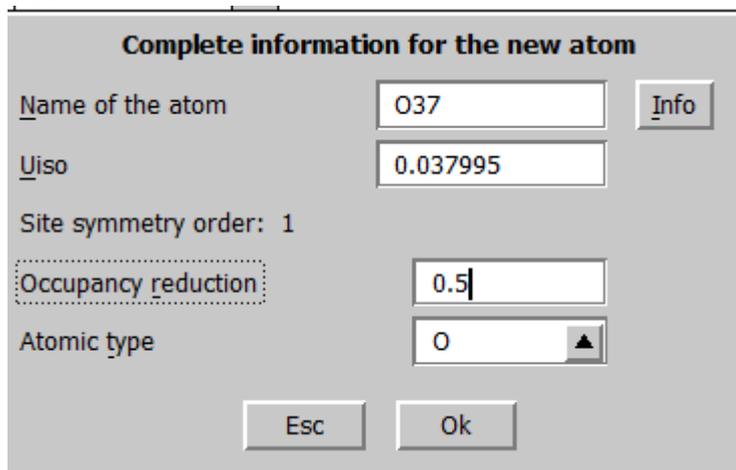
Go to „Parameters“ → „Twin fractions“ and allow the refinement of the „twvol2“. OK, Yes

Start refinement

You can see that the twin fractions are changing dramatically and R values drop down significantly to ~5.03% and GOF ~1.6 for 218 parameters. The refined twin ratios are about 85/15.

Check difference Fourier

Include the resting maximum Max1 (~ 2.6 Å to oxygen), as O atom. Reduce its occupancy to 0.5.



Run the refinement

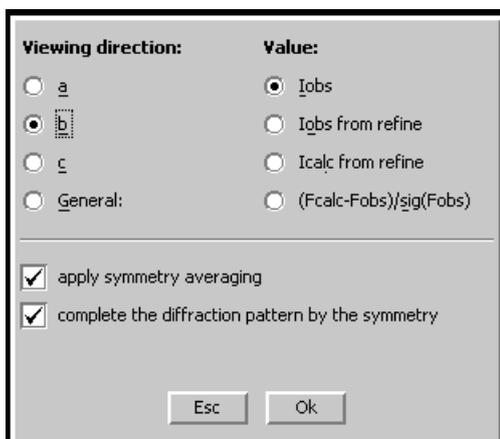
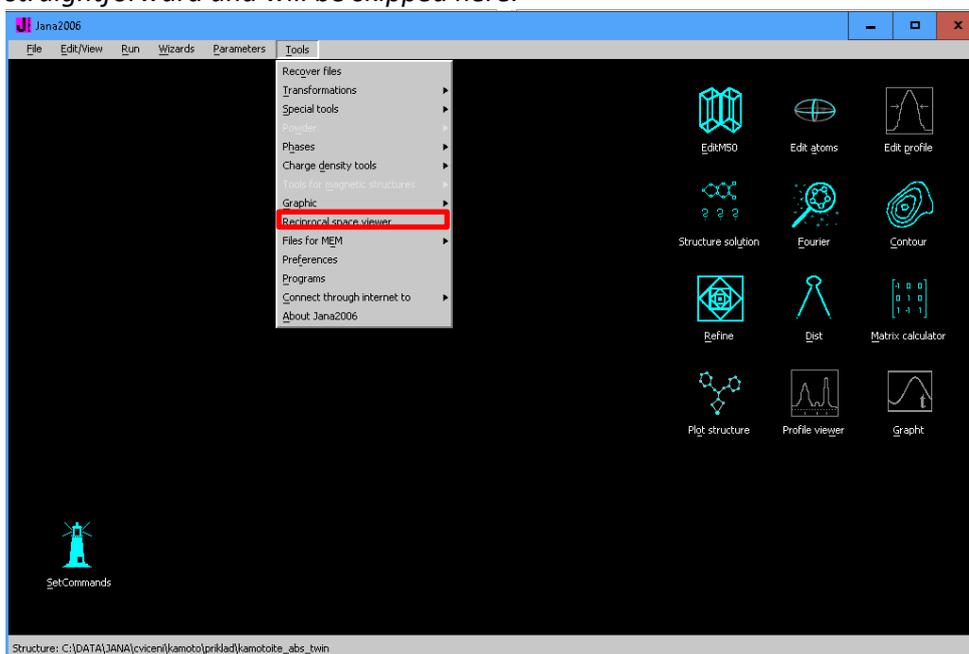
The refinement converged to the final values of 4.96% and GOF = 1.5 for 222 refined parameters; highest difference Fourier peak is now about 4 eÅ<sup>-3</sup>.

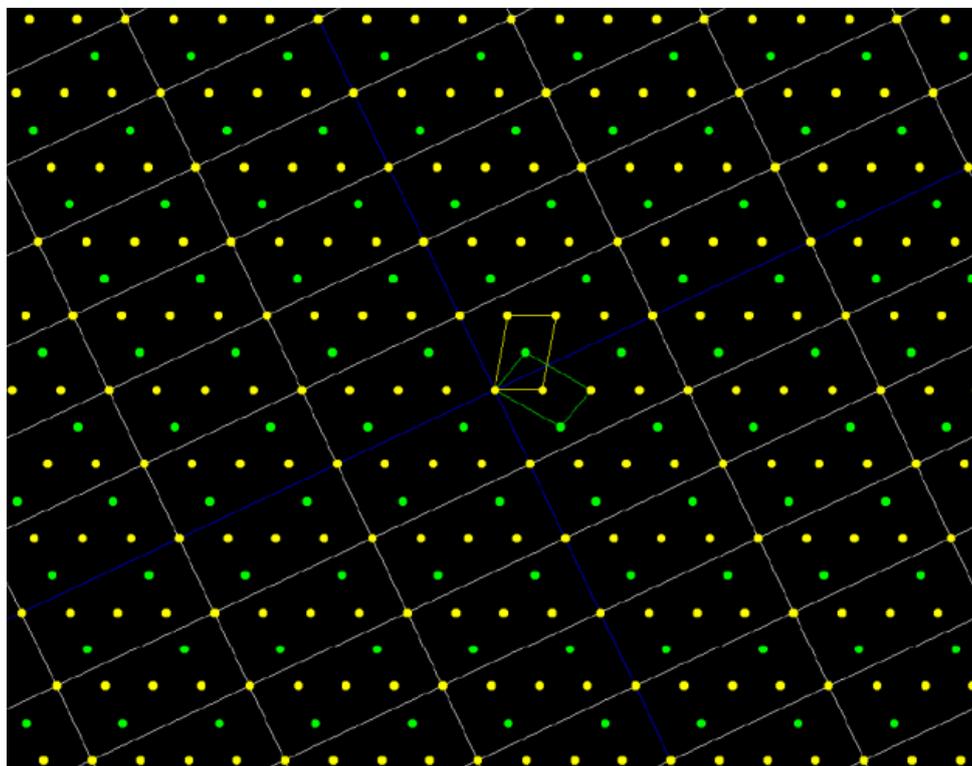
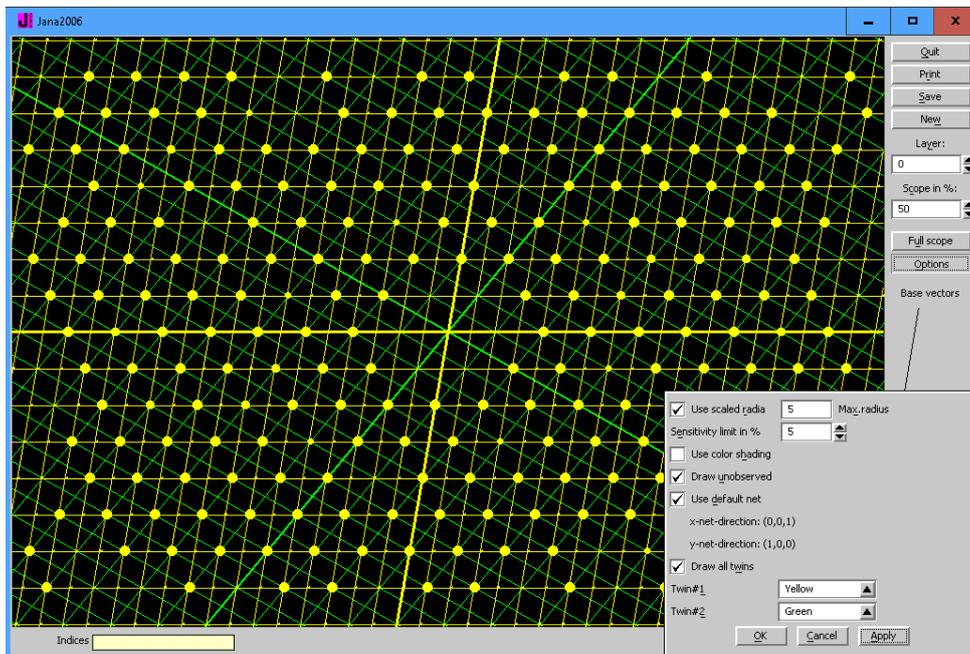
Refinement of anisotropic ADP for oxygen cannot be done from this data set. Making  $O^*$  anisotropic introduces 185 new parameters but leads to negligible decrease of R-factor and non-positive definite ADPs.

Crystal structure of kamotoite-(Y) possesses many H atoms, present both as (OH) and molecules of  $H_2O$ , however, they cannot be localized from this X-ray dataset. Therefore the model we obtained is a final one.

You can obtain the information about atomic composition in „Edit atoms“ → „Composition“ → click on „Formula from M40“ →  $Y1.375 U4 O36.5 C4 Dy0.625$ .

Both twins can be visualized in Jana, using Reciprocal space viewer in Tools. The way how to visualize corresponding observed reflections for the second (and vice versa) twin-domain is not straightforward and will be skipped here.





*Reciprocal-space view of the two contributing twin domains in kamotoite-(Y) crystal; yellow = reflections of the larger domain, green = smaller domain. The grid corresponds to the simulated orthorhombic super-lattice.*

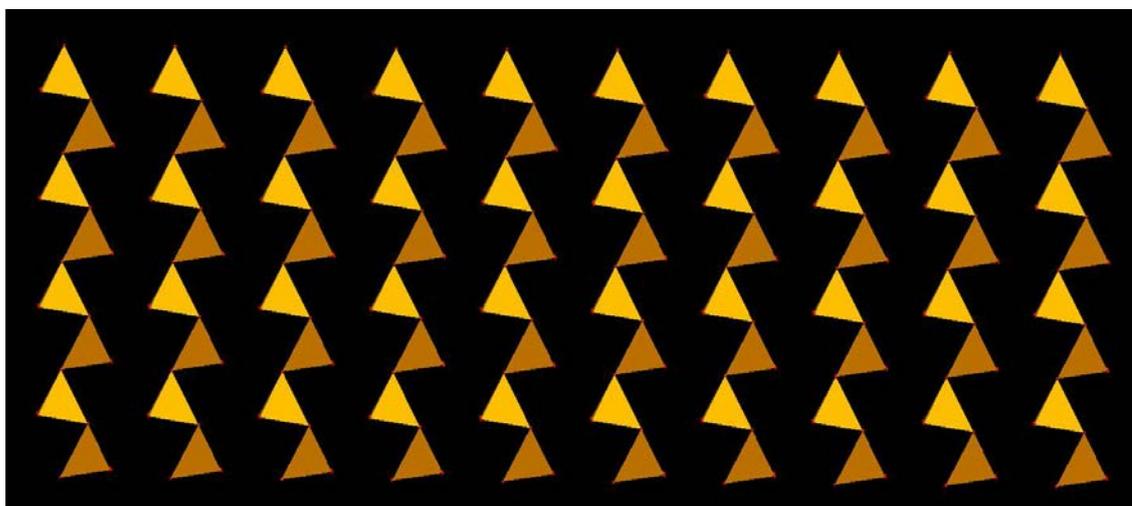


# Example 3.4: $\text{Ca}_2\text{Fe}_2\text{O}_5$

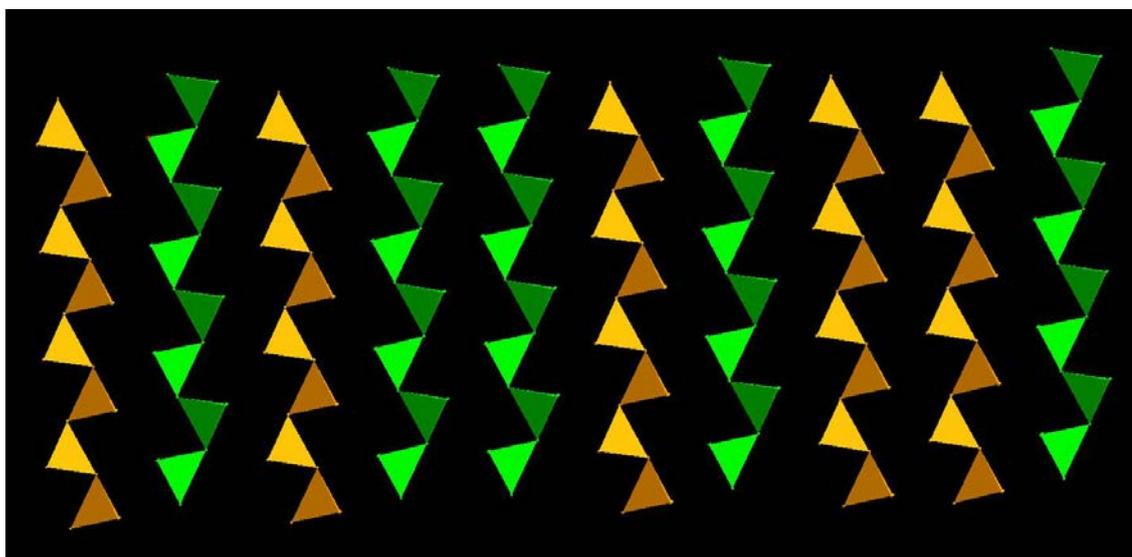
HT structural phase transition, coexistence of two phases in single crystal with strong overlaps.

H. Kruger, V. Kahlenberg, V. Petříček, F. Phillipp & W. Wertl, *J. Solid State Chem.*, **182**, (2009), 1515-1523.

LT phase – orthorhombic,  $Pnma$ , cell parameters  $\sim 5.4707, 14.9897, 5.6302 \text{ \AA}$   
In one layer of Fe tetrahedrons there is only one type orientation (e.g. Left)



HT phase ( $>710^\circ\text{C}$ ) – orthorhombic, modulated,  $Imma(00\gamma)s00$ , cell parameters  $\sim 5.4707, 14.9897, 5.6302 \text{ \AA}$ ,  $\mathbf{q}=(0,0,0.58)$ . In one layer of Fe tetrahedrons there are two different orientations (Left and Right) alternating with the period incommensurate to the basic cell.



Diffraction pattern: Strong 1<sup>st</sup> order, no 2<sup>nd</sup> order and some weak 3<sup>rd</sup> order satellites → crenel like modulation with  $\Delta \approx 1/2$ .

Main features of the solution for the HT phase: The atoms Fe2 and O3 are occupying the positions close to the Wyckoff position 4(e), point group  $mm2$ . The mirror  $m$ , with normal along  $a$  axis, having half shift along the internal  $x_4$  axis, transforms the “left” oriented ribbon of Fe tetrahedrons to the “right” ones and the occupational modulations of both atoms have a crenel like shape.

During the first order phase transition both phases (LT and HT) are coexisting in a wide region of temperatures and with x-ray diffraction they both contribute to the same diffraction pattern. In this example we shall start from the known structures of both phases and we shall demonstrate that the generalized twinning option in Jana2006 can also be applied to single crystals composed from two or more phases.

As a starting point you have at disposal the HT structure refined against the data set having the highest possible fraction of the HT phase from all measured data sets. In the first part of the example it is demonstrated main features of the solution. In the second part the LT phase will be read in from the supplied CIF file and then the final refinement will be performed.

Input files: HT\_phase.m40, HT\_phase.m50, HT\_phase.m90, HT\_phase.m95 and LT\_phase.cif.

### 1. Open the modulated phase

Start Jana2006

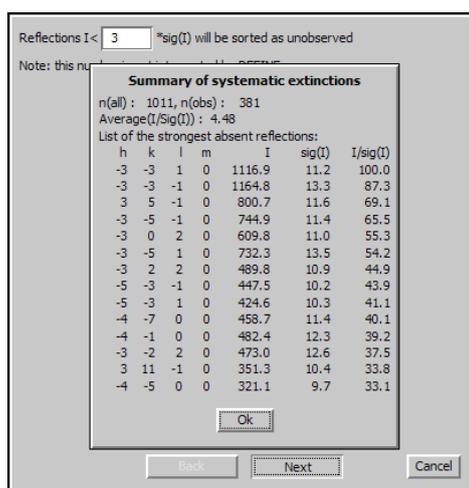
“File → Structure → Open” opens a file manager

Left pane: locate directory with input files

Right pane: double-click HT\_Phase

### 2. Check systematically extinct reflections

“File → Reflection file → Create refinement reflection file”



*There are 381 observed reflections, some of them relatively strong, which do not follow the extinction rules for  $Imma(00\gamma)s00$ . This means that the reflections of the second “P-centered” phase are really present.*

### 3. Run refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine.

[On the screen: refinement options]

Define 100 of cycles, Damping factor 1; OK

Choose "YES+START"

The refinement converges with  $R(\text{obs})$  about 5.98%, 4.48% and 9.12%.

### 4. Check the refinement model

[On the screen: basic Jana window]

Start "Edit atoms"

[On the screen: list of atoms]

Double-click on the first atom Fe1

[On the screen: list of atoms]

Go through all atoms (using arrows of the top-left text box) and check the modulation model.

All atoms except Fe2 and O3 have just one harmonic positional wave. Atoms Fe2 and O3 have one crenel function.

Write down coordinates of Fe2 and O3 and then go to "Edit" thumbnail, press the button "Occupancy" and write down also the values of delta and x40

Fe2 (-0.052,0.25,0.568) delta=0.5 (fixed) x40~0.6404

O3 (-0.402,0.25,0.625) delta=0.5 (fixed) x40~0.6755

Escape the form;

### 5. Run dist

[On the screen: basic Jana window]

Right-click the icon of Dist.

[On the screen: distance commands]

Use the default parameters except for the listing form which should be changed to "With symmetry code".

OK; Start the program;

Open the listing and look for Fe2 coordination;

The atom Fe2 is coordinated by the atom O2, O2#s2, O3 and O3#s4c2t0,0,1.

### 6. Draw modulation curves in Contour for Fe2 and O3

[On the screen: basic Jana window]

Double-click the icon Contour; Press the button "New plot" if active;

Select "Fourier map" and "Draw maps as calculated"; OK

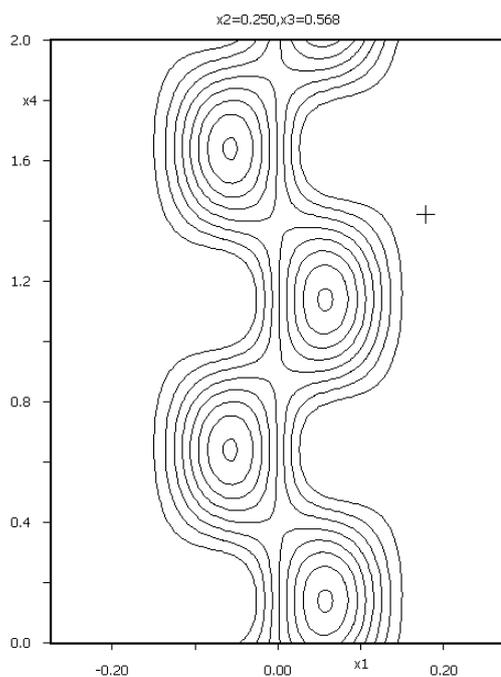
In thumbnail "Basic" select "F(obs) – Fourier" and in thumbnail "Scope" select "by a central point";

Center "0 0.25 0.568"; Section 1<sup>st</sup> → x1, 2<sup>nd</sup> → x4, 3<sup>rd</sup> → x2, 4<sup>th</sup> → x3;

x4 minimum → 0, maximum → 2, step 0.02

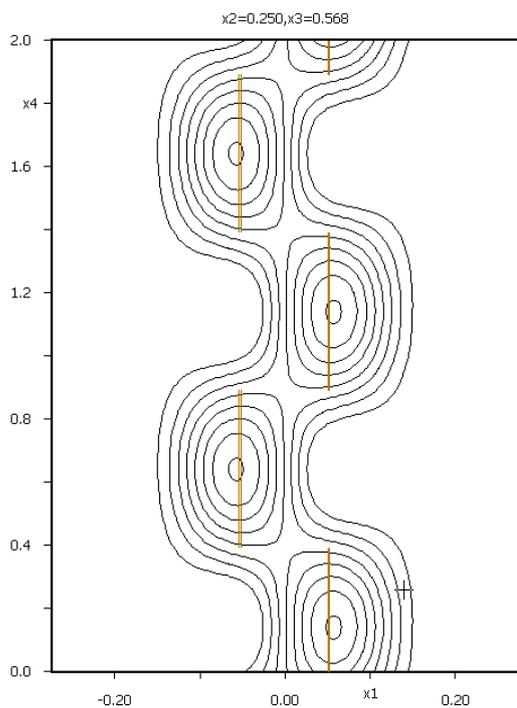
Scope → 3 0 0; Step → 0.02; OK

[On the screen: the following map]



Press “Atom edit” and add two atoms Fe2 and Fe2#s8. The second one is the position generated by the eighth symmetry operation i.e. by  $-x_1 \ x_2 \ x_3 \ x_4+1/2$ ;

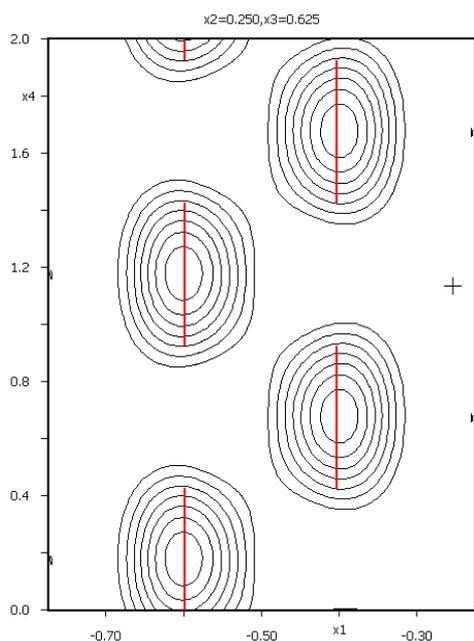
*[On the screen: the following map]*



Repeat it for the center at  $-0.5 \ 0.25 \ 0.625$  (a position close to O3);  
 Press the button “Atoms edit” to show the modulation curves for O3 and the symmetry related atom O3#s8t-1,0,0. The translation part  $-1,0,0$  returns the symmetry related atom

back to vicinity of O3.

[On the screen: the following map]



The crenel function for atoms Fe2 and O3 assures the alternation between the “Left” and “Right” configurations of Fe tetrahedrons. During the refinement the “delta” values were fixed to 0.5 for both atoms. But there were no restrictions applied to x40. Now we have to check:

(a) if there is no overlap between two symmetry related positions of Fe2 and Fe2#s8 and O3 and O3#s8t-1,0,0.

The symmetry operation #8 has the following form:  $-x_1, x_2, x_3, x_4+1/2$

for the atom Fe2 we have:  $t_{\min} = x_{40} - \Delta/2 - \mathbf{q} \cdot \mathbf{r}$   $t_{\max} = x_{40} + \Delta/2 - \mathbf{q} \cdot \mathbf{r}$  and for the symmetry related Fe2#s8:  $t_{\min} = x_{40} + 1/2 - \Delta/2 - \mathbf{q} \cdot \mathbf{r}'$   $t_{\max} = x_{40} + 1/2 + \Delta/2 - \mathbf{q} \cdot \mathbf{r}'$

From the fact that the modulation vector is  $(0,0,\gamma)$  and that the third component of the symmetry related atoms remains the same for both positions, it follows that the  $t$  intervals are fully separated with no overlaps.

The same conclusion is valid also for the atom O3.

(b) if the  $t$  intervals in which exist atom Fe2, O3 and O3#s4c2t0,0,1 are identical.

For Fe2 and O3 this means:

$$t_{\min}(\text{Fe } 2) = x_{40}(\text{Fe } 2) - \Delta(\text{Fe } 2)/2 - \mathbf{q} \cdot \mathbf{r}(\text{Fe } 2) = t_{\min}(\text{O } 3) = x_{40}(\text{O } 3) - \Delta(\text{O } 3)/2 - \mathbf{q} \cdot \mathbf{r}(\text{O } 3) =$$

taking into account the fact that  $\Delta(\text{Fe } 2) = \Delta(\text{O } 3) = 1/2$  we have:

$$x_{40}(\text{Fe } 2) - \mathbf{q} \cdot \mathbf{r}(\text{Fe } 2) = x_{40}(\text{O } 3) - \mathbf{q} \cdot \mathbf{r}(\text{O } 3) \Rightarrow x_{40}(\text{O } 3) = x_{40}(\text{Fe } 2) - \mathbf{q} \cdot [\mathbf{r}(\text{Fe } 2) - \mathbf{r}(\text{O } 3)]$$

$$\text{and finally } x_{40}(\text{O } 3) = x_{40}(\text{Fe } 2) - \gamma \cdot [z(\text{Fe } 2) - z(\text{O } 3)] \quad (1)$$

Numerically:  $x_{40}(\text{O3}) = 0.6755 \approx 0.6404 - 0.6101 \cdot [0.568 - 0.625] = 0.6752$  and  
 $t_{\min}(\text{O3}) = 0.6755 - 0.6101 \cdot 0.625 = 0.0442$

This means that the refined value was really close to the ideal value

For  $\text{O3}\#s4c2t0,0,1$  the symmetry operation  $s4c2t0,0,1$  is  $x_1+1/2 -x_2+1/2 -x_3+3/2 -x_4+1/2$  modifies  $t_{\min}$  to:

$$t_{\min} = x_{40}(\text{O3}\#s4c2t0,0,1) - \Delta(\text{O3}\#s4c2t0,0,1)/2 - \mathbf{q} \cdot \mathbf{r}(\text{O3}\#s4c2t0,0,1)$$

Numerically:  $z(\text{O3}\#s4c2t0,0,1) = 3/2 - z(\text{O3}) = 0.825$   
 $x_{40}(\text{O3}\#s4c2t0,0,1) = 1/2 - x_{40}(\text{O3}) = -0.1755$

This means that:  $t_{\min} = -0.1755 - 0.6101 \cdot 0.825 - 0.25 = -0.959$  and therefore we have to modify the equation by adding one:

$$t_{\min}(\text{Fe2}) = x_{40}(\text{Fe2}) - \Delta(\text{Fe2})/2 - \mathbf{q} \cdot \mathbf{r}(\text{Fe2}) =$$

$$x_{40}(\text{O3}\#s4c2t0,0,1) - \Delta(\text{O3}\#s4c2t0,0,1)/2 - \mathbf{q} \cdot \mathbf{r}(\text{O3}\#s4c2t0,0,1) + 1 \Rightarrow$$

$$x_{40}(\text{O3}\#s4c2t0,0,1) = x_{40}(\text{Fe2}) - \mathbf{q} \cdot [\mathbf{r}(\text{Fe2}) - \mathbf{r}(\text{O3}\#s4c2t0,0,1)] - 1$$

and by applying the symmetry operation  $s4c2t0,0,1 \sim x_1+1/2 -x_2+1/2 -x_3+3/2 -x_4+1/2$ :

$$1/2 - x_{40}(\text{O3}) = x_{40}(\text{Fe2}) - \gamma \cdot [z(\text{Fe2}) - 3/2 + z(\text{O3})] - 1 \Rightarrow$$

$$x_{40}(\text{O3}) = -x_{40}(\text{Fe2}) + \gamma \cdot [z(\text{Fe2}) - 3/2 + z(\text{O3})] + 3/2 \quad (2)$$

Combining (2) with the previous one we have for  $x_{40}(\text{Fe2})$ :

$$x_{40}(\text{Fe2}) = 3/4 \cdot (1 - \gamma) + \gamma \cdot z(\text{Fe2}) \Rightarrow t_{40}(\text{Fe2}) = 3/4 \cdot (1 - \gamma)$$

$$x_{40}(\text{O3}) = 3/4 \cdot (1 - \gamma) + \gamma \cdot z(\text{O3}) \Rightarrow t_{40}(\text{O3}) = 3/4 \cdot (1 - \gamma)$$

Numerically:  $x_{40}(\text{O3}) = 0.6755 \approx 0.75 \cdot 0.3899 + 0.6101 \cdot 0.625 = 0.6737$

This means that both  $t_{40}$  parameters can be fixed to the same constant value as Fe2.

## 7. Run restricted refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine.

[On the screen: refinement options]

Select thumbnail “Various” and press the button “Equations”:

Define equations:

t40[Fe2]=0.75-0.75\*cq3

t40[O3]=0.75-0.75\*cq3

OK; Start Refinement;

*The refinement converges with R(obs) about 5.99%, 4.49% and 9.14% which means that it had almost no effect.*

Open the listing to check the applied equation:

*Equations defined by user:*

x40[Fe2]=0.2924+0.6101\*z[Fe2]

x40[O3]=0.2924+0.6101\*z[O3]

### **8. Continue with a new structure name**

*[On the screen: basic window of Jana]*

Start Jana2006

“File → Structure → Save as” opens a file manager

Right pane: Write a new structure name e.g. “Both\_Phases”

*[On the screen: “Continue with the new structure?”]*

Yes;

### **9. Adding of the LT phase**

*[On the screen: basic window of Jana]*

“Tools → Phases → New phase”;

Select “Import from CIF format”; Press “Browse” and select the file LT\_Phase.cif;

OK

### **10. Define the twinning matrices**

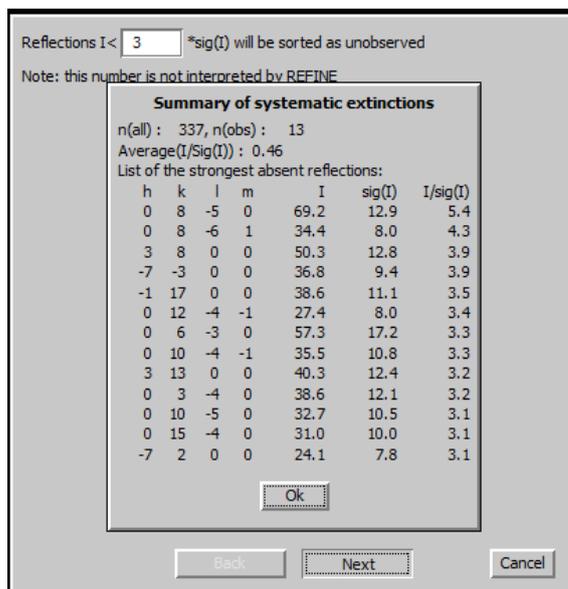
*[On the screen: the form for defining of twinning matrices]*

*The “twinning” matrices define relationship between the phases and the reference cell parameters. Unlike real twinning they may change the unit cell. In our case both phases are defined in the same cell.*

Both matrices are unit ones. The first is to be applied to the first phase and the second to the second phase.

OK; follow the wizard for creating the refinement reflection file

*Systematic extinctions are now much better fulfilled:*



### 11. Run refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine.

[On the screen: refinement options]

Change the damping factor to 0.5.

OK; Save and run the refinement;

The refinement converges with R(obs) about 4.99%, 4.09% and 7.37%.

### 12. Refine anisotropic ADP of atoms from the second phase

[On the screen: basic window of Jana]

Switch the phase to the Phase#2 (thumbnails in the lower-left corner)

Using "Edit atoms": select all atoms and change ADP to harmonic;

OK;

### 13. Run refinement

[On the screen: basic window of Jana]

Double-click the icon of Refine.

The refinement converges with R(obs) about 4.60%, 3.78% and 6.75%.

### 14. Check the phase fraction factor

[On the screen: basic window of Jana]

"Parameters → Twin fractions"

The fraction of the second domain was refined to 0.276

# Example 3.5: Cd-HPO

Updated 9 March 2019

Data	Topic	Level
X-ray single crystal data	Local disorder	Intermediate

## Tasks

---

Group-subgroup transformation with application of local symmetry.

## Initial data

---

### Data

Single crystal data measured with Oxford Diffraction four-cycle diffractometer

### Input files:

Cd-HPO.hkl

Cd-HPO.cif\_od

### Additional information:

Chemical formula:  $\text{Cd}(\text{H}_2\text{PO}_3)(\text{HPO}_3)(\text{CH}_3\text{OH})$

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# Instructions

---

## I. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → **New**” opens a file manager

Left pane: locate directory with input files;

Right pane: double-click **Cd-HPO**

### 2. Import wizard

Select “Known diffractometer formats”; **NEXT**

Select “Oxford Diffraction → CCD”; **NEXT**

Select “Input from “cif\_od” file”; **OK**

Leave all settings unchanged; **NEXT**

Leave all settings unchanged; **NEXT**; **OK**;

*The program reads 5291 reflections from hkl file*

For absorption correction select “None or done before importing”; **NEXT**

**FINISH**;

### 3. Data Repository

**OK**; **YES** to accept the data set

**NEXT**;

### 4. Symmetry wizard

[On the screen: “Tolerances for crystal system recognition”.]

Leave all settings default; **NEXT**; **OK**

[On the screen: Select Laue symmetry]

Select **Hexagonal 6/mmm** Laue symmetry; **NEXT** (Step 1)

#### Step 1

Select Laue symmetry				
Crystal system	Point group	Rint(obs/all)	#averaged	Redundancy
Tridinic	-1	2.58/2.66	1385/1713	3.089
Monoclinic-setting "c"	2/m	12.84/12.90	799/937	5.647
Orthorhombic-setting "a,2b-a"	mmm	13.14/13.20	466/551	9.603
Orthorhombic-setting "b,-2a-b"	mmm	13.03/13.09	474/566	9.348
Orthorhombic-setting "-a-b,a+b"	mmm	13.08/13.15	464/556	9.516
Trigonal	-3	2.90/2.97	520/627	8.439
Trigonal	-31m	2.97/3.04	299/377	14.034
Trigonal	-3m1	13.17/13.23	353/411	12.873
Hexagonal	6/m	13.24/13.30	294/344	15.381
Hexagonal	6/mmm	13.30/13.36	206/246	21.508

ordered by Laue symmetry       ordered by Rint

Averages made from 4208/5291 reflections

Back      Next      Cancel

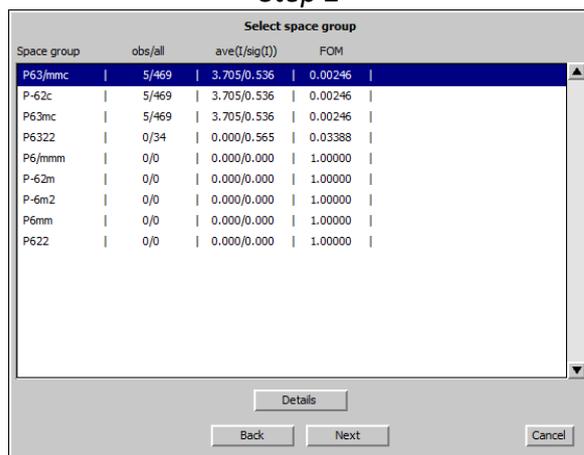
Select centering **P** unit cell; **NEXT**  
 [On the screen: Select space group]  
 Select **P63/mmc**; **NEXT** (Step 2)

#### Notes

*Superflip will give us hexagonal space group during processing that is why we chose hexagonal setting even if the trigonal setting seems better. Another reason for starting with hexagonal setting is that we get possibility to transform the structure to a trigonal twin.*

Leave all settings unchanged; **FINISH**

#### Step 2



### 5. Creating refinement reflection file

**NEXT** to confirm threshold 3sigma; **OK**; **OK**

#### Notes

<p><b>Import statistics - obs/all</b></p> <p>4208/5291 reflections read from input file          4203/4822 reflections written to output file          5/469 reflections rejected as systematically extinct.</p> <p><input type="button" value="OK"/></p>	<p><b>Summary of systematic extinctions</b></p> <p>n(all) : 469, n(obs) : 5          Average(I/sig(I)) : 0.36          List of the strongest absent reflections:</p> <table border="1"> <thead> <tr> <th>h</th> <th>k</th> <th>l</th> <th>I</th> <th>sig(I)</th> <th>I/sig(I)</th> </tr> </thead> <tbody> <tr> <td>2</td> <td>-1</td> <td>7</td> <td>2157.3</td> <td>457.2</td> <td>4.7</td> </tr> <tr> <td>2</td> <td>-1</td> <td>5</td> <td>1392.9</td> <td>348.7</td> <td>4.0</td> </tr> <tr> <td>-1</td> <td>-1</td> <td>7</td> <td>1169.8</td> <td>339.2</td> <td>3.4</td> </tr> <tr> <td>-2</td> <td>1</td> <td>-5</td> <td>1154.4</td> <td>349.8</td> <td>3.3</td> </tr> <tr> <td>2</td> <td>-4</td> <td>5</td> <td>711.8</td> <td>232.2</td> <td>3.1</td> </tr> </tbody> </table> <p><input type="button" value="OK"/></p>	h	k	l	I	sig(I)	I/sig(I)	2	-1	7	2157.3	457.2	4.7	2	-1	5	1392.9	348.7	4.0	-1	-1	7	1169.8	339.2	3.4	-2	1	-5	1154.4	349.8	3.3	2	-4	5	711.8	232.2	3.1
h	k	l	I	sig(I)	I/sig(I)																																
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-2	1	-5	1154.4	349.8	3.3																																
2	-4	5	711.8	232.2	3.1																																

[On the screen: settings for merging of reflections]

**NEXT**

The program reports *Rint* 13.30% for 203 observed reflections merged from 217 reflections.

#### Notes

*We have a high value of *Rint*, which may be due to the presence of twinning, which may explain why Jana2006 found the trigonal setting better. We will try this approach later in this exercise.*

**OK**;

Select "Accept the new data block and calculate coverage"; **FINISH**; **OK**

## II. Structure solution and Refinement model 1

### 1. Structure solutions wizard

[On the screen: Structure solution]

In "Formula" textbox type list of chemical elements: **Cd P O C H**

Select **"Use Superflip"**;

Check **"Repeat Superflip: Number of runs"** leave **10**

Leave other settings default; press **"Run solution."**

[On the screen: first, you will see the window of Superflip and, after the calculation reaches convergence, it is replaced the listing of Superflip results]

Press **CLOSE** to leave the listing (Step 1)

Press **Accept last solution**

#### Step 1

```
=====
Space group derived from the symmetry operations:
R3m
R3m symbol: R3m
Formula: CdP2O6
Space group: R3m(198)14720 (0,0,0)
Symmetry operations:
  1 1 1
  2 1/2 1/2 1/2
  3 1/3 2/3 1/3
  4 1/4 3/4 1/4
  5 1/5 4/5 1/5
  6 1/6 5/6 1/6
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```

OK; YES  
Run Refine;

#### Notes

$R$  factors [217=203+14/9]

$GoF(obs) \approx 9.64$ ;  $R(obs) \approx 8.85$ ;  $wR(obs) \approx 12.89$ ;  $R(all) \approx 9.26$ ;  $wR(all) \approx 12.94$

Start **Edit atoms**;

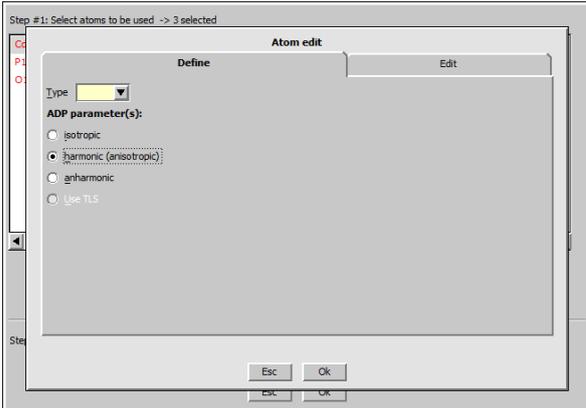
Press “**Select all**” → “**Action**” → “**Edit/Define atoms.**”

Change the ADP parameter(s) from isotropic to **harmonic** (anisotropic); (Step 2)

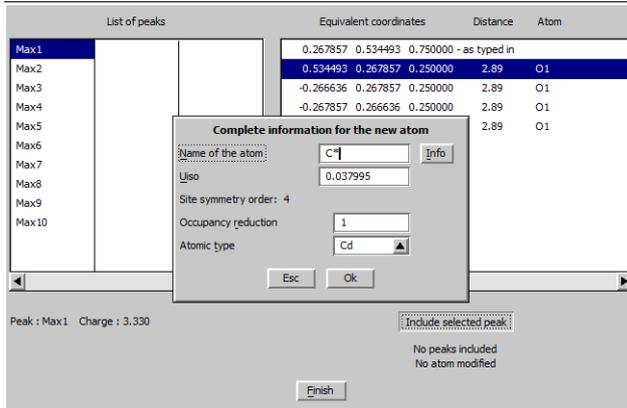
OK; OK; YES

Run Refine;

**Step 2**



**Step 3**



Peak	Equivalent coordinates	Distance	Atom
Max1	0.267857 0.534493 0.750000 - as typed in		
Max2	0.534493 0.267857 0.250000	2.89	O1
Max3	-0.266636 0.267857 0.250000	2.89	O1
Max4	-0.267857 0.266636 0.250000	2.89	O1
Max5			
Max6			
Max7			
Max8			
Max9			
Max10		2.89	O1

#### Notes

$R$  factors [217=203+14/16]

$GoF(obs) \approx 6.13$ ;  $R(obs) \approx 5.14$   $wR(obs) \approx 8.05$ ;  $R(all) \approx 5.51$ ;  $wR(all) \approx 8.10$

**Warning** due to Negative ADP of some atoms

*We have a negative ADP on some atoms. Due to the initial high value of  $R_{int} \approx 13\%$ , we should try to determine if the presence of twin might be the cause of this negative value.*

File → structure → Save as (Create backup copy) **Cd-HPO\_hexa**

**NO** (you don't want to continue with the new structure)

### III. Structure solution and Refinement model 2

#### 1. Change space group

#### Notes

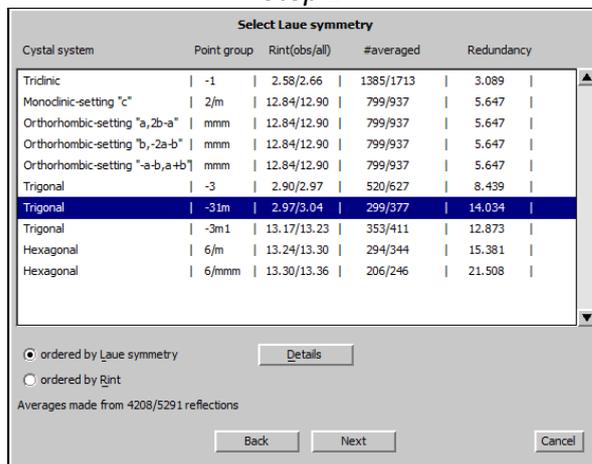
There are two options for lowering the symmetry, both of them being able to generate corresponding twinning matrices:

- Transformation of the current structure model to subgroup
- New symmetry check and structure solution

Here, we will use the second approach as solution of the hexagonal structure model was effortless and might be biased by using improper symmetry.

File → reflection file → make space group test; Yes  
 [On the screen: "Tolerances for crystal system recognition"]  
 Check "Introduce twin laws in case of subgroups"; **NEXT**; **OK**  
 [On the screen: Select Laue symmetry]  
 Select **Trigonal -31m** Laue symmetry; **NEXT** (Step 1)

### Step 1



Select centering **P** unit cell; **NEXT**  
 [On the screen: Select space group]  
 Select **P-31c**; **NEXT**  
 Tick "Accept twinning matrices induced by the space group test", leave all other settings unchanged; **FINISH**; **YES**

## 2. Creating refinement reflection file

**NEXT** to confirm threshold 3sigma; **OK**; **OK**

Notes																																					
<p><b>Import statistics - obs/all</b></p> <p>4208/5291 reflections read from input file            4203/4822 reflections written to output file            5/469 reflections rejected as systematically extinct.</p> <p style="text-align: center;"><input type="button" value="Ok"/></p>	<p><b>Summary of systematic extinctions</b></p> <p>n(all) : 469, n(obs) : 5            Average(I<sub>hkl</sub>/I<sub>001</sub>) : 0.36</p> <p>List of the strongest absent reflections:</p> <table border="1"> <thead> <tr> <th>h</th> <th>k</th> <th>l</th> <th>I</th> <th>sig(I)</th> <th>I/sig(I)</th> </tr> </thead> <tbody> <tr> <td>2</td> <td>-1</td> <td>7</td> <td>2157.3</td> <td>457.2</td> <td>4.7</td> </tr> <tr> <td>2</td> <td>-1</td> <td>5</td> <td>1392.9</td> <td>348.7</td> <td>4.0</td> </tr> <tr> <td>-1</td> <td>-1</td> <td>7</td> <td>1169.8</td> <td>339.2</td> <td>3.4</td> </tr> <tr> <td>-2</td> <td>1</td> <td>-5</td> <td>1154.4</td> <td>349.8</td> <td>3.3</td> </tr> <tr> <td>2</td> <td>-4</td> <td>5</td> <td>711.8</td> <td>232.2</td> <td>3.1</td> </tr> </tbody> </table> <p style="text-align: center;"><input type="button" value="Ok"/></p>	h	k	l	I	sig(I)	I/sig(I)	2	-1	7	2157.3	457.2	4.7	2	-1	5	1392.9	348.7	4.0	-1	-1	7	1169.8	339.2	3.4	-2	1	-5	1154.4	349.8	3.3	2	-4	5	711.8	232.2	3.1
h	k	l	I	sig(I)	I/sig(I)																																
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2	-1	5	1392.9	348.7	4.0																																
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-2	1	-5	1154.4	349.8	3.3																																
2	-4	5	711.8	232.2	3.1																																
<p>We obtained the same values and errors as for the hexagonal unit cell</p>																																					

[On the screen: settings for merging of reflections]  
**NEXT**  
 The program reports Rint 2.97% for 297 observed reflections merged from 327 reflections.  
**OK**;  
 Select "Accept the new data block and calculate coverage"; **FINISH**; **OK**

Notes
<p>The twin matrix was automatically added corresponding to the twinning by merohedry, with the twin law:</p>

$$\begin{pmatrix} 1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

### 3. Structure solutions wizard

#### Notes

*In case the Structure solution tab does not open automatically, you can open it manually from Run – Structure solution.*

*[On the screen: Structure solution]*

In “Formula” textbox type list of chemical elements: **Cd P O C H**

Select “**Use Superflip**”;

Check “**Repeat Superflip: Number of runs**” leave **10**

Leave other settings default; press “**Run solution.**”

*[On the screen: the window of Superflip replaced after reaching the convergence with the listing of Superflip]*

Press **CLOSE** to leave the listing

Press **Accept last solution**

### 4. Refinement

#### Notes

*We obtain similar solution as previously*

Start **Edit atoms**;

Select **C1** → “Action” → “**Edit/Define atoms**” → Type **O**; OK

Press “**Select all**” → Action → **Rename selected atoms to “atom\_type” + number**

Press “**Select all**” → “Action” → “**Edit/Define atoms.**”

Change the ADP parameter(s) from isotropic to **harmonic** (anisotropic);

**OK; OK; YES**

Run **Refine**;

#### Notes

*R factors [327=297+30/20]*

*GoF(obs) ≈ 13.10; R(obs) ≈ 11.44; wR(obs) ≈ 18.53; R(all) ≈ 12.47; wR(all) ≈ 18.58*

*There are still warnings about negative ADP of some atoms*

Select **Parameters** → Twin fractions and check **twvol2**

Run **Refine**

#### Notes

*R factors [327=297+30/20]*

*GoF(obs) ≈ 2.82; R(obs) ≈ 2.84; wR(obs) ≈ 3.99; R(all) ≈ 3.43; wR(all) ≈ 4.01*

*Using Parameters → Twin fraction, you can see the refined twvol2 is nearly zero and the structure corresponds to trigonal structure without twinning. No atoms has negative ADP!*

Start **EditM50**

**Uncheck** Twinning ; **OK**

Yes “**Re-create refinement reflection file**” and follow the ensuing procedure.

**Run Refine**

#### Notes

*R factors [327=297+30/20]*

*GoF(obs)  $\approx$  2.83; R(obs)  $\approx$  2.83; wR(obs)  $\approx$  4.01; R(all)  $\approx$  3.40; wR(all)  $\approx$  4.11*

*No atom has negative ADP but C1 exhibits disorder manifested by a huge ADP ellipsoid.*

*This corresponds to a disordered methanol and will be further analyzed.*

File → structure → Save as (Create backup copy) **Cd-HPO\_trigo1**

**NO** (you don't want to continue with the new structure)

### 5. Solvent modelling

#### Notes

*C1 exhibits a large ADP but even from difference Fourier map it is not clear if this is a split position. However, modelling this electron density with anharmonic ADP will clearly show the particular atomic positions.*

Start **Edit atoms**;

Select **C1** → “Action” → “**Edit/Define atoms**”

Change the ADP parameter(s) from harmonic to **anharmonic**.

*We will make different tests with different numbers of anharmonic terms*

**OK; OK; YES**

**Run Refine**;

#### Notes

*With the 3<sup>rd</sup> order anharmonic tensors*

*R factors [327=297+30/24]*

*GoF(obs)  $\approx$  2.76; R(obs)  $\approx$  2.79; wR(obs)  $\approx$  3.88; R(all)  $\approx$  3.40; wR(all)  $\approx$  3.99*

*With the 4<sup>th</sup> order anharmonics tensors*

*R factors [327=297+30/33]*

*GoF(obs)  $\approx$  2.35; R(obs)  $\approx$  2.15; wR(obs)  $\approx$  3.25; R(all)  $\approx$  2.67; wR(all)  $\approx$  3.36*

*With 4 anharmonics we arrived at the maximum number of parameters that we can refine. To refine 1 parameter we generally need 10 independent reflections. Here we need to refine 33 parameters and we have 327 independent reflections. If we increase once more the number of anharmonics, we would need to refine 42 parameters in total.*

Start **Contour**;

Press **New plot** and draw **j.p.d.f** map; **OK**(Step 2)

**Refresh** and select **C1** and **check** Calculate deformation **j.p.d.f** (joint probability density function); **Next**; (Step 3)



In Page Define, change ADP parameter(s) to **harmonic**  
OK; OK; Yes  
Run **Refine**  
Start **Edit atoms**  
Select **C1** → Action → Select **C1** → Action → **Split atomic position**  
Press Apply; OK  
Run Refine

Notes

*R factors [327=297+30/22]*

*GoF(obs) ≈ 2.58; R(obs) ≈ 2.33; wR(obs) ≈ 3.64; R(all) ≈ 2.87; wR(all) ≈ 3.76*

Skip warnings, OK

Notes

*The special position of C1 and C1' atom are at the origin of this warning*

Start **Edit atoms**  
Select **C1/C1'** → Action → **Edit/Define atoms**  
In page Edit check **ai** refinement  
OK; OK; YES  
Run **Refine** (Here use only 10 cycles)

Notes

*R factors [327=297+30/23]*

*GoF(obs) ≈ 2.69; R(obs) ≈ 2.34; wR(obs) ≈ 3.79; R(all) ≈ 2.88; wR(all) ≈ 3.91*

*Due to the splitting, C1 leaves the special position and therefore 12 instead of six atoms is generated. After occupation refinement, occupancy of one of the atoms (C1 or C1') decreases to zero, giving rise to the expected six atoms like indicated in the previous VESTA plot j.p.d.f.*

Start **Edit atoms**  
Select **C1** → Action → **Edit/Define atoms**  
In page Edit uncheck **ai** refinement and change the value to 0.5  
Select **C1'** → Action → Delete selected atoms → Yes to all  
OK; Yes  
Run Refine

Notes

*R factors [327=297+30/19]*

*GoF(obs) ≈ 2.59; R(obs) ≈ 2.35; wR(obs) ≈ 3.67; R(all) ≈ 2.89; wR(all) ≈ 3.79*

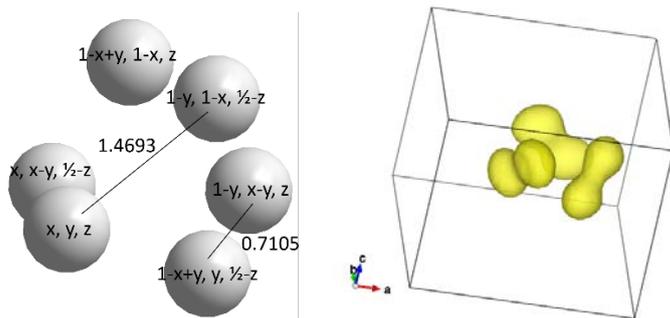
Start **Edit atoms**;  
Select **C1** → "Action" → **"Edit/Define atoms"**  
Change the ADP parameter(s) from isotropic to **harmonic**.  
**OK; OK; Yes**  
Run **Refine**

Notes

*R factors [327=297+30/24]*

*GoF(obs) ≈ 2.57; R(obs) ≈ 2.32; wR(obs) ≈ 3.60; R(all) ≈ 2.88; wR(all) ≈ 3.72*

At the end of this step, C1 is split with occupation 0.5 like this following picture (Diamond) which is similar to the previous Vesta representation.



The distance between C1 (x,y,z) and C1(1-y, 1-x, 1/2-z) correspond to the distance between C-C or C-O.

## 6. Add Hydrogen

Start **Edit atoms**;

Select **C1** → Action → Adding of hydrogen atoms

**Uncheck** “try automatic run for carbon atoms”; **OK**

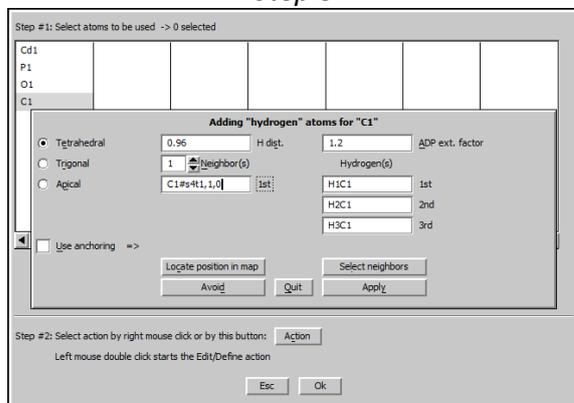
Select **Tetrahedral** configuration with **1** Neighbour(s)

Click into the box “1<sup>st</sup>”, Press select neighbours and chose **C1** with distance **1.469 Å**; **OK**  
(Step 8)

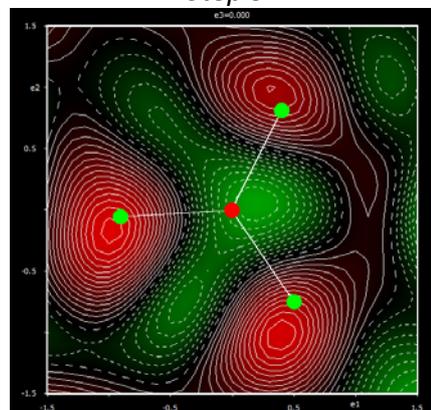
Press **Locate position in map**;

Press **Optimal** and **Apply**(Step 9) we can observe the presence of hydrogen

Step 8



Step 9



Press **Apply** ; **OK**; **Yes**

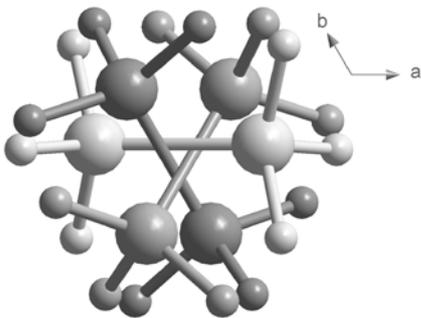
Run **Refine**

### Notes

$R$  factors [327=297+30/24]

$GoF(obs) \approx 3.28$ ;  $R(obs) \approx 2.66$ ;  $wR(obs) \approx 4.61$ ;  $R(all) \approx 3.23$ ;  $wR(all) \approx 4.71$

You will obtain this following configuration:



*Adding hydrogen increased the value of R-factor. This model corresponds to an ethane molecule but we know that the solvent is a methanol molecule. However, it is impossible to make difference between C and O atoms because they are symmetry equivalent. In order to stay at the trigonal symmetry, we have to accept that each separated molecule at the figure consists of two methanol molecules with CH<sub>3</sub> in one and opposite side. This is possible but first we should test if this is reality or just result of improper trigonal symmetry. In the next step, we will transform the structure model to a monoclinic subgroup to see what is happening with the disordered methanol.*

File → structure → Save as (Create backup copy) **Cd-HPO\_trigo2**

**NO** (you don't want to continue with the new structure)

#### **IV. Refinement model 3**

##### **1. Group subgroup transformation**

Start **Edit atoms**;

Select **All H** → Action → Delete selected atoms → **Yes to all**

**OK; Yes**

Run **Refine**

##### **Notes**

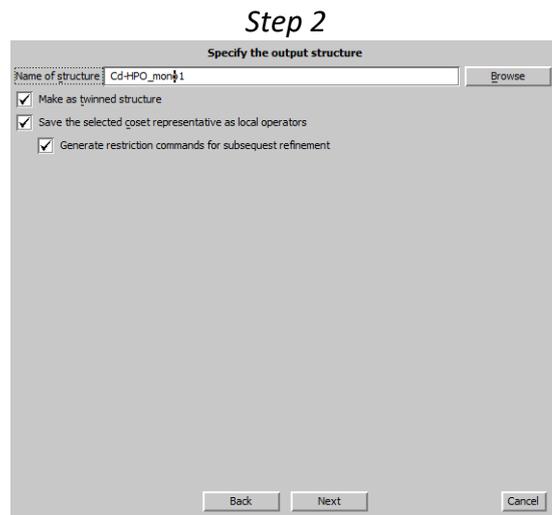
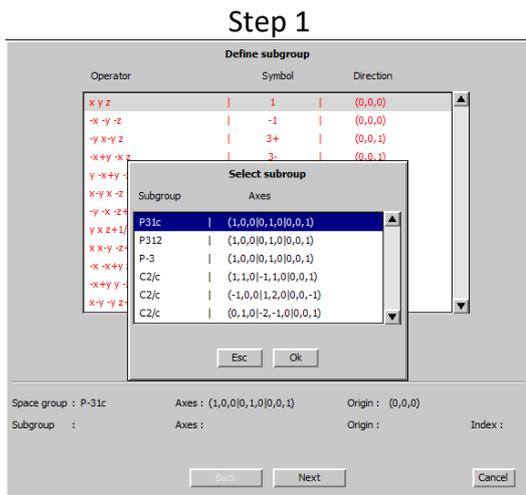
*R factors [327=297+30/24]*

*GoF(obs) ≈ 2.57; R(obs) ≈ 2.33; wR(obs) ≈ 3.60; R(all) ≈ 2.88; wR(all) ≈ 3.72*

*We deleted the hydrogen atoms to get a simpler initial disordered model .*

Select **Tools** → Transformations → Go to subgroup structure

Press **Select non-isomorphic subgroup** (Step 1)



Select the first monoclinic subgroup (all the three are equivalent) ; OK  
 Next; Next; Next; Next  
 Check “save the selected coset representative as local operators”

#### Notes

*This option is very important because the nearly trigonal structure could not be refined for technical reasons. The omitted but in fact existing for most atoms trigonal symmetry would cause oscillating refinement and almost singular normal matrix. Thus, in the formally monoclinic structure positions and ADP of all atoms will still be connected with the trigonal symmetry applied as local symmetry operators.*

Write the Name of structure : **Cd-HPO\_mono1** (Step 2)

**Next; Finish;**

**Next; OK; OK;**

**Next; OK**

*The program reports Rint 2.58% for 1385 observed reflections merged from 1706 reflections.*

**Finish; Yes “I want to apply this transformation”**

**Yes “ I want to continue with the new structure”**

**Refine**

#### Notes

*R factors [1706=1385+321/24]*

*GoF(obs) ≈ 1.73; R(obs) ≈ 2.58; wR(obs) ≈ 3.38; R(all) ≈ 3.64; wR(all) ≈ 3.70*

*The applied local symmetry operations are listed in Refinement options → Various → Restrictions. They keep coordinates and ADP in the former trigonal positions but allow to distinguish carbon and oxygen of methanol because occupancy is not restricted.*

**Start Edit atoms;**

**Select C1\_1/C1\_2/C1\_3 → Action → Edit/Define atoms**

**In page Edit check ai refinement**

OK;OK:YES

Run **Refine** (skip warning if necessary)

Notes

$R$  factors [1706=1385+321/27]

$GoF(obs) \approx 1.55$ ;  $R(obs) \approx 2.38$ ;  $wR(obs) \approx 3.03$ ;  $R(all) \approx 3.30$ ;  $wR(all) \approx 3.21$

Start **Edit atoms**;

Check resulting occupancy (“ai”) of C1\_1, C1\_2 and C1\_3. The  $ai > 0.5$  means the atom is oxygen;  $ai \sim 0$  means the atom should be deleted.

**Change chemical type** of the carbon with  $ai > 0.5$  to **oxygen**; change its **occupancy to 0.5**; **disable refinement of ai**

**Delete the carbon** with occupancy close to zero

Change the **occupancy of the remaining carbon to 0.5**; **disable refinement of ai**

Select all → Action → **Rename selected atoms to “atom\_type + number**

**Ok**; Yes

Run **Refine**

Notes

$R$  factors [1706=1385+321/24]

$GoF(obs) \approx 1.68$ ;  $R(obs) \approx 2.42$ ;  $wR(obs) \approx 3.27$ ;  $R(all) \approx 3.39$ ;  $wR(all) \approx 3.49$

## 2. Add hydrogen atoms

Start **Edit atoms**;

Select **C1** → Action → Adding of hydrogen atoms

**Uncheck** “try automatic run for carbon atoms”; **OK**

Select **Tetrahedral** configuration with **1** Neighbour(s)

Press select neighbours and chose **O4** with distance **1.425 Å**; **OK**

Press **Locate position in map**;

Press **Optimal** and **Apply**; **Apply**

Run **Refine**

Notes

$R$  factors [1706=1385+321/24]

$GoF(obs) \approx 1.54$ ;  $R(obs) \approx 2.35$ ;  $wR(obs) \approx 3.00$ ;  $R(all) \approx 3.34$ ;  $wR(all) \approx 3.29$

Select **O4** → Action → Adding of hydrogen atoms

Select **Apical** configuration with **1** Neighbour(s)

Press select neighbours **C1** with distance **1.425**; **OK**

**Apply**

Select **P1** → Action → Adding of hydrogen atoms

Select **Tetrahedral** configuration with **3** Neighbour(s), distance to H **1.2 Å**

Press select neighbours and chose **O1,O2,O3** with distance **1.521 Å**; **OK**

**Apply**; **Ok**; **Yes**

Run **Refine**

Notes

$R$  factors [1706=1385+321/24]

$GoF(obs) \approx 1.57$ ;  $R(obs) \approx 2.33$ ;  $wR(obs) \approx 3.07$ ;  $R(all) \approx 3.33$ ;  $wR(all) \approx 3.35$

## Right Click on Refine

In page various select **Keep commands**

**Disable** “Keep hydro tetrahed” for P1 and “Keep hydro apical” for O4; **OK**

In page various select Distance restrains

“Fix to the specified” value **0.82** for **O4 H1o4** distance; **Add**

“Fix to the specified” value **1. 2** for **P1 H1p1** distance; **Add**

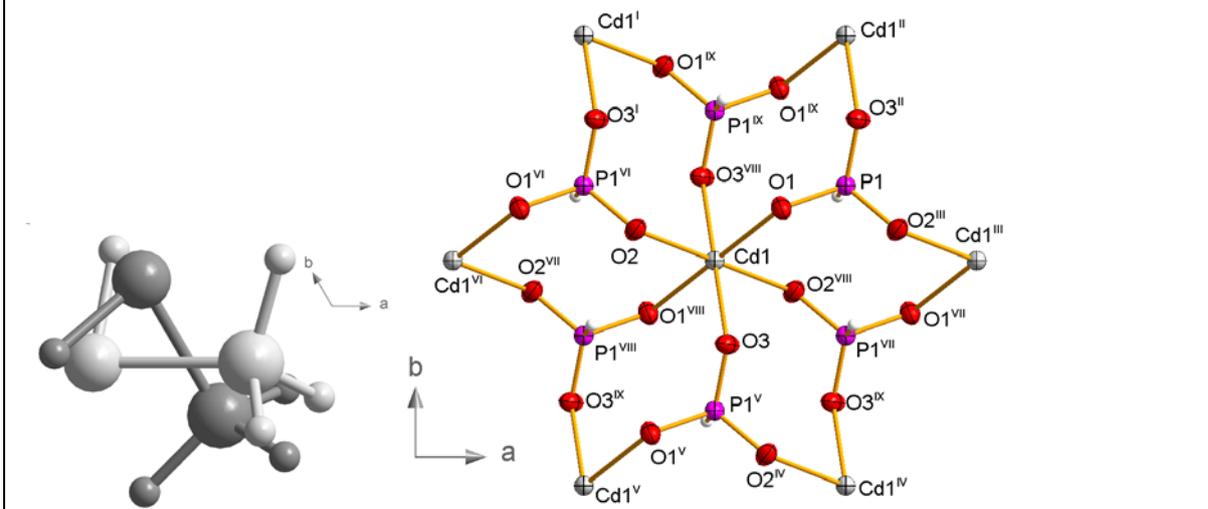
**OK;OK; Yes +start**

### Notes

*R factors [1706=1385+321/24]*

*GoF(obs)  $\approx$  1.52; R(obs)  $\approx$  2.25; wR(obs)  $\approx$  2.96; R(all)  $\approx$  3.24; wR(all)  $\approx$  3.22*

*The final structure is composed by two methanol molecules:*



## References

# Example 4.1: PtCu

Disordered structure.

Revised 26 September 2017

[Cu(CH<sub>3</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>)<sub>2</sub>] [Pt(CN)<sub>4</sub>]

Polyhedron 2011, 30, 269-278.

Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: PtCu.hkl, PtCu\_red.sum

Frame scaling, absorption correction: done with software of diffractometer

## 1. *Creating new jobname*

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click PtCu

## 2. *Import Wizard*

Select "Known diffractometer formats"; NEXT

Select "Oxford Diffraction-CCD"; NEXT

[On the screen: "Define basic input file"]

Use "input from sum file"; OK

[On the screen: "Your sum file consists of 6 appended data reduction runs"]

OK;

[On the screen: "Complete/correct experimental parameters"]

Leave all settings unchanged; NEXT

[On the screen: "Define the reference cell/split by twinning"]

Leave all settings unchanged; NEXT

For absorption correction select "None or done before importing"; NEXT

FINISH

## 3. *Data Repository*

The line in data repository window corresponds to one data set.

OK; YES to accept the data set

## 4. *Symmetry Wizard*

[On the screen: "Tolerances for crystal system recognition"]

Leave all settings default; NEXT

[On the screen: Select Laue symmetry]

Select Tetragonal Laue symmetry 4/m; NEXT

Select primitive unit cell; NEXT

[On the screen: Select space group]

Using the criteria described in the first example Select P42/m; NEXT

Select "Accept the space group transformed into the original cell"

**Clear** "Accept twinning matrices induced by the space group test"

The highest Laue symmetry consistent with the unit cell parameters is  $4/mmm$  while the selected Laue symmetry is lower –  $4/m$ . This opens possibility for twinning, but in this case twinning does not occur (as one would find during refinement of twin volume fractions).

FINISH

The original cell is used because the suggested transformation does not change the unit cell and the space group symbol

YES to create refinement reflection file M90

#### 5. Creating refinement reflection file

NEXT to confirm threshold  $3\sigma$

[On the screen: settings for merging of reflections]

Leave all settings default; NEXT

Accept the data block; FINISH

#### 6. Structure Solution Wizard

[On the screen: window of Structure solution]

In "Formula" textbox type chemical composition  $C_{10}H_{20}CuPtN_6$ , two formula units

Select "Use Superflip"

Check "Repeat Superflip", number of runs 10

Leave other settings default; "Run Solution"

[On the screen: listing of Superflip]

Superflip converges rapidly with  $R \sim 14\%$  and very good (i.e. low) fit for the symmetry elements of  $4_2/m$

The suggested centering vector  $(0,0,1/2)$  is in contradiction with found systematic absences, it cannot be used. It is a pseudosymmetry caused by positions of platinum (heavy atom).

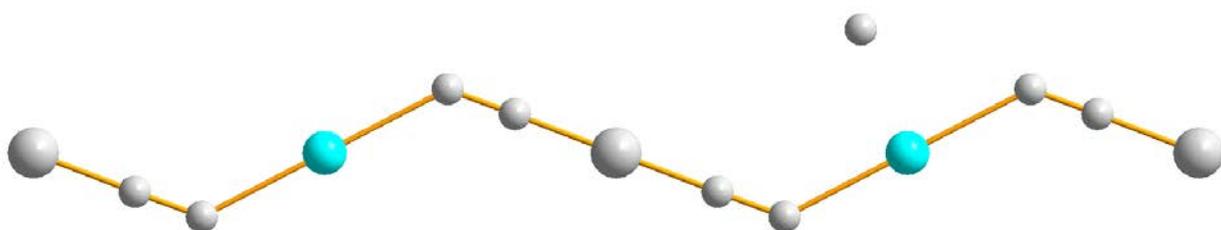
Close listing of Superflip

Press "Accept last solution" to leave the Structure solution wizard

#### 7. Completing the structure model

Plot the structure found by Superflip

There should be a chain  $Pt - C - N - Cu$  visible in the plot.



Open Refinement options, change number if refinement cycles to 100

Run Refine

Refinement converges with  $R$  value about 12%

Start "Edit atoms" and define harmonic ADP for Pt1 and Cu1

Delete rejected atoms (in case the button "Select rejected" is active)

Run Refine

Refinement converges with  $R$  value about 9%

Open Fourier options (right button on Fourier icon) and select "F(obs)-F(calc) - difference Fourier", OK, YES+Start to execute Fourier calculation

YES to start the procedure for including of the new atoms

The same tool could be started separately by “Parameters → Atoms → New”

[On the screen: Inserting/replacing of atoms]

For “Show distances up to” type 4 Å

OK

[On the screen: list of peaks]

List of peaks	Equivalent coordinates	Distance	Atom
Max1	0.104386 0.287890 0.000000 - as typed in		
Max2	0.104386 0.287890 0.000000	3.12	Pt1
Max3	-0.104386 -0.287890 0.000000	3.12	Pt1
Max4	0.104386 0.287890 0.000000	3.70	C2
Max5	0.712110 0.104386 0.500000	3.71	C3
Max6	-0.104386 -0.287890 0.000000	3.76	C2
Max7	-0.287890 0.104386 -0.500000	3.79	C1
Max8	-0.287890 0.104386 0.500000	3.79	C1
Max9	0.104386 0.287890 0.000000	3.79	C3
Max10	0.287890 -0.104386 0.500000	3.85	C3
	-0.287890 0.104386 -0.500000	3.94	C2
	-0.287890 0.104386 0.500000	3.94	C2

Peak : Max1 Charge : 2.830

In the left panel, Max1 is focused. Its integrated charge is displayed at the bottom. In the right panel, we can see distances of symmetry equivalent positions of Max1 to already existing atoms of the structure model, up to the previously defined limit 4Å. We can expect distances ~2 Å for Pt-C, ~1.5 Å for C-C, ~1 Å for C-N of cyano group and ~3 Å for Pt-N. Therefore, the maximum Max1 is probably nitrogen.

In the left panel, focus Max1 (or other peak if in your case Max1 has no good distance)

In the right panel, focus its reasonable position having good distance to some existing atom

Press “Include selected peak”

[On the screen: Complete information for the new atom]

For “Name of atom” type C\* (even for nitrogen); TAB; OK

We will intentionally add all atoms like carbon, it will help later on to analyse disorder.

The chemical type was assigned to carbon, the name will be C+sequence number.

Repeat the procedure for other maxima. Skip distances below 1 Å as well as maxima with too small charge or strange distances. At this point, all atoms should be added as carbon, we will distinguish between C and N later on.

FINISH; YES to include the new atoms

Finally the structure model should contain 9 symmetry-independent atoms. In case some improper maxima have been added, they will be probably discarded during refinement based on large isotropic ADP.

Run Refine

Refinement converges with R value about 4%

Start “Edit atoms” and check if the button “Select rejected” is enabled.

If “Select rejected” is enabled some atoms have zero occupancy. It was set by Refine because their Uiso was refined above the limit defined in the Refinement options (default limit is 0.2).

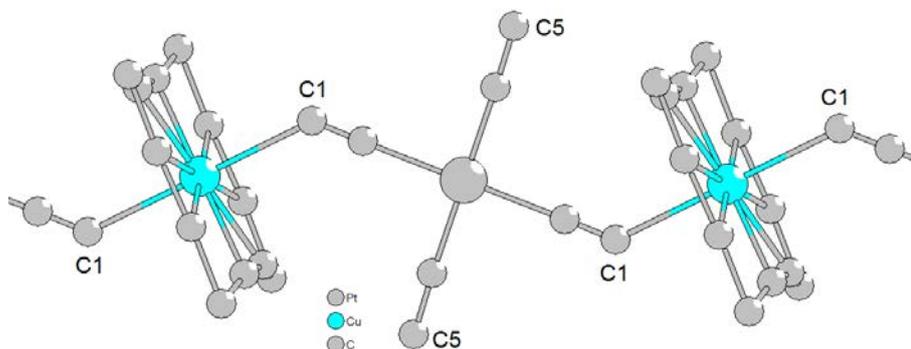
Delete rejected atoms.

Check with "Select all" that the structure contains 9 atoms

If the structure model does not contain all 9 atoms, repeat calculation of difference Fourier

Leave "Edit atoms"

Plot structure in Diamond



Note names of atoms (C1, C5 in our example) which should be nitrogen of cyano groups

Leave Diamond and change chemical type and names of C1, C5

Run Refine

### 8. Solution of disorder

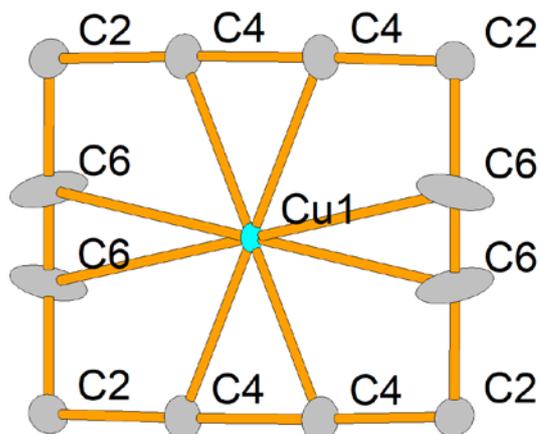
Open "Edit atoms" and define harmonic ADP for all atoms

Double-click is necessary in the locked yellow-indicated options

Run Refine

Refinement converges with R value ~3% for 60 parameters

Plot the disordered part of the structure: press ; click on Pt; Ctrl-M selects the Pt "molecule"; Delete deletes it – remaining atoms are coordinated to Cu



Using "Action → Rename selected atoms manually", rename atoms according to this plot

This is not necessary but will help to follow easily the cookbook

Start "File → Structure → Save As" and create a backup copy, for instance PtCu\_completed

Open "Edit atoms", select C6

"Action" → "Split atomic position"

[On the screen: split atomic position window]

Leave all settings default; Apply

[On the screen: list of atoms in "Edit atoms"]

Select C6, go to "Edit/define atoms", switch to the page "Edit", activate refinement of occupancy (the parameter ai)

Close "Edit atoms", YES to save changes

The next steps show automatically created restriction for C6, C6'

Open Refinement options, go to the page "Various", press "Restrictions"

Focus the line "restric C6 2 C6'

Press Load

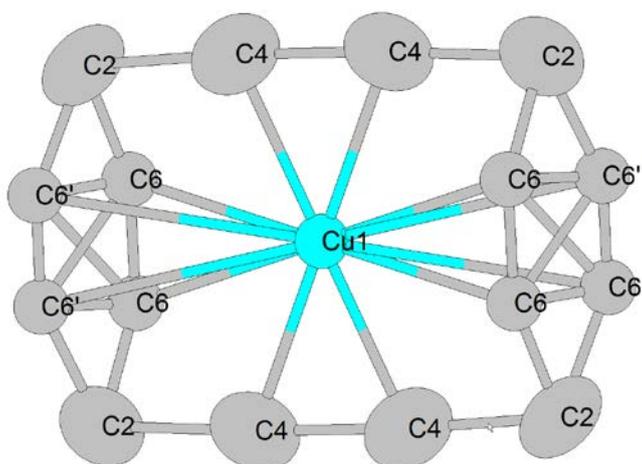
In the lower part of the window there are listed properties of the restriction. The atom C6 was split to two positions, C6 and C6'. Both atoms will have the same ADP and their occupancy will be complementary.

Leave Refinement options

Run Refine

Refinement converges with  $R \sim 2\%$  for 59 parameters

Plot the same part of the structure



Open "Edit atoms"

Using "Action → Rename selected atoms manually", rename atoms according to this plot

This is not necessary but will help to follow easily the cookbook

Enable refinement of occupancy for C2 and C4

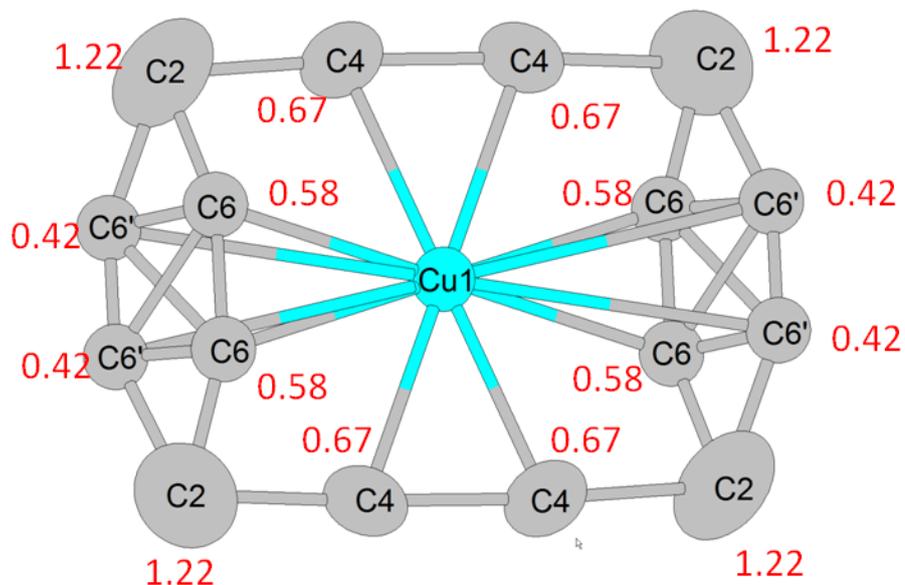
Run Refine

Refinement converges with  $R = 1.8\%$  for 61 parameters

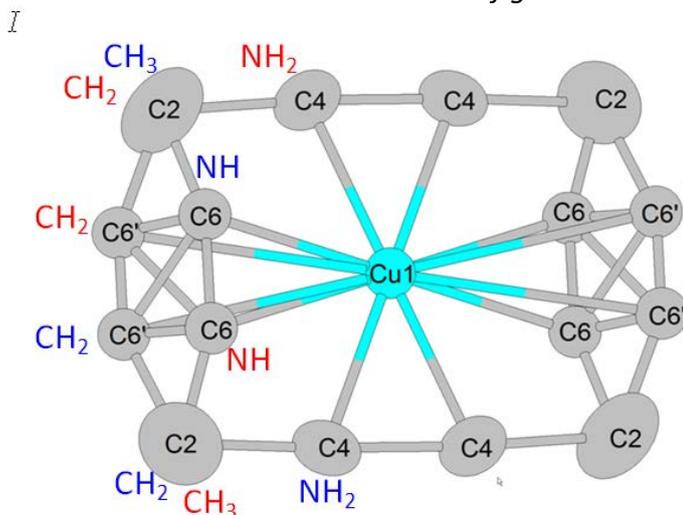
Note refined occupancies

Plot the same part of the structure and compare occupancies of carbons

(Diamond shows occupancies when hovering the mouse on the atom)



We are looking for two symmetry-related half-occupied methyl-ethylenediamine chains. Atoms with occupancy above 0.5 will be half-occupied atoms of nitrogen. In positions with occupancy above 1 atoms of two disordered chains coincide. Occupancy of C2 and C4 positions also reflects the missing hydrogen atoms while occupancy C6, C6' keeps the sum 1.0. Based on these considerations, we can speculate that the methyl-ethylenediamine chains will be oriented like in the next figure:



Open "Edit atoms" and change chemical type of C4 and C6 to nitrogen. Using "Action → Rename selected atoms manually", rename C4 to N4 and C6 to N6 and C6' to C6.

The atom names in the restrictions (page Various of the refinement commands) are renamed automatically

Run Refine

Open "Edit atoms"

Change occupancy of C2 to 1

Split the position of C2 (using the same procedure like previously for C6)

Enable refinement of occupancy for C2

The reason for changing the occupancy to 1 is that the generated restriction will keep the sum of actual occupancies.

## Run Refine

A slight increase of R value is due to change of ADP to isotropic during splitting.

Open "Edit atoms" and change ADP of C6 and N6 from isotropic to harmonic

Open Refinement options, go to the page "Various", press "Restrictions"

Load the restriction C6-N6 and uncheck "ADP parameters"; press "Rewrite"

The atoms C6 and N6 are so far from each other that their ADP can be refined independently

OK; OK; YES+Start to save changes and run refinement

Refinement converges with R=1.7% for 70 parameters

Plot the structure

Atom N4 represents through its symmetry equivalent positions the terminal nitrogen of both methyl-ethylenediamine groups. From this follows that the chains are symmetry-equivalent and must have the same occupation 0.5

Open "Edit atoms" and select all atoms of both methyl-ethylenediamine groups (N4,C2,C2',C6,N6 in our example)

Rewrite their occupancy to 0.5 and disable its refinement

Double-click will be necessary for the locked yellow-indicated fields

Run Refine

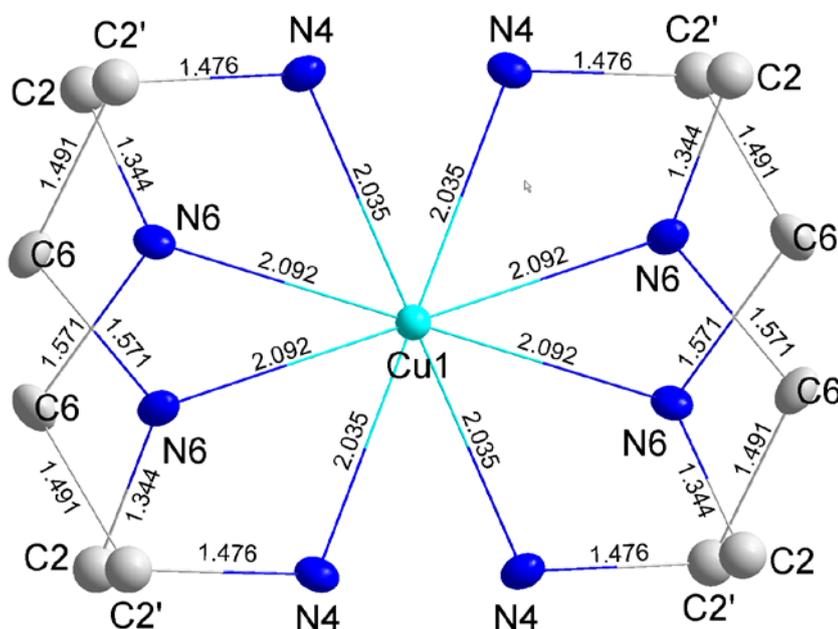
Refinement converges with R=1.7% for 67 parameters

Create backup copy, for instance PtCu\_beforeH

Plot the result

## 9. Adding hydrogen atoms

For adding hydrogen atoms the automatic procedure cannot be used because of the disorder. In the following plot, we can find how many hydrogen atoms we need for carbons and nitrogens. Warning: In your structure model, the distances may slightly differ because of missing hydrogen atoms. It may also happen that C2 and C2' are swapped (in such case it is better to rename them).



C2 belongs to methyl

C2' and C6 belong to CH<sub>2</sub>

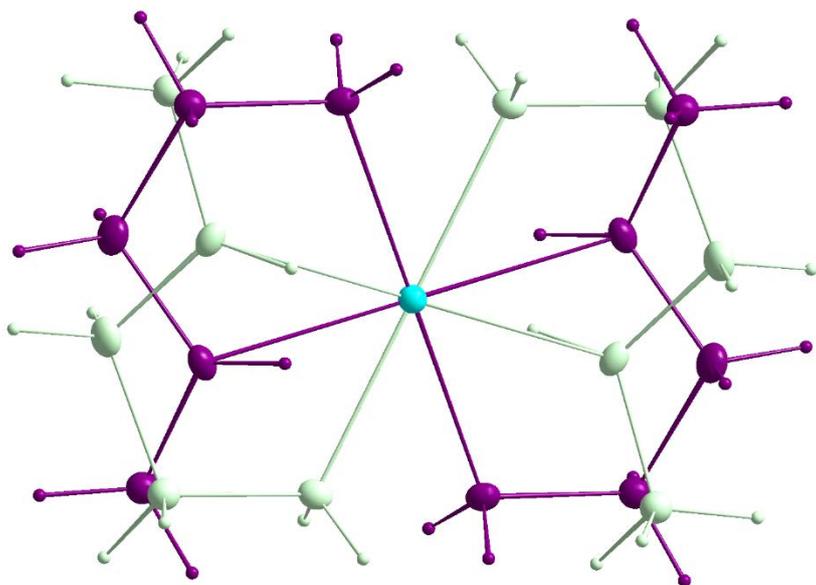
N4 belongs to NH<sub>2</sub>

N6 belongs to NH

Open "Edit atoms"  
 Select C2, C2', C6, N4 and N6  
 Start "Action → Adding of hydrogen atoms"  
 Clear "Try automatic run"; OK  
*[On the screen: Adding hydrogen atoms for C2]*  
*C2 belongs to methyl, therefore it has one neighbor and three hydrogen atoms*  
 Select "Tetrahedral"  
 Change number of neighbors to 1  
 Click in the textbox for the neighbor: this activates the button "Select neighbors" in the lower right corner  
 Press "Select neighbors"  
 Select N6; OK  
 In the textboxes for hydrogens type H1C2, H2C2 and H3C2  
 Press "Apply → Go to next"  
*[On the screen: Adding hydrogen atoms for C2']*  
*C2' belongs to CH2, therefore it has two neighbors and two hydrogen atoms*  
 Select "Tetrahedral"  
 Change number of neighbors to 2  
 Click in the textbox of the first neighbor; button "Select neighbors" will be activated  
 Press "Select neighbors"  
 Select N4 and C6; OK  
 In the textboxes for hydrogens type H1C2' and H2C2'  
 Press "Apply → Go to next"  
*Similarly, continue for C6. For C6 two atoms N6 will be shown as neighbors but the one with too short distance belongs to the second chain*  
*Similarly, continue for N4 belonging to NH<sub>2</sub>. Here one of the neighbors will be copper.*  
*Similarly, continue for N6 belonging to NH. Geometry for N6 is trigonal, not tetrahedral.*  
 Leave "Edit atoms"  
 Check in Diamond geometry of hydrogens (needs manually deleting of unwanted distances using Table of created bonds)  
 Run Refine  
*Refinement converges with R value 1.6% for 67 parameters*

*At this structure model, hydrogen atoms attached to nitrogen are strictly kept in idealized geometry. This is correct for carbon but not for nitrogen. In the next step, we will redefine constraints (keep commands) to restraints.*

Start refinement commands; select the page Various; open "Keep commands"  
 Disable the command "keep hydro tetrahed N4"  
 Disable the command "keep hydro triang N6"  
*The commands "keep ADP riding N4" and "keep ADP riding N6" will be retained*  
 OK; open "distance restraints"  
 Select "Fix to the specified value" and for the "Value" type 0.87  
 In the textbox "Atoms", type: N4 H1N4; N4 H2N4; N6 H1N6  
 Press "Add"; OK; OK; "YES+START"  
*In case of bad convergence, change the damping factor to 0.5.*  
*Refinement converges with R value ~1.5% for 76 parameters*



*This plot in Diamond requires a lot of manual work*



# Example 4.2: NaNiFe

Revised: 07 March 2018

Data	Topic	Level
X-ray single crystal data	Structure with mixed sites.	Intermediate

## Tasks

---

Solving simple structure with mixed sites

- Split atoms

## Initial data

---

### Data

Single crystal data measured with Oxford Diffraction four-circle diffractometer

### Input files:

NaNiFe.hkl, NaNiFe.cif\_od.sum

### Additional information:

Frame scaling, absorption correction: done by the diffractometer software

Chemical Formula : NaNiFe

## Contents

---

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# Instructions

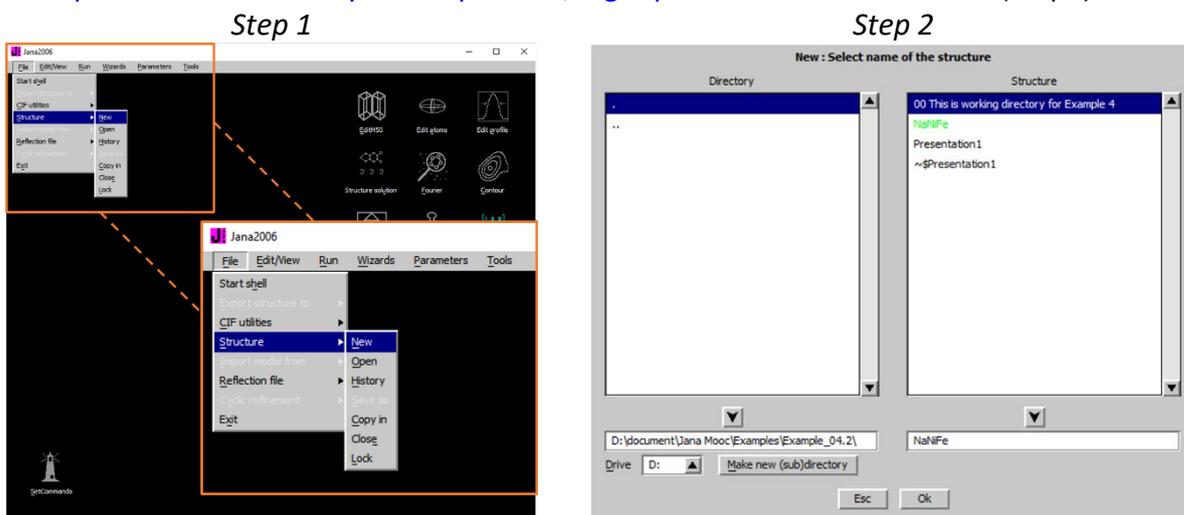
## I. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager (*Step1*)

Left pane: locate directory with input files; Right pane: double-click NaNiFe (*Step2*)

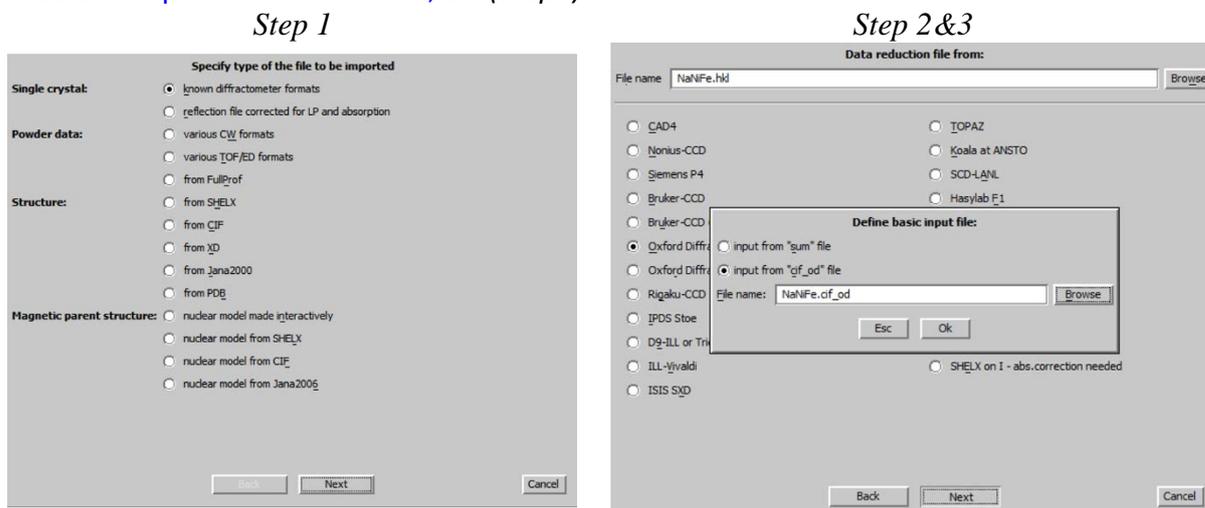


### 2. Import wizard

Select “Known diffractometer formats”; NEXT (*Step1*)

Select “Oxford Diffraction → CCD”; NEXT (*Step2*)

Select “Input from “sum” file”; OK (*Step3*)



Leave all settings unchanged; NEXT (*Step4*)

Leave all settings unchanged; NEXT; OK; (*Step5*)

The program reads 7999 reflections from hkl file

### Step 4

**Complete/correct experimental parameters**

Cell parameters: 11.6458 12.3536 6.4144 90.04 113.797 89.947

Number of input indices: 3

1st modulation vector:

2nd modulation vector:

3rd modulation vector:

X-ray tube

Wave length: 0.7107

Temperature: 299.1

**Polarization correction:**

Circular polarization

Perpendicular setting

Parallel setting

Guinier camera

Linearly polarized beam

**Monochromator parameters:**

Perfection: 0.5

Glancing angle: 6.081886

### Step 5

**Define the reference cell/split by twinning**

Cell parameters: 11.6458 12.3536 6.4144 90.040 113.797 89.947

Target dimension: 3

Twinning

Number of domains:

1st modulation vector:

2nd modulation vector:

3rd modulation vector:

Data related to domain #:

Max. satellite index:

Accuracy:

Multiply input F(hkl)/I(hkl) by: 1

**INFORMATION**

All 7999 input reflections were properly handled

For absorption correction select "None or done before importing"; NEXT (Step6)  
FINISH (Step7)

### Step 6

**Define parameters for absorption and scaling procedure**

None or done before importing

Correction for spherical sample  radius of the sphere [mm]

Gaussian integration method  integration grid

Empirical correction and/or frame scaling

Define absorption coefficient =>

Define formula =>

Number of formula units:

### Step 7

**INFORMATION**

The import wizard is complete. As a next step you can import another file or modify the previously imported ones.

## 3. Data Repository

OK; YES to accept the data set (Step1)  
Nest; (Step2)

### Step 1

**Data repository**

File	Type	Radiation
NalNFe.hkl	Single crystal	X-rays Mo K(alpha)

### Step 2

**INFORMATION**

Now the program will open a wizard for a space group test which can determine interactively the symmetry. In the case that later you will need to modify your first choice the same procedure can be run by the command 'File->Reflection file->Make space group test' without necessity to reimport the data.

## II. Symmetry and data merging

Go through the steps of the Symmetry wizard,

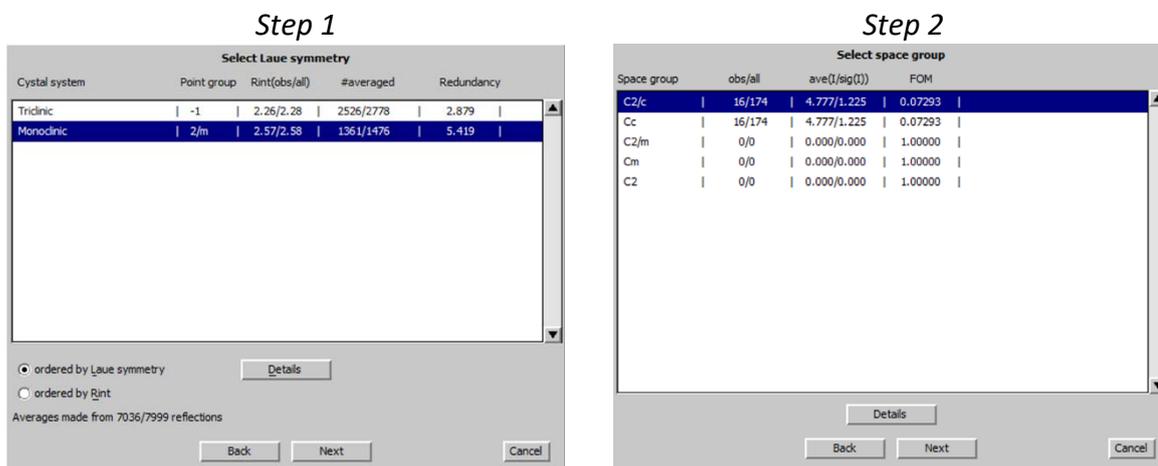
Select Laue symmetry 2/m, (Step1)

C centering and space group C2/c (Step2)

Accept the space group transformed into the original cell; FINISH

Go through the steps of the Merging wizard leaving all settings default

Rint will be 2.57%



## III. Structure solution

[On the screen: window of Structure solution]

In "Formula" textbox type chemical composition Na Ni Fe P O, 4 formula units

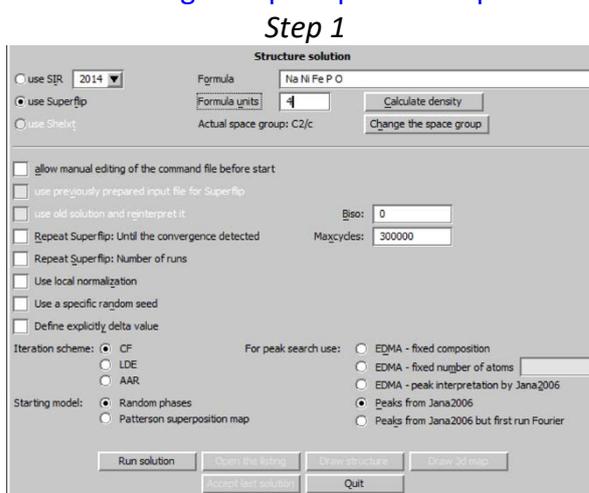
Select "Use Superflip"

Leave other settings default; OK (Step1)

[On the screen: listing of Superflip]

Superflip converges rapidly with R~18% and very good (i.e. low) agreement factors for the symmetry C2/m

Close listing of Superflip and accept the results



## IV. Refinements and model improvement

### 1. Checking the structure model

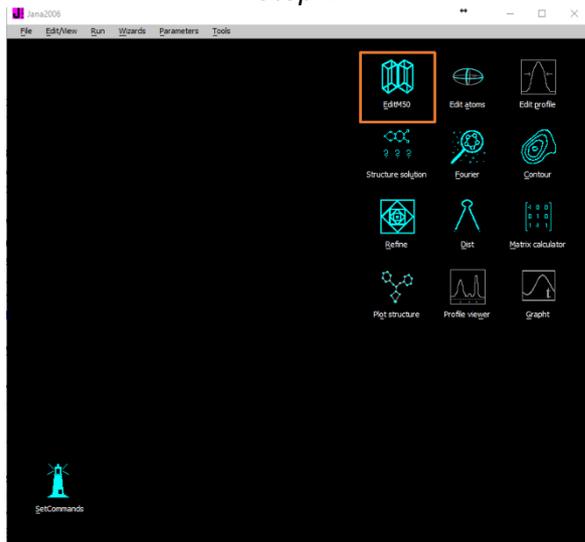
Start EditM50, page Composition, (Step1)  
press "Formula from M40" (Step2)

#### Notes

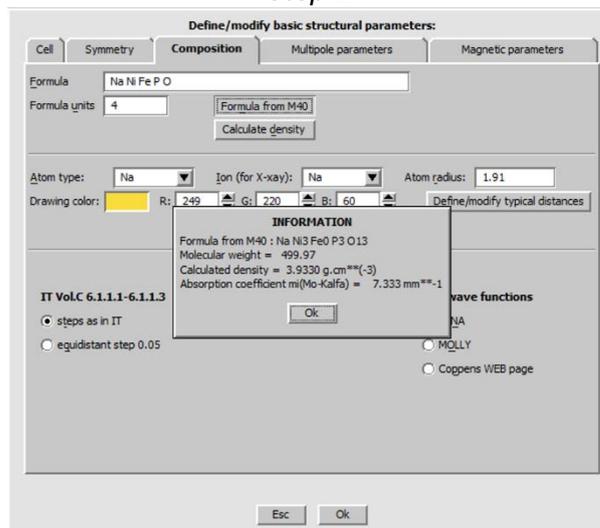
It shows the formula "Na Ni<sub>3</sub> Fe<sub>0</sub> P<sub>3</sub> O<sub>13</sub>" (for Z=4). However, the expected disphosphate unit is P<sub>2</sub>O<sub>12</sub> with negative charge -9. The positive charge NaNi<sub>3</sub> is only 7. Why do we have 13 oxygens? Where is Iron?

Leave to the basic window of Jana2006

#### Step 1



#### Step 2



Start refinement

Refinement converges with  $R \sim 5.7\%$ .

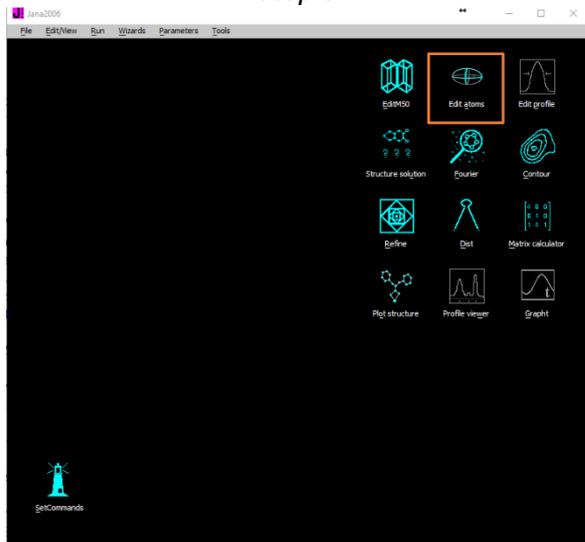
Using "Edit atoms" (Step3)

Select all → Action → Edit/Define atoms

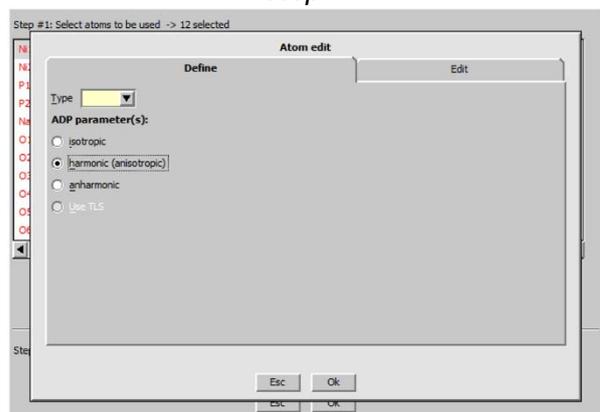
Change all ADP to harmonic and repeat the refinement (Step4)

Refinement converges with  $R \sim 4.4\%$

#### Step 3

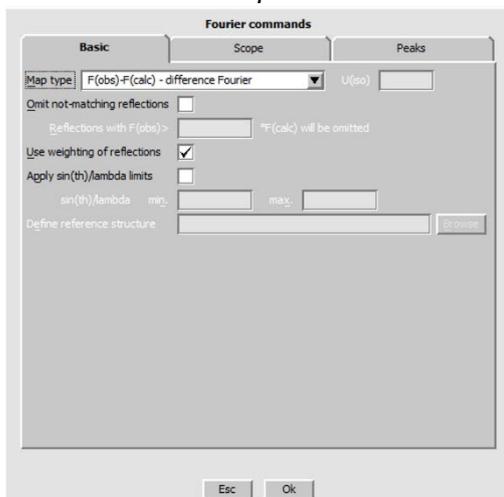


#### Step 4

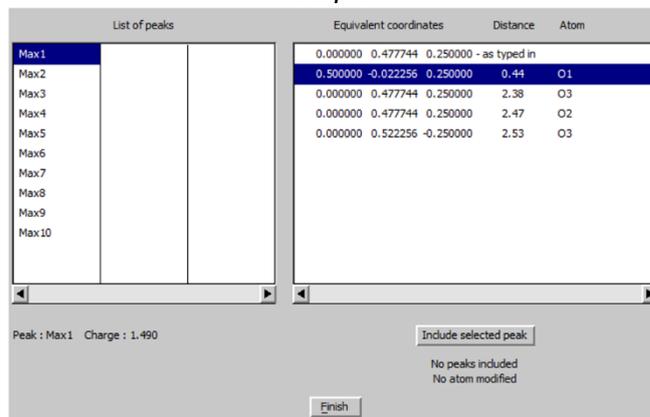


Open Fourier options and select Difference Fourier (Step5)  
 “Yes+Start” to save changes and start Fourier  
 YES to include new atoms (Step6)

Step 5



Step 6

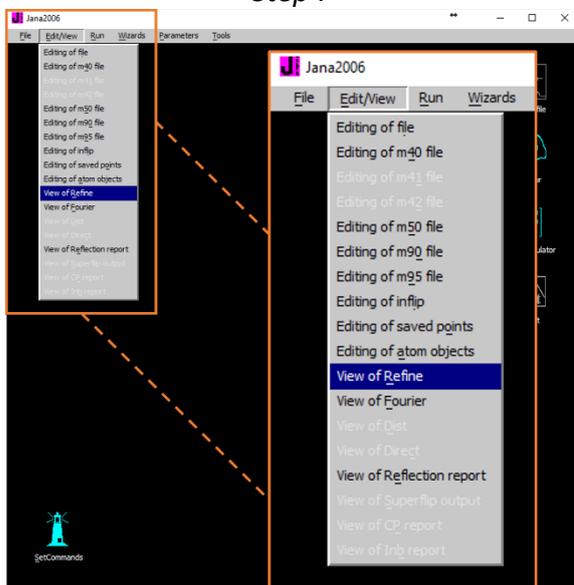


### Notes

The list of Fourier maxima does not display any useful maximum. The structure is complete.

Return to the basic window of Jana2006 without adding new atoms  
 Open refinement listing (Step7)  
 Go To → list of serious warnings (Step8)  
 The listing says that ADP of Na1 and O1 are not positive definite

Step 7



Step 8



Return to the basic window of Jana2006

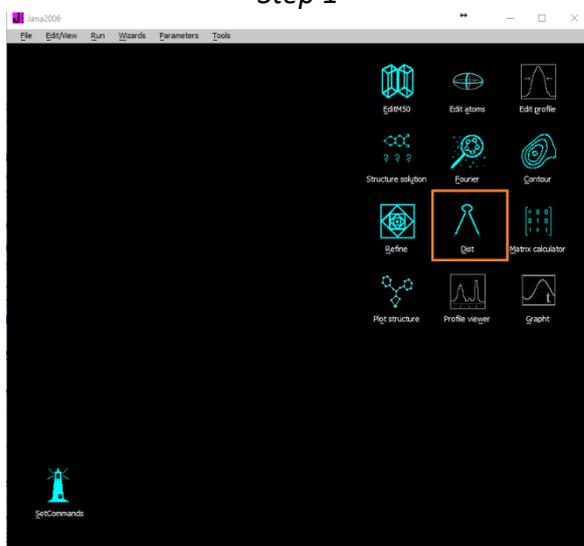
## 2. Calculation of distances and bond valences

Open Distances options (right-click the icon Dist) (Step1)

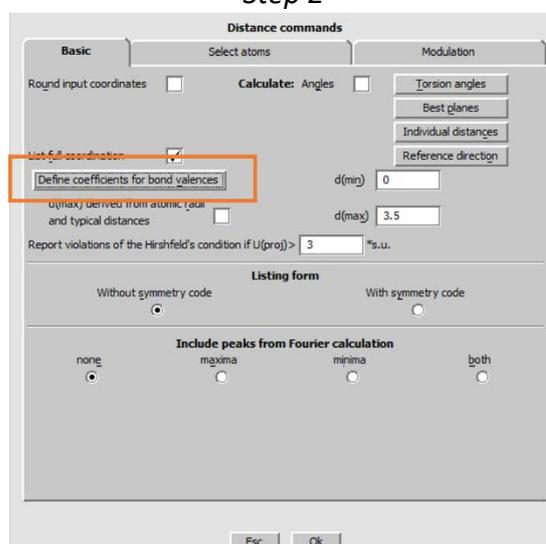
Uncheck “d(max) derived from...”

For “d(max)” type 3.5 (Step2)

Step 1



Step 2



Press the button “Define coefficients for bond valences”

Select “1<sup>st</sup> atom type” Na; “2<sup>nd</sup> atom type” O (Step3)

Press the button “From file” and select the first line for bond valences coefficients

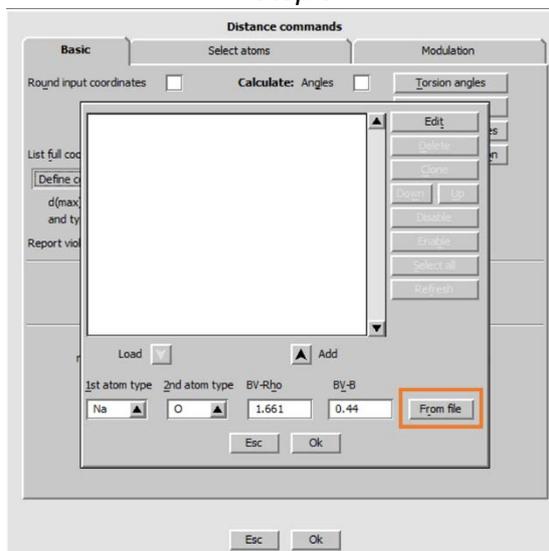
### Notes

*The list shows the coefficients like published in various sources. We are interested only in differences in coordinations and not in absolute values of bond valences sums. Therefore, we can use the first line for all cases.*

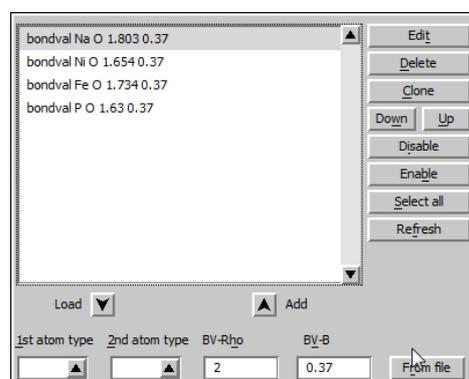
Press Add

Do the same for the pairs Ni-O, P-O and Fe-O (Step4)

Step 3



Step 4

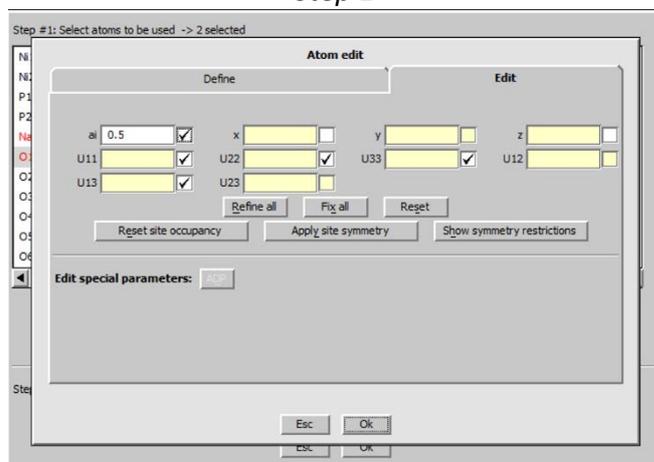




### 3. Refinement of occupancy Na1, O1

Using “Edit atoms” select that occupancy of Na1 and O1 will be refined (Step1)

#### Step 1



#### Start refinement

Refinement converges with  $R=3.4\%$

Occupancy of Na1 refines to 0.62

Occupancy of O1 refines to 0.69

#### Notes

From refinement listing we can see there are no warnings about negative ADP  
Na1 must be mixed with Ni or Fe because the refined occupancy exceeds the site occupancy. The BVS larger than 1 support this idea.  
For oxygen  $0.69 * 2 * 8 = 11$ ; 2 is the site multiplicity, 8 is number of electrons. The result is not too far of 10, which is sum of electrons for water. Therefore, O1 could be a water molecule.

Using “Edit atoms” change chemical type of O1 to Na without renaming

Run refinement

Calculate distances

#### Notes

R value is the same. Occupancy of O1 (now chemical type Na) refines to 0.46. BVS of O1 is 1.0. Therefore O1 could be also sodium, but partially occupied because there is no lighter element available for mixing.  
**In the next part, we shall consider O1 to be oxygen of a water molecule.**

### 4. Mixed site Na1-Ni3

Start “Edit Atoms”

Change chemical type of O1 back to oxygen

Change occupancy of Na1 back to 0.5

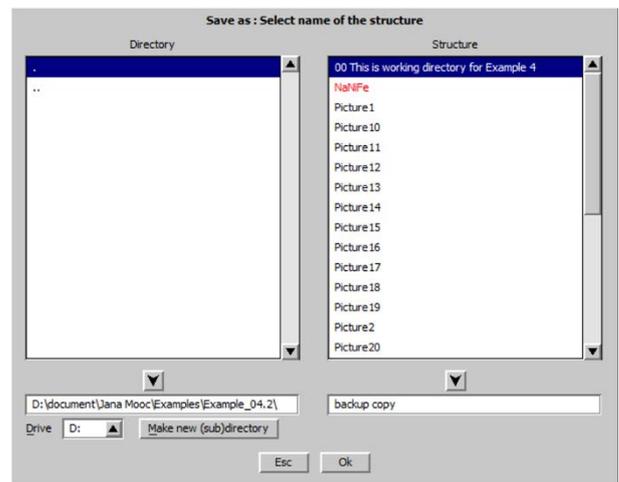
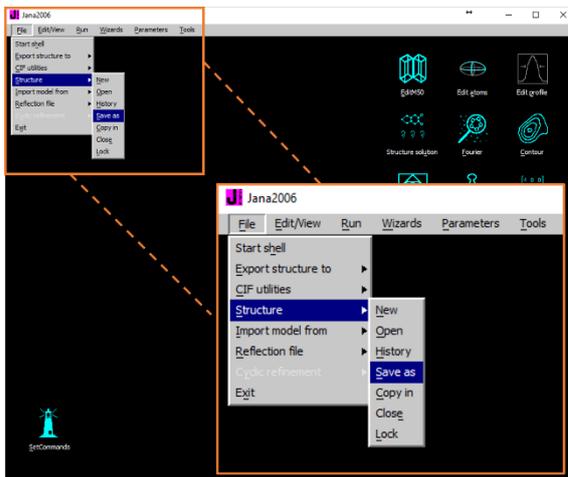
Close “Edit Atoms”, save changes

Using “File → Structure → Save As” (Step1)

Create a **backup copy** of the structure but continue with the original one (Step2)

Step 1

Step 2



Start “Edit Atoms”

Right-click Na1 and select “Split atomic position” (Step3)

For name of the split atom, type Ni3

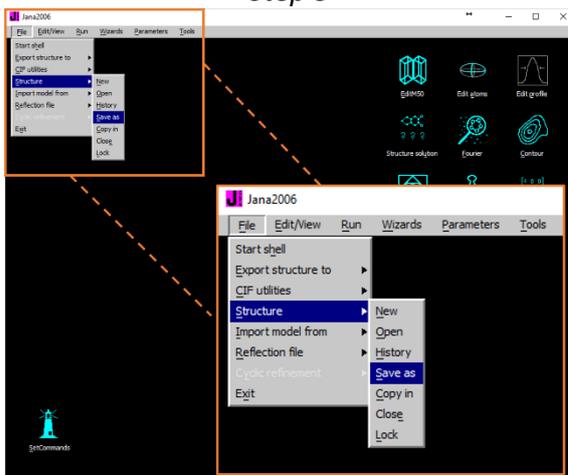
For its atomic type, select Ni

For Shift of the split atom, select “defined manually” and use the pre-defined translation “0 0 0”

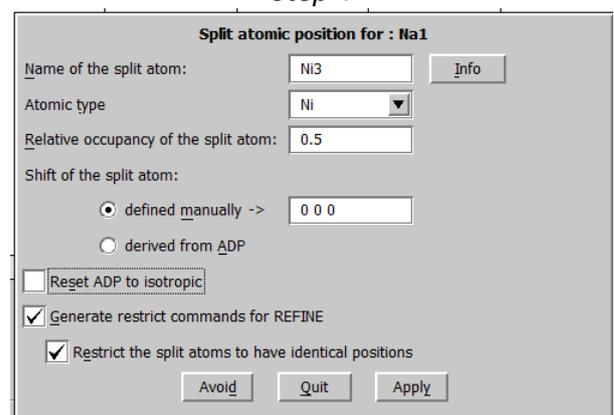
Uncheck “Reset ADP to isotropic” (Step4)

Press Apply

Step 3



Step 4



## Notes

*We have splitted the Na1 position to two identical positions, Na1 and Ni3. The initial occupancy of these positions is  $\frac{1}{4}$ , because the original occupancy was  $\frac{1}{2}$ . The tool generated a refinement restriction keeping for both atoms the same position and occupancy and constant sum of occupancies (i.e.  $\frac{1}{2}$ ).*

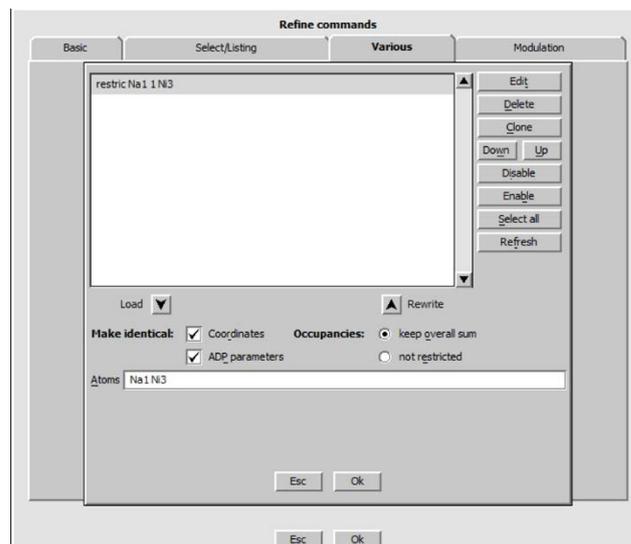
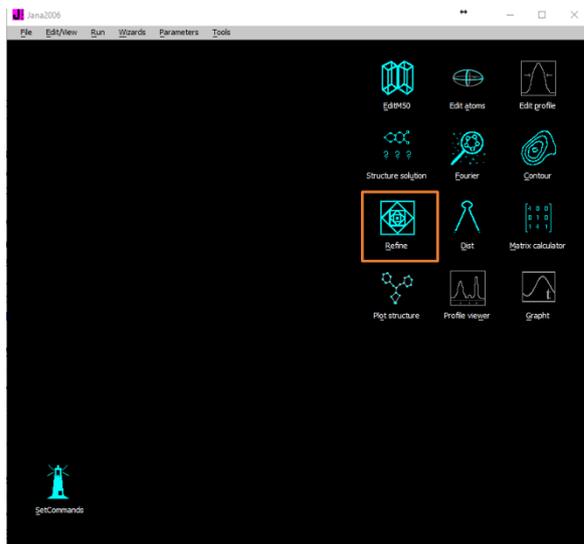
Close “Edit Atoms” and open Refinement options (Step5)

Switch to page “Various” and press “Restrictions”

Load the previously defined restriction to check it (Step6)

Step 5

Step 6



Close refinement options, run refinement

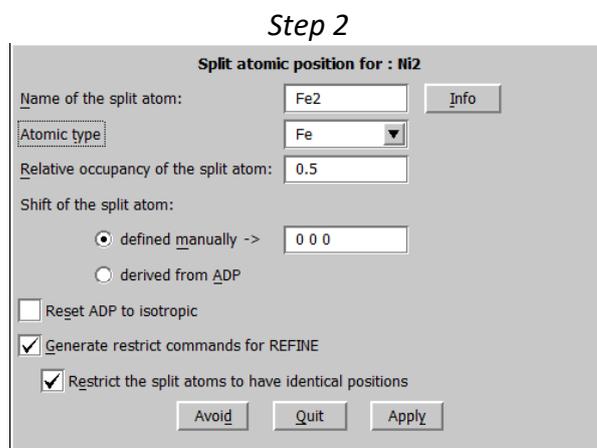
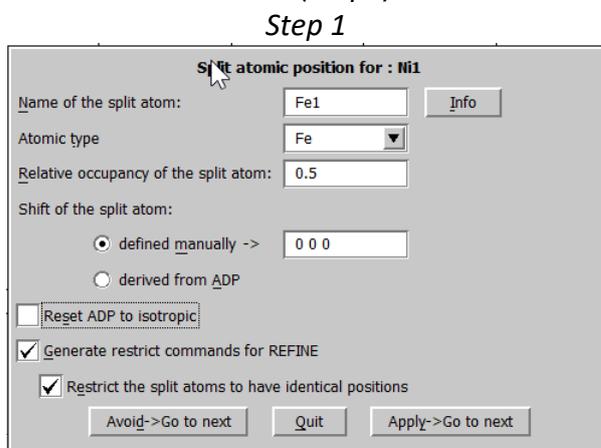
*Refinement converges with R value still around 3.4%*

*Site occupancies refined to 0.43 for Na1 and 0.07 for Ni3*

*Similar results could be achieved with iron so at this point the chemical type of the metal is either nickel or iron*

## 5. Mixed sites Ni1-Fe1 and Ni2-Fe2

Using "Edit atoms" and the same tools like before, split Ni1 to Ni1-Fe1, (Step1) and Ni2 to Ni2-Fe2. (Step2)



Activate refinement of site occupancies for Ni1, Ni2

Run refinement

*Refinement converges with R~3.2% (slight improvement)*

*Occupancy of the pair Ni1-Fe1 refines to 0.24, 0.26*

*Occupancy of the pair Ni2-Fe2 refines to 0.36, 0.64*

## 6. Calculation of the charge

Start "EditM50", page "Composition"

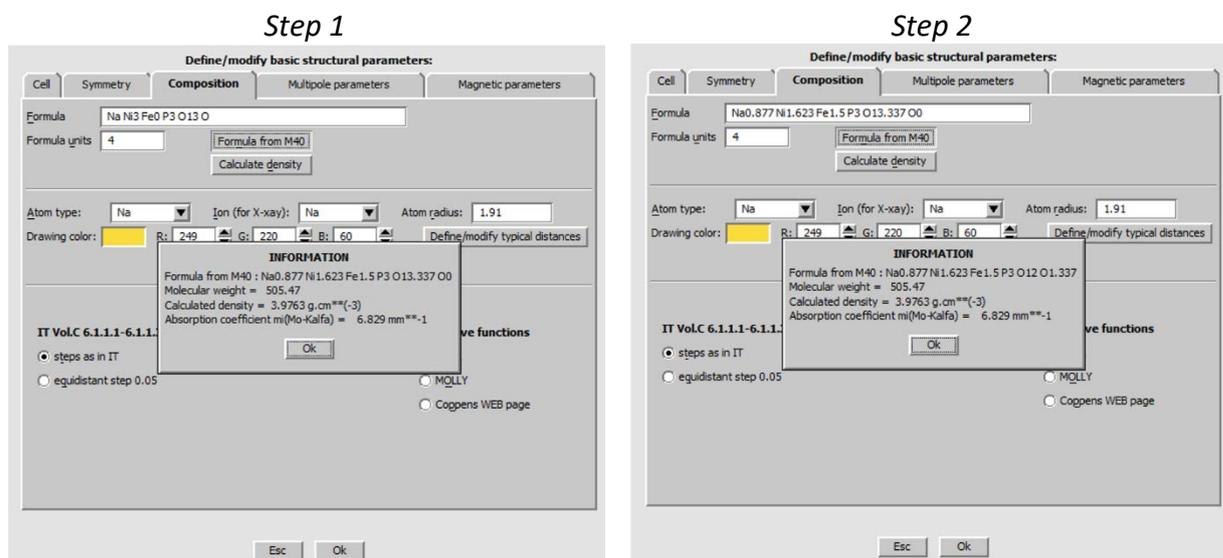
Press "Formula from M40"

It prints  $\text{Na}_{0.878} \text{Ni}_{1.306} \text{Fe}_{1.817} \text{P}_3 \text{O}_{13.332}$

In order to subtract easily water, we should define a separate chemical type for water

In the "Formula" textbox, add "O" (another oxygen) at the end of the formula (Step1)

Using "Edit atoms", redefine chemical type of O1 to be "O#2" (Step2)



Start "EditM50", page "Composition"; Press "Formula from M40"

### Notes

It prints " $\text{Na}_{0.878} \text{Ni}_{1.306} \text{Fe}_{1.817} \text{P}_3 \text{O}_{12} \text{O}_{1.332}$ ", where  $\text{O}_{1.332}$  is water with hydrogen atoms omitted, causing the increased occupancy of oxygen

Assuming that the valence of iron is three, we can calculate:

$1.82 \cdot 3 + 1.31 \cdot 2 + 0.88 + 3 \cdot 5 - 12 \cdot 2 = -0.04$ . This is very close to the charge balance.

By this way, we have established one possible structure model. However, there are other possibilities which should also be checked, for instance:

The water could be partially occupied sodium (it slightly decreases R value to 3.07%) and the valence of the iron mixed with Ni could be 2+. The composition would be  $\text{Na}_{1.769} \text{Ni}_{1.27} \text{Fe}_{1.844} \text{P}_3 \text{O}_{12}$ .

$1.844 \cdot 3 + 1.27 \cdot 2 + 1.769 + 3 \cdot 5 - 12 \cdot 2 = 0.84$ , i.e. an exceed of positive charge

Unfortunately, data quality does not allow for confirming the lack or presence of hydrogens bonded to O1. Moreover, microprobe analysis was not sufficiently accurate and no additional information was supplied by the chemist. Therefore, we finished with structure model, which cannot be reliably confirmed.

## References



# Example 5.1: YPO

Simple modulated structure with crenel

Revised 3 December 2018

$\text{Y}(\text{PO}_3)_3$

Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: YPO.hkl, YPO\_red.sum

Frame scaling, absorption correction: done

## 1. Creating new jobname

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click YPO

## 2. Import Wizard

Select "Known diffractometer formats"; NEXT

Select "Oxford Diffraction → CCD"; NEXT

[On the screen: "Define basic input file:"]

Select "Input from sum file"; file name "ypo\_red.sum"; OK

[On the screen: "Warning about appended data reduction runs"]

OK

[On the screen: "Complete/Correct experimental parameters"]

Leave all settings unchanged; NEXT

[On the screen: "Define the reference cell/split by twinning"]

Leave all settings unchanged; NEXT

For absorption correction select "None or done before importing"; NEXT

FINISH

## 3. Data Repository

The line in data repository window corresponds to one data set.

OK; YES to accept the data set

[On the screen: "Information about starting symmetry wizard"]

NEXT

## 4. Symmetry Wizard

[On the screen: "Tolerances for crystal system recognition".]

Symmetry wizard can be started separately by "File → Reflection file → Make space group test".

Leave all settings default; NEXT

[On the screen: Select supercell]

Select "Continue with the basic cell"; NEXT

[On the screen: Select Laue symmetry]

Select Monoclinic Laue symmetry; NEXT

[On the screen: Select cell centering]

Select I centered unit cell; NEXT

[On the screen: Select space group]

Select C2/c; NEXT

[On the screen: Select superspace group]

C2/c(0b0)s0

[On the screen: Final step of the superspace test]

Accept the superspace group in the standard setting: C2/c(0b0)s0; FINISH

#### 5. **Creating refinement reflection file**

We have finished creation of the file M95 (reflections converted from diffractometer format to Jana format) and M50 (cell parameters, symmetry). At this step we shall create the file M90 containing data set merged by symmetry, with extinct reflections omitted.

NEXT to confirm threshold 3sigma

[On the screen: settings for merging of reflections]

Leave all settings default; NEXT

Accept the data block and calculate coverage; FINISH

[On the screen: Information that structure solution will start]

#### 6. **Structure Solution Wizard**

[On the screen: window of Structure solution]

In "Formula" textbox type list of chemical elements for  $Y(PO_3)_3$ : Y P O

Select "use Superflip"; "Peaks from Jana2006"

Select "Use a specific random seed" and type value 5555

"Run solution"

Superflip converges (after noise suppression) with R value 21%. It confirms the symmetry C2/c(0b0)s0.

Fixing the random seed to 5555 guarantees for most processors that the Superflip returns the same results like described in this cookbook. Otherwise, each run of Superflip would return slightly different electron density. For normal work, random seed should be automatic because the convergence of charge flipping is not guaranteed for every value of random seed.

Close the listing and press "Accept last solution" to leave the structure solution wizard

#### 7. **Verification of the structure solution**

Start "Edit/View → editing of M40 file". It shows the structure parameter file

Start "Edit atoms". It shows the same in a graphical interface; parameters of atoms can be accessed by double clicking on atom or by "Action → Edit/Define atoms";

OK

Start EditM50, go to page Composition, change "Formula units" to 4

Press "Formula from M40"

[On the screen: Information about formula]

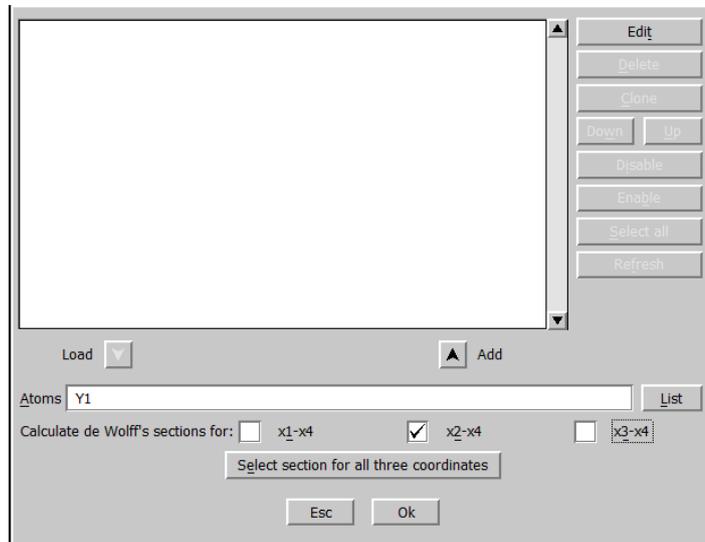
With previously used "randomseed 5555" the formula should be Y P3 O8 (for Z=4).

OK; YES for updating the formula

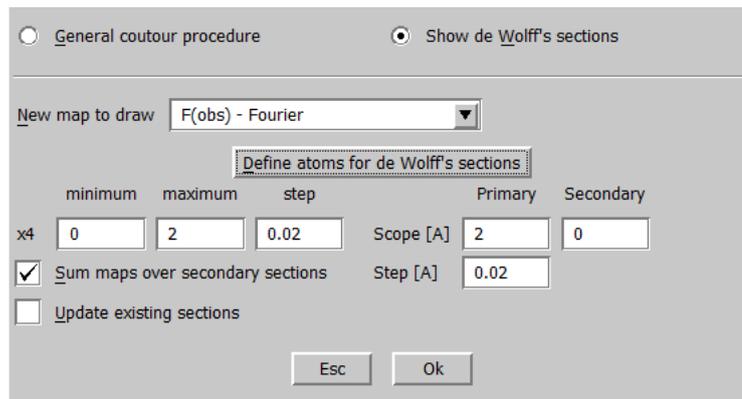
Modify the formula to Y P3 O9; OK, YES to rewrite M50 file

Correct numbers of elements helps to find correct number of atoms in Fourier maps. It is also important for the final CIF generation.

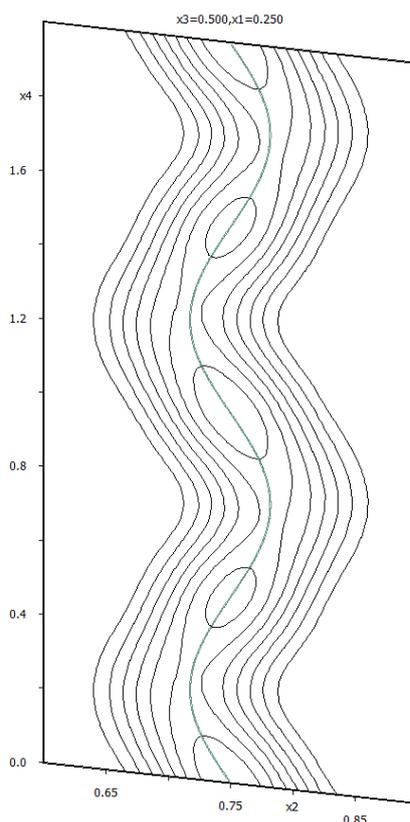
Run Contour; start “New plot”; select “Show de Wolff’s sections”;  
 New map to draw “F(obs) – Fourier”;  
 Press “Define atoms for de Wolff’s sections”;  
 Select atom Y1 and section x2-x4:



Press “Add”; OK  
 Leave rest stting default;



OK;  
 Then the modulation density will appear. With “Atoms edit” define the Y1 atom to be visualized.



The plot illustrates that the electron density from Superflip contains reliable information about position modulation. The modulation curve results by interpretation of the electron density map by Jana.

[Quit Contour](#)

### 8. Origin shift to the position of Y

The atom Y should be localized at the inversion center in one of the following Wyckoff positions:

4d  $(1/4, 1/4, 1/2); (3/4, 1/4, 0) + (1/2, 1/2, 0)$

4c  $(1/4, 1/4, 0); (3/4, 1/4, 1/2) + (1/2, 1/2, 0)$

4b  $(0, 1/2, 0); (0, 1/2, 1/2) + (1/2, 1/2, 0)$

4a  $(0, 0, 0); (0, 0, 1/2) + (1/2, 1/2, 0)$

In the next step we shall shift the origin to the position of the Y atom. This step is not necessary for the structure solution and refinement but it assures that the coordinates and plots will look as described in this cookbook

Start [“Tools → Transformations → Origin shift”](#)

[On the screen: Move the origin to:]

Select Atom Y1 and press OK.

Run [“Edit atoms”](#); Select P and O atoms;

Press [“Action”](#) and choose [“Make symmetrically contiguous motifs”](#);

This will not only make an contiguous motif from PO, but also it will move motifs to the basic cell.

### 9. Verification of modulated functions found by Superflip

Right-click the icon of Refine and select thumbnail "Various". Use the button "Fixed commands", select "Modulation parameters" and type \* to the Atoms/parameters textbox.

*This fixes modulation parameters for all atoms.*

Press the button "Add"; OK; OK

Start Refinement.

*The refinement should finish with R(obs) factors about 13%, 11%, 15% and 22% for all, main, 1<sup>st</sup> order satellite and 2<sup>nd</sup> order satellite reflections. This means that we have reasonably good starting point to continue the solution.*

*The screen output of Refine is closed after a delay. It is saved in refinement listing ("Edit/View → View of Refine → Go to → R-factors overview")*

### 10. Refinement of the modulated structure

Right-click the icon of Refine and select thumbnail "Various". Use the button "Fixed commands" and disable or delete the previously used "Fixed command"

Run refinement.

*You should get R values about 13%, 10%, 14% and 20%.*

Start "Edit atoms"

Press "Select all" and "Action → Edit/define"

Choose "harmonic" for ADP parameters.

OK; OK; Yes to rewrite changes

Start Refinement.

*Refinement converges with R value about 11%, 8%, 12% and 20% for 94 parameters.*

### 11. Localization of the missing oxygen atom

Right-click the icon of Fourier and select thumbnail "Basic" – select "Map type" "F(obs)-F(calc) – difference Fourier"

In the thumbnail "Scope" select: "Automatically" and "Use default map orientation"

OK

Run Fourier

*The modulation curve of this additional atom is rather complicated and therefore we have to look at the density maps to see more details. First, we should check if the peak, representing possible position of the new oxygen atom, has been really localized in the difference Fourier map.*

*[On the screen: Do you want to start the procedure for including of new atoms?]*

Answer yes.

*[On the screen: Inserting/replacing of atoms – setting of distance limits]*

Use default 3 Å; OK

*(The dialogue for adding maxima is also available through "Parameters → Atoms → New")*

*The dominating maximum (with the largest charge) should be close to the special position at (3/4,3/4,1/2) or to some of its equivalents, with reasonable distances to the atom P1 (about 1.5 Å).*

Note the coordinates of the dominating maximum in equivalent position close to P1

For the current structure model (random seed 5555) it should be 0.749, 0.725, 0.495

Round the coordinates to the closest special position and note them

For the current structure model (random seed 5555) it should be: 0.75, 0.75, 0.5

Leave the form **without** adding the new atom.

*Adding new atoms would add oxygen to a general position because its special position is not*

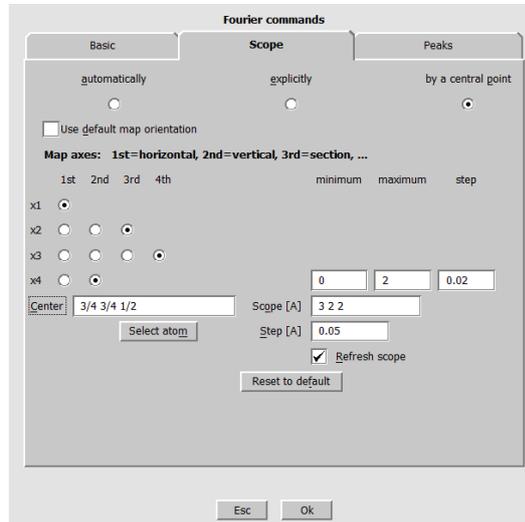
properly recognized.

Use Contour to see difference Fourier sections through the point (3/4, 3/4, 1/2).

Start Contour, press "New plot"; Select "General contour procedure"

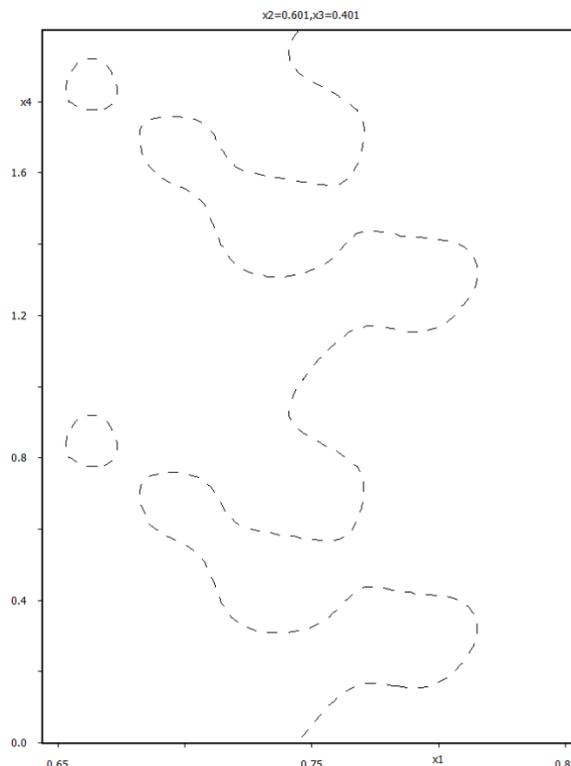
Select "Calculate new ones" and "Draw maps as calculated"; OK

In Basic thumbnail select "F(obs)-F(calc) – difference Fourier" and in the thumbnail "Scope" define the vicinity of the point (3/4, 3/4, 1/2):



OK starts Fourier calculation

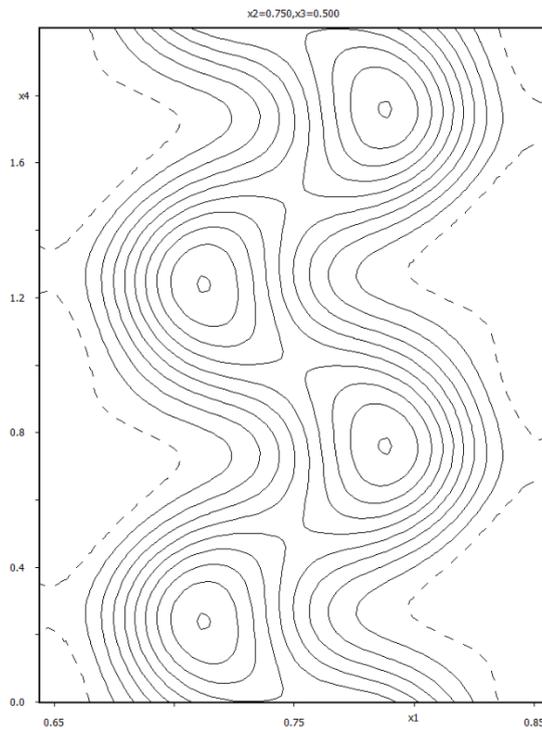
The first section is immediately plotted:



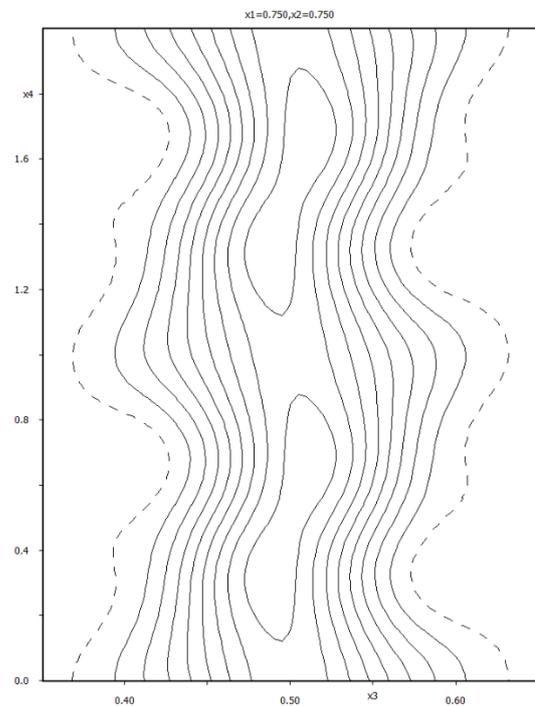
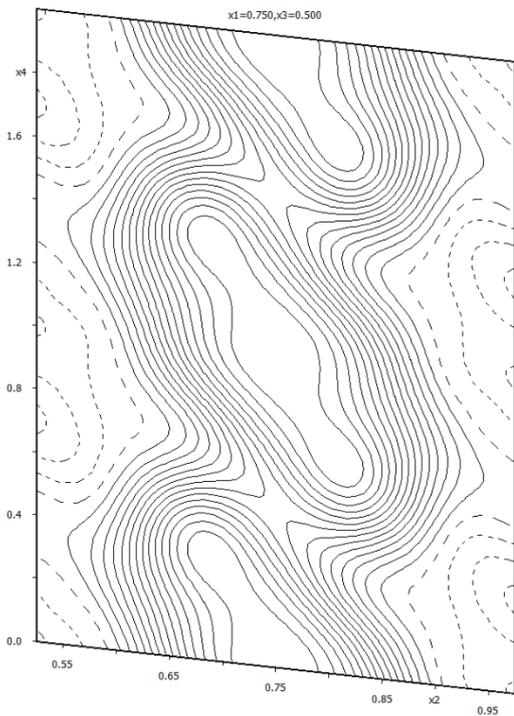
The resulting map must be summed over x2, x3 direction to see the correct modulation curve

Press "Sum ON"; select "x2" and "x3" leaving the intervals defaults; OK

The resulting map shows the shape of modulation:



Analogously (starting with button “New plot” followed by “Calculate new ones”), calculate and plot the section  $x_2$ - $x_4$  and the section  $x_3$ - $x_4$ :



*The modulation has a discontinuity at the point with  $x_4=0.5$ . This is clearly visible from the map showing evolution of the  $x_2$  atomic coordinate (the  $x_2$ - $x_4$  section).*

As the difference Fourier is more sensitive to light oxygen atom we should save the temporary result for a final check of the refined modulation of that oxygen atom.

Close "Contour"

"File → Structure → Save as" and use a new name for example "YPO-for-maps" but do not continue with the new structure.

## 12. Inserting the missing oxygen atom

From the previous we know that the modulation function of the new atom at  $(-1/4, -1/4, -1/2)$  has a discontinuity and therefore a crenel function will be used. In the  $x_2$ - $x_4$  difference section we found that the length (delta) of crenel is one and its center ( $x_{40}$ ) is located at 0.

"Parameters → Atoms → New", select "Coordinates from keyboard"; OK

Type the coordinates  $3/4, 3/4, 1/2$ , press "Use new coordinates"

Select the symmetrical position making the shortest distance to P1 and press "Include selected peaks".

[On the screen: Complete information for the new atom]

For "Name of atom" type "O\*" followed by TAB

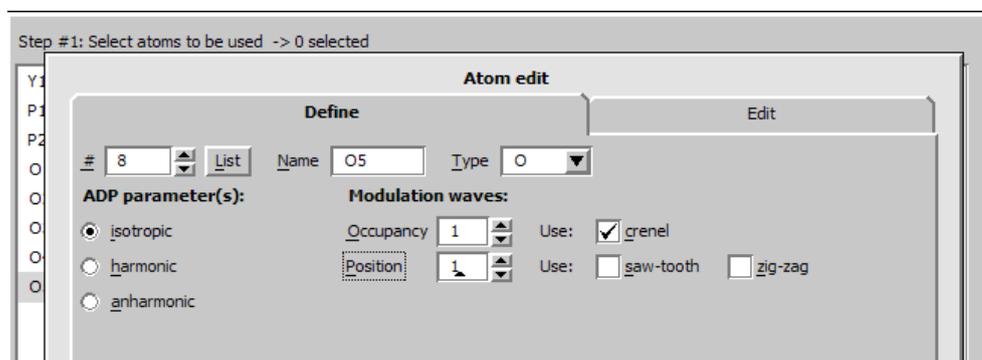
This selects the chemical type oxygen and the label with the first available sequence number.

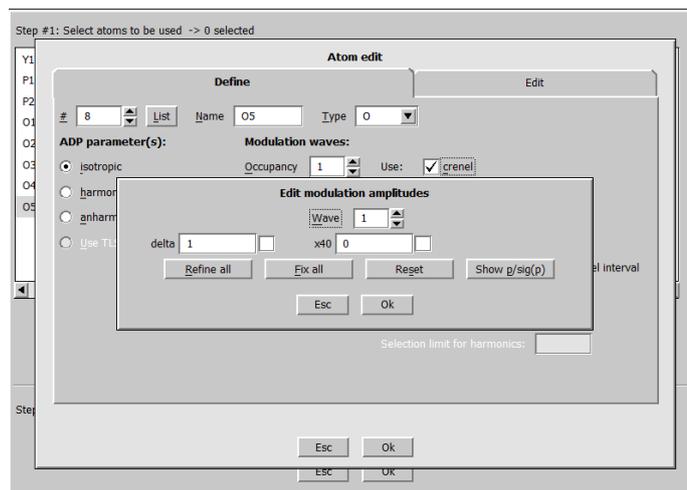
OK; Finish; YES to include new atom

Now we have to define the crenel function

Run "Edit atoms" and select the new atom (probably O5).

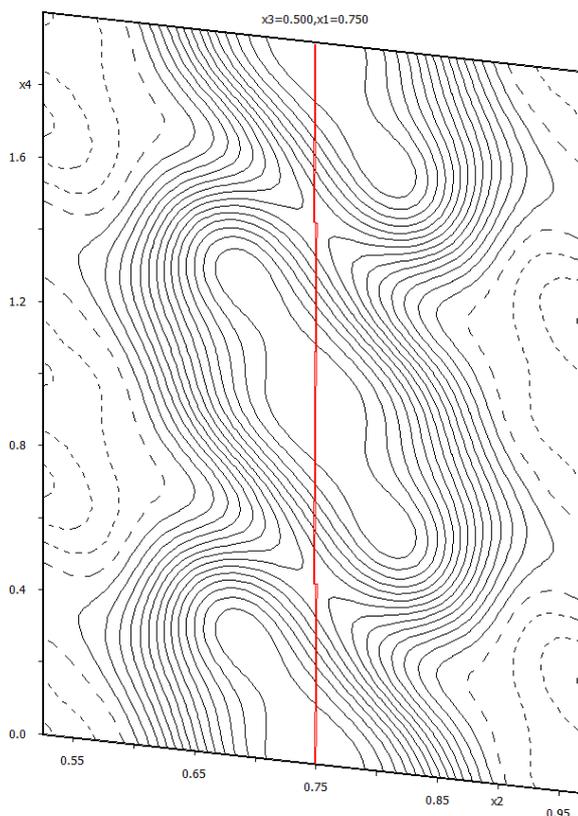
"Action → Edit/define" check "crenel" and add also one position modulation wave in the textbox "Position"





define "1" for "delta" and "0" for "x40"; OK  
 This is width and centre of the crenel function  
 Select "Legendre polynomials in crenel interval"  
 OK; OK; Yes to rewrite

Draw Contour section x4-x2 for (3/4 3/4 1/2) - like previously  
 Press "Atoms edit" and add O5; OK  
 The Contour plot shows the initial modulation function for O5



### 13. Refinement of the complete structure

Right click on the Refine icon, switch to "Basic"  
 Define there number of cycles 100 and damping factor 0.2.

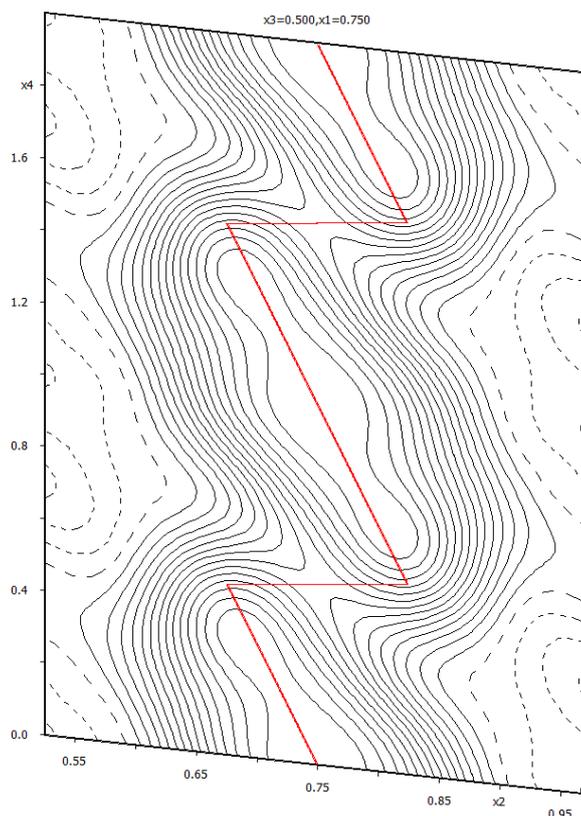
*Damping factor multiplies the parameters changes*

Start refinement

→ R about 9%, 6%, 10%, 20%

Draw Contour section (without Fourier calculation!)  $x_4$ - $x_2$  for (3/4 3/4 1/2) - like previously  
Press "Atoms edit" and add O5; OK

*The Contour plot shows the crenel modulation function for O5 combined with one modulation wave*



Run "Edit atoms", select all atoms, press "Action" and select "Edit/Define atoms"  
Modify all ADP parameters to harmonic ones by double-clicking the corresponding radio button

*Yellow indicates locked objects. Locking occurs when the corresponding parameters are not the same (or of the same type) for the selected atoms. In our case ADP is harmonic for most of atoms but isotropic for the newly added O5, this is the reason for locking of radio buttons. The text box for site occupancy is also locked because some atoms are in special positions. A locked object can be unlocked by double-click.*

Add another one positional modulation wave for all atoms using the textbox "Position".  
Save changes and start refinement

→ R about 5.6%, 3.4%, 6%, 18%

Run "Edit atoms", select all atoms and (using the button "ADP<sup>2nd</sup>") define two ADP modulation waves for all atoms.

Start refinement

→ R about 3.4%, 2.5%, 3.5%, 9.0% for 297 refined parameters

“File → Structure → Save as” make a backup copy with name e.g. ypo-final

#### 14. Check modulation curves with maps for O5

In this part we will check whether the refined modulation function for oxygen O5 corresponds to the electron density map found previously by Superflip. We are making this check because refinement of sawtooth function for oxygen in the structure containing the heavy yttrium could be unreliable

Return to the result saved previously (YPO-for-maps):

“File → Structure → Open”: select the name of the previously saved structure (“YPO-for-maps”)

Run Refine to re-generate phases

(R factors 11%, 8%, 12% and 20%.)

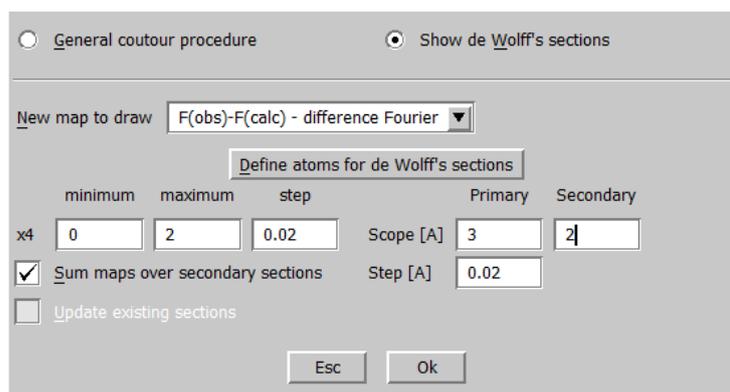
“File → Structure → Copy in” copy only (!!!) m40 from the final structure

**(From this point Refine must not be started)**

Run “Contour”; Choose “Show de Wolff’s sections” and difference Fourier;

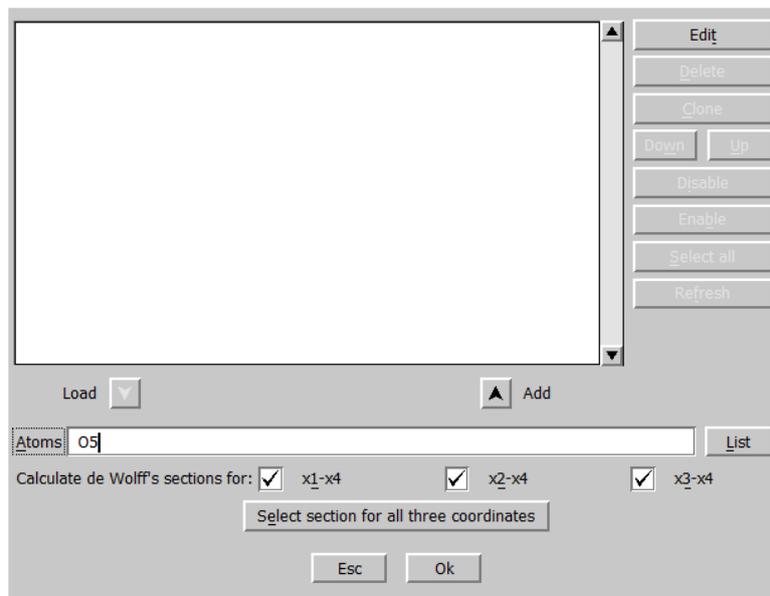
Define primary and secondary scope, 3 and 2 respectively;

Activate summation of the maps over secondary directions:

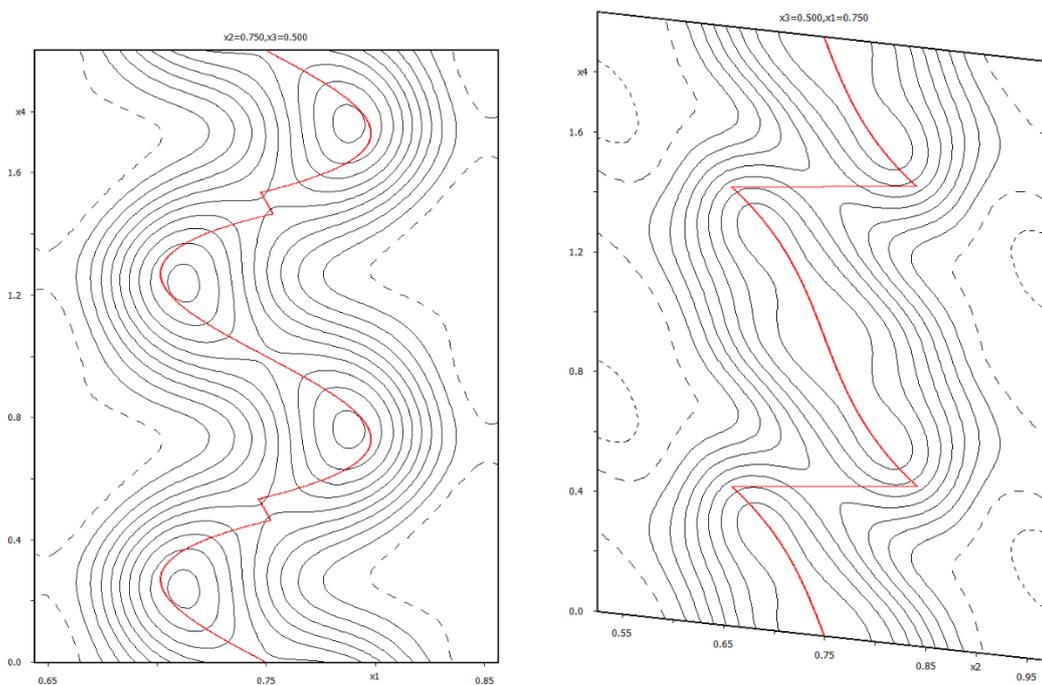


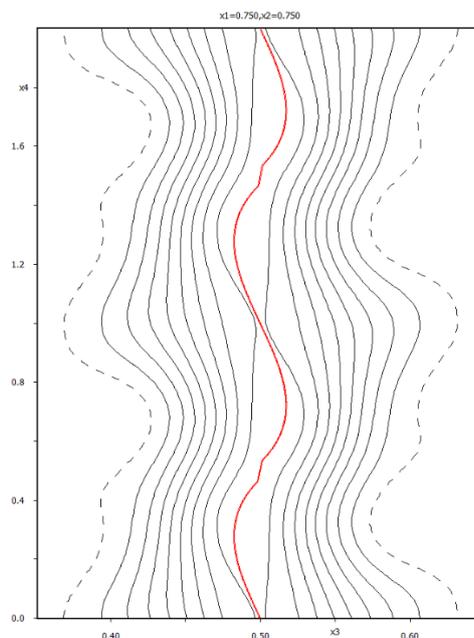
Press the button “Define atoms for de Wolff’s section:

Select atom O5 and activate calculations for all three sections x1-x4, x2-x4 and x3-x4:



The following maps will be obtained:





By this procedure, we plot the final refined modulation curve of O5 together with the previously calculated Fourier map. The technical trick consists in the fact that Fourier calculation does not use M40; it uses M80 created by Refine. Only the modulation curve displayed by Contour is based on parameters from M40.

### 15. Drawing of refined modulated structure

Return back to the refinement result using “File → Structure → History”

Drawing programs such as Diamond cannot draw a modulated structure directly. Jana2006 creates an approximant based on the refined modulated functions. During this process, the superspace symmetry is used to generate all atomic positions and the symmetry is reduced to P1. The size of approximant and the starting  $t$  value are to chosen to visualize different portions of the non-periodic matter. In our case the most convenient supercell is  $1 \times 8 \times 1$  as follows from the modulation vector being close to  $(0, 3/8, 0)$ .

#### “Plot structure”

In Diamond, symmetry operations cannot be used for the approximant (no automatic structure, no supercell, no coordinations .... ). This is because Diamond does not know modulation displacements of newly created positions.

#### Checking of refinement listing

Start “Edit/View → View of Refine”

Press “GoTo → List of serious warnings”

The listing contains information that modulation of ADP leads to non-positive values for some values of  $t$  coordinate:

```

*****
* List of serious warnings *
*****

Modulated harmonic ADP tensor of the atom "O1" is not positive in some regions
  For more details run "Grapht" and draw U(min) value
Modulated harmonic ADP tensor of the atom "O4" is not positive in some regions
  For more details run "Grapht" and draw U(min) value
Modulated harmonic ADP tensor of the atom "O5" is not positive in some regions
  For more details run "Grapht" and draw U(min) value

There were no correlations larger than 0.900 in the last refinement cycle

```

Start "Grapht"

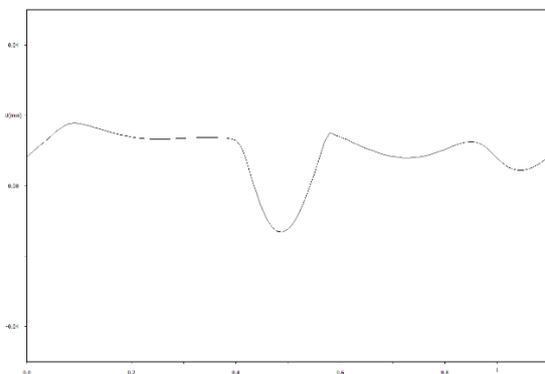
Press New/Edit

For "Parameter to draw" select "ADP parameter"

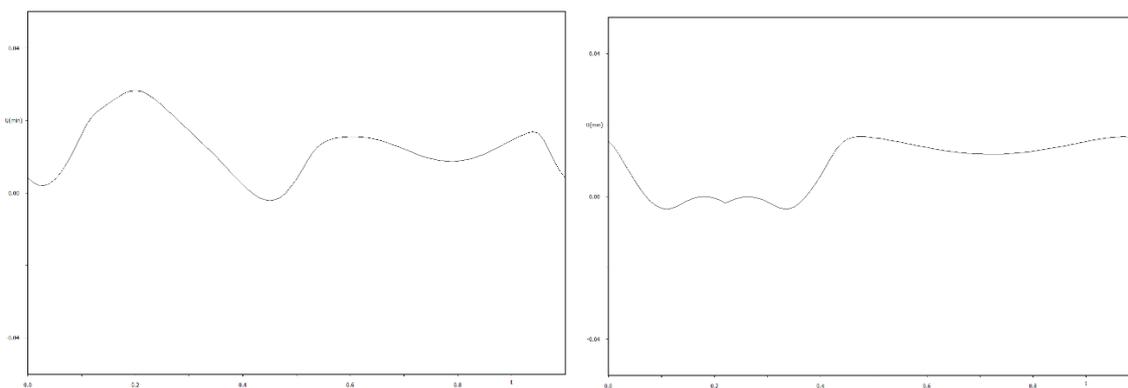
For "Central atom" use "O1" (the label may differ)

For "Principal" select "U(min)"; OK

The following plot shows that  $U(\min)$  is negative for a small region of  $t$



Create the same graphs for O4 and O5



Decreasing of number of ADP modulation waves often solves such situation:

In Atoms/Edit select all oxygen atoms and decrease number of ADP modulation waves to 1

Check refinement listing and Grapht graphs

In our case it only helps for O4. The reason for bad ADP modulation of some oxygen atoms is probably caused by the fact the sample is more complicated than presented here. High

*exposition reveals another set of weak satellites, which needs another  $q$ -vector for their indexing. The five-dimensional structure remains unsolved.*



# Example 5.2: Na<sub>2</sub>CO<sub>3</sub>

Revised: 10 March 2019

Data	Topic	Level
X-ray single crystal data	Simple modulated structure from single crystal data	Intermediate

## Tasks

---

Solving a modulated structure from single crystal data

- **Structure solution and refinement**
- **De Wolff sections**
- **Interpretation of results using Grapht**

## Initial data

---

### Data

Single crystal data measured with KUMA four-circle diffractometer (KUMA has changed to Oxford Diffraction, later on Varian, later on Agilent, now Rigaku Oxford Diffraction)

### Input files:

naco.hkl, naco.cif\_od

### Additional information:

Frame scaling, absorption correction: done by the diffractometer software

Chemical Formula : Na<sub>2</sub>CO<sub>3</sub>

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# Instructions

## I. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files; Right pane: double-click naco

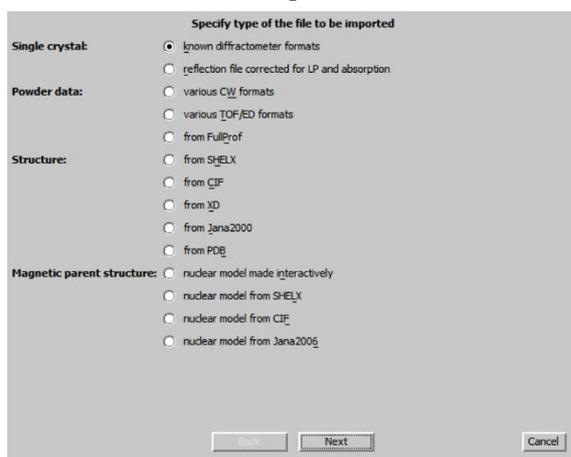
### 2. Import wizard

Select “Known diffractometer formats”; NEXT (Step 1)

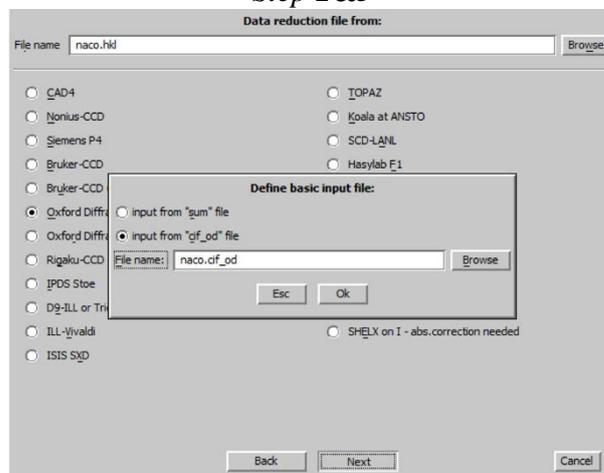
Select “Oxford Diffraction → CCD”; NEXT (Step 2)

Select “Input from “cif\_od” file”; OK (Step 3)

*Step 1*



*Step 2&3*



Leave all settings unchanged; NEXT (Step 4)

*q*-vector read from the cif\_od file should be: 0.1776 0 0.3252

Leave all settings unchanged; NEXT; OK; (Step 5)

The program reads 555555 reflections from hkl file

**Step 4**

**Complete/correct experimental parameters**

Cell parameters: 8.9338 5.2678 6.0565 90.1018 101.551 89.7404

Number of input indices: 4 Info about metrics parameters

1st modulation vector: 0.1776 0 0.3252

2nd modulation vector:

3rd modulation vector:

X-ray tube

Wave length: 0.7107

Temperature: 293

**Polarization correction:**

Circular polarization

Perpendicular setting Info

Parallel setting Info

Guinier camera

Linearly polarized beam

**Monochromator parameters:**

Perfectness: 0.5

Glancing angle: 6.081886 Set glancing angle

Back Next Cancel

**Step 5**

**Define the reference cell/split by twinning**

Cell parameters: 8.9338 5.2678 6.0565 90.102 101.551 89.740

Target dimension: 4 Twinning Twinning matrix

1st modulation vector: 0.1776 0.0000 0.3252

2nd modulation vector:

3rd modulation vector:

Max. satellite index:

Accuracy:

Number of domains:

Data related to domain #:

Multiply input F(hkl)/I(hkl) by: 1

Import only satellites:

Define transformation matrix

Back Next Cancel

For absorption correction select “None or done before importing”; NEXT  
FINISH

### 3. Data Repository

OK; YES to accept the data set  
NEXT;

## II. Symmetry and data merging

### 1. Symmetry Wizard

[On the screen: “Tolerances for crystal system recognition”.]

#### Notes

Symmetry wizard can be started separately by “File ? Reflection file ? Make space group test”.

**Change “Maximal deviation for cell angles” to 0.3 (Step 1)**

*Without this change unit cell angles will not be recognized as monoclinic*

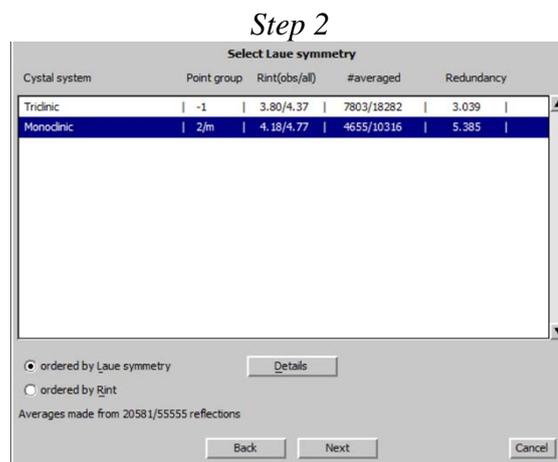
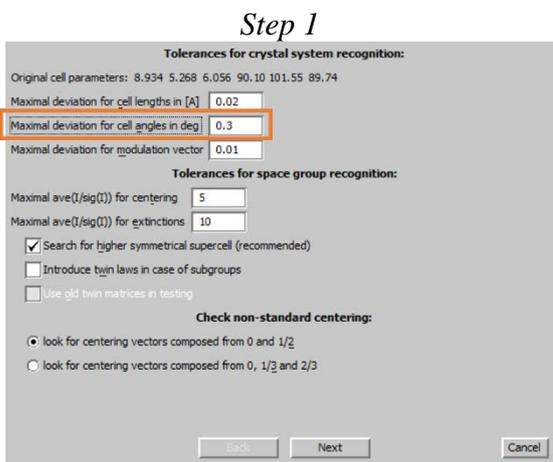
Leave all other settings default; NEXT

[On the screen: “Select supercell”.]

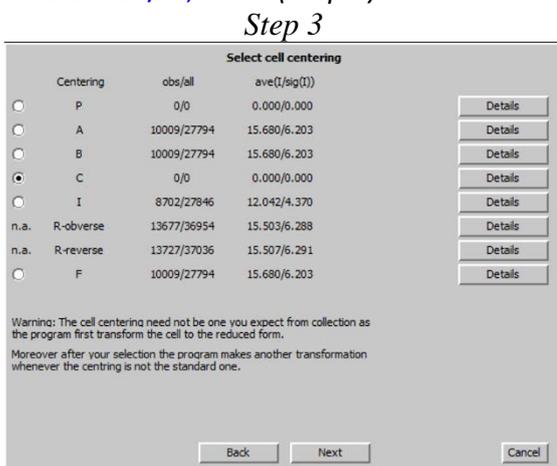
Leave all settings default; NEXT

[On the screen: Select Laue symmetry]

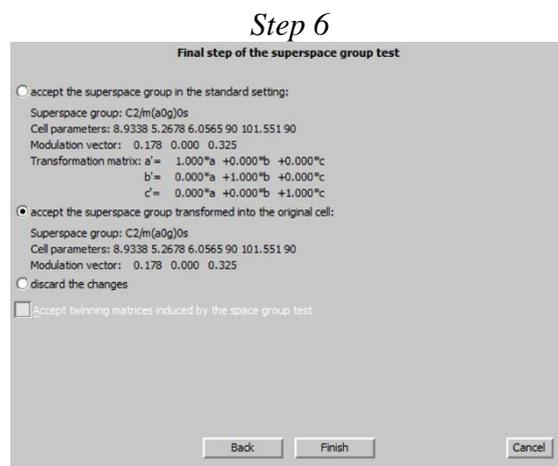
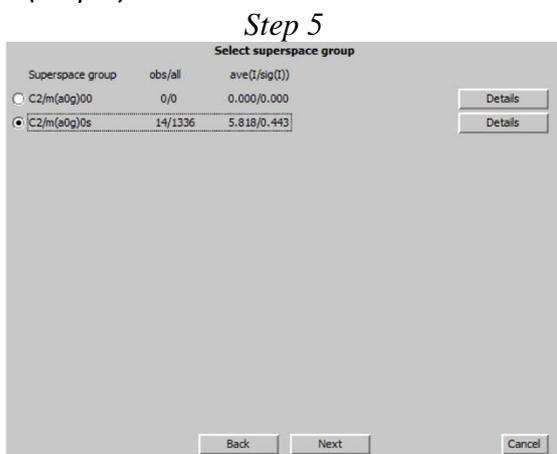
Select Monoclinic Laue symmetry; NEXT (Step 2)



[On the screen: Select cell centering]  
 Select C centered unit cell; NEXT (Step 3)  
 [On the screen: Select space group]  
 Select C2/m; NEXT (Step 4)



[On the screen: Select superspace group]  
 C2/m(a0g)0s (Step 5)  
 [On the screen: Final step of the superspace test]  
 Accept the superspace group transformed into the original cell: C2/m(a0g)0s; FINISH (Step 6)



## 2. Creating refinement reflection file

### Notes

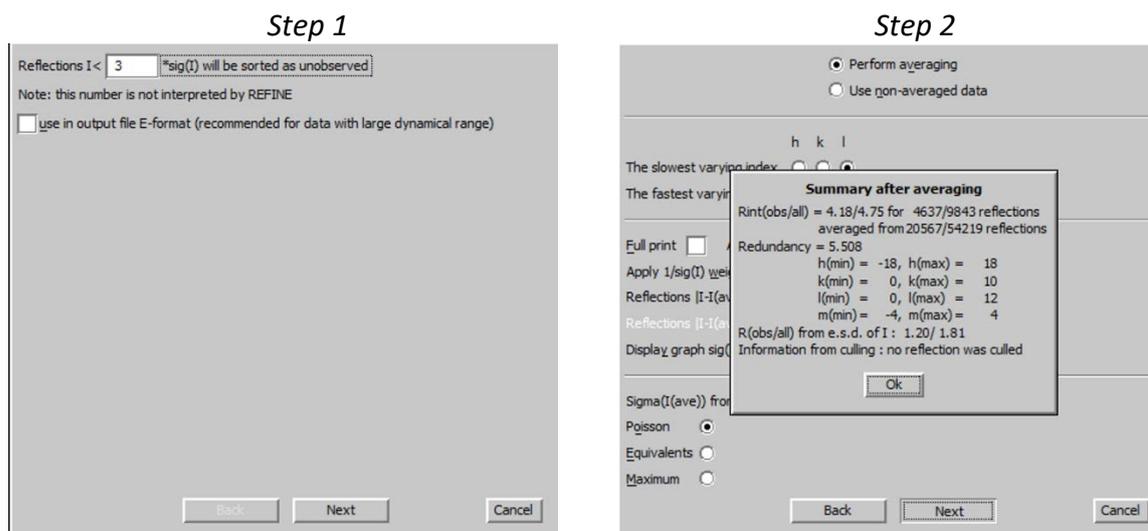
We have finished creation of the file M95 (reflections converted from diffractometer format to Jana format) and M50 (cell parameters, symmetry). At this step, we will create the file M90 containing data set merged by symmetry, with forbidden reflections omitted.

NEXT to confirm threshold 3sigma (Step1)

[On the screen: settings for merging of reflections]

Leave all settings default; NEXT (Step2)

The  $R_{int}$  for observed reflections will be 4.18%



Accept the data block and calculate coverage; FINISH

[On the screen: Information that structure solution will start]

## III. Structure solution

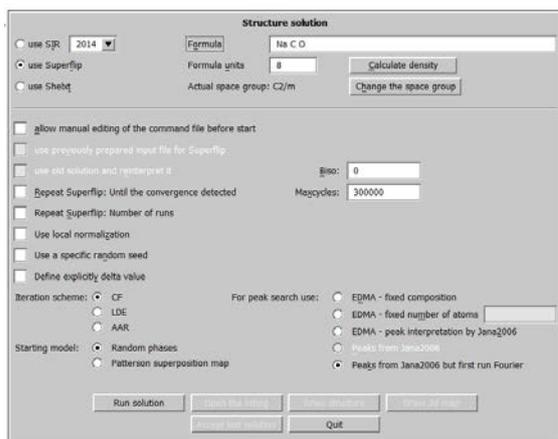
### 1. Structure Solution Wizard

[On the screen: window of Structure solution]

In "Formula" textbox type list of chemical elements: Na C O

Select "use Superflip"; "Peaks from Jana2006 but first run Fourier" (Step 1)

## Step 1



### Notes

Superflip converges (after noise suppression) with R value 21%. It confirms the symmetry C2/m(a0g)0s.

```

Jana2006
Find Find next Go to Print PgTop Open in editor Close
#####
# Checking the density for symmetry #
#####

Centering vectors:
0.000 0.000 0.000 0.000
0.500 0.500 0.000 0.000

Symmetry operations compatible with the lattice and centering:
Symmetry operation agreement factor
m|s(0,1,0): x1 -x2 x3 1/2+x4 0.147
2|0(0,1,0): -x1 x2 -x3 -x4 0.951
-1: -x1 -x2 -x3 -x4 1.090
c|s(0,1,0): x1 -x2 1/2+x3 1/2+x4 58.468
m|0(0,1,0): x1 -x2 x3 x4 62.926
c|0(0,1,0): x1 -x2 1/2+x3 x4 71.357

-----
Space group derived from the symmetry operations:
-----
Tentative HM symbol: C12/m1(a0g)0s
Fingerprint: 431222C0R960028dXM1 (0,0,0,0)
Centering vectors:
0.000 0.000 0.000 0.000
0.500 0.500 0.000 0.000
Symmetry operations:
1: x1 x2 x3 x4
m|s(0,1,0): x1 -x2 x3 1/2+x4
2|0(0,1,0): -x1 x2 -x3 1/2-x4
-1: -x1 -x2 -x3 -x4

#####
# Search for the origin of the space group #
#####

Position of the origin in the CF map:
0.6542 0.9549 0.8401 0.9741
Agreement factors of individual generators:
Number smb agreement
4 m|s 0.15
2 2|0 0.95

Overall agreement factor: 0.73

You can obtain more information about the reconstructed reflection phases by using 'expandedlog yes'.

Electron density written to file naco_Superflip.m81.

-----
End of the calculation: 12.MAR 2018, 17:00:19
-----
Superflip version: 05/17/16 12:53
  
```

This is symmetry found by Superflip in the electron density map

This is fit of symmetry elements supplied by user (small numbers = good fit)

Close the listing and press “Accept last solution”

## 2. Reflection report

Start “Edit/View → View of Reflection report” (Step1)

### Notes

Reflection report shows which symmetry operations were used for merging of reflections and which extinction rules were applied

#### Step 1

```
Creating of the JANA reflection file
structure :

*****
* Basic information *
*****

*****
* Structure data *
*****

Cell parameters      :      8.9338      5.2678      6.0565      90.000      101.551      90.000      Volume :      279.3
Reciprocal parameters :      0.114248      0.189833      0.168525      90.000      78.449      90.000      Volume :      0.003581

Modulation vector q(1):      0.177600      0.000000      0.325200

Centrosymmetric super-space group: C2/m(a0g)0s Number : 12

List of centring vectors:

0.000000 0.000000 0.000000 0.000000
0.500000 0.500000 0.000000 0.000000

Symmetry operators:

x1      x2      x3      x4
-x1     x2     -x3     -x4+1/2
-x1     -x2     -x3     -x4
x1      -x2     x3      x4+1/2
```

## 3. Verification of the structure solution

Start “Edit/View → editing of M40 file”.

### Notes

This is the file of structure parameters. Each atom has one modulation wave (number of waves and six parameters are indicated in red) found by Jana2006 in the electron density map from Superflip.

```
Na1      1      1      0.500000 0.670666 0.000000 0.246168      000 0 1 0
0.037995 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
0.000000 0.066260 0.000000 0.000000-0.004772 0.000000      000000
0.000000
```

Note that there is no oxygen in M40 – later on some carbon atoms will be changed to oxygen. The coordinates may differ from the ones shown here dependent on which equivalent origin position was used by Superflip.

Close the editor  
Start "Edit atoms".

#### Notes

*It shows the same information in a graphical interface; parameters of atoms can be accessed by double clicking on atom or by "Action → Edit/Define atoms";*

OK

Start "Plot structure"

Select "Draw average structure"

Start "Draw+continue"

*With this option the basic 3d structure will be plotted*

#### [On the screen: window of Diamond]

In Diamond use Ctrl-A and Delete to remove an automatically created plot (if present)

In Diamond use  to include all symmetry independent atoms from M40

Delete Na atoms

In Diamond use  to add coordinated atoms

Using mouse cursor and rotations  identify atoms which should be oxygens of CO<sub>3</sub> group: C1 and C2

Quit Diamond (without saving the plot)

Start "Edit atoms"

Change chemical type of C1, C2 to oxygen

Use "Action → Rename selected atoms to atom type + number" for oxygens and carbon

*The structure now contains: Na1, Na2, Na3, O1, O2, C1*

Return to the basic window

## IV. Refinements and model improvement

### 1. Refinement of modulated structure with modulations of positions

In Refinement commands set 100 refinement cycles  
Run refinement.

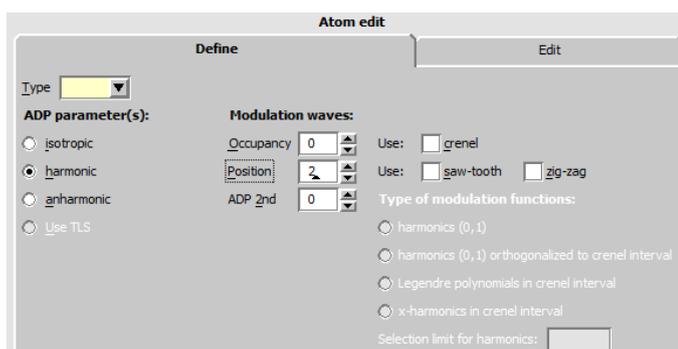
Notes	
<i>Modulation waves are refined from the starting values found by charge flipping. Refinement converges with <math>R_{obs}</math> factors 17%, 13%, 14%, 24%, 30% and 49% for all reflections, main reflections, 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> order satellites, respectively.</i>	
R factors : [9843=4637+5206/30], Damping factor: 1.0000 GOF(obs)= 9.15 GOF(all)= 6.43 R(obs)= 17.20 wR(obs)= 22.58 R(all)= 25.78 wR(all)= 23.11 R factors for main reflections : [1147=904+243] R(obs)= 12.60 wR(obs)= 17.69 R(all)= 14.25 wR(all)= 17.85 R factors for satellites +(1) : [2068=1436+632] R(obs)= 14.39 wR(obs)= 17.83 R(all)= 17.79 wR(all)= 18.12 R factors for satellites +(2) : [2294=1220+1074] R(obs)= 24.45 wR(obs)= 29.05 R(all)= 35.89 wR(all)= 29.74 R factors for satellites +(3) : [2049=719+1330] R(obs)= 29.70 wR(obs)= 38.35 R(all)= 55.27 wR(all)= 39.63 R factors for satellites +(4) : [2285=358+1927] R(obs)= 49.25 wR(obs)= 62.77 R(all)= 86.46 wR(all)= 63.21 Last wR(all): 23.11 Maximum change/s.u. : -0.0073 for z[C1]	

Start "Edit atoms" and change ADP of all atoms to harmonic  
Repeat refinement

$R_{obs}$  factors: 13%, 8%, 11%, 21%, 26% and 49%

Start "Edit atoms" and add another position modulation wave for all atoms (Step1)

#### Step 1



Repeat refinement

$R_{obs}$  factors: 12%, 7%, 10%, 16%, 23%, 48%

Start "Edit atoms" and add a 3<sup>rd</sup> position modulation wave for all atoms

Repeat refinement

$R_{obs}$  factors: 8%, 8%, 7%, 9%, 15%, 25%

Start "Edit atoms" and add a 4<sup>th</sup> position modulation wave for all atoms

Repeat refinement

$R_{obs}$  factors: 8%, 6%, 7%, 9%, 14%, 21%

## Notes

Refinement with four position modulation waves is reasonable because there are satellites up to the 4<sup>th</sup> order in data. However, it is not sure at this point that all atoms really need so many waves.

Use “File → Structure → Save As” and create backup copy “naco\_posmod”  
(Continue with the original structure)

## 2. De Wolff sections – manual setup

### Notes

In the next step, modulation functions will be checked against observed and difference Fourier map.

Start Fourier commands

For “Map type” select “F(obs) – Fourier” (Step 1)

Switch to the page “Scope”

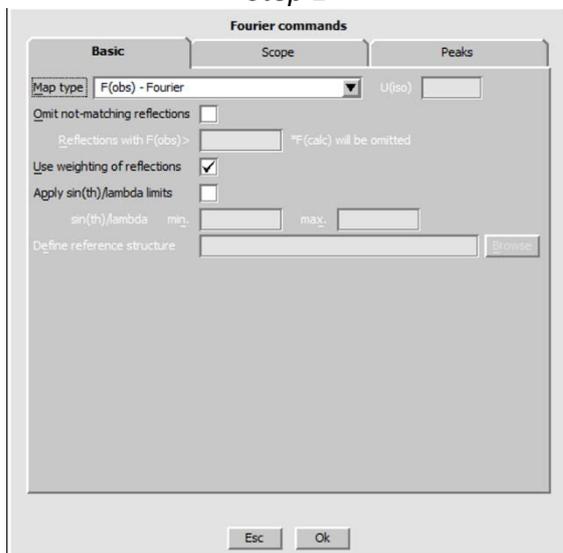
Select “by a central point”; For “Map axes” select x1 for “1<sup>st</sup>” column and x4 for “2<sup>nd</sup>”

For “Center” type Na1

For “Scope [A]” type 2 1 1

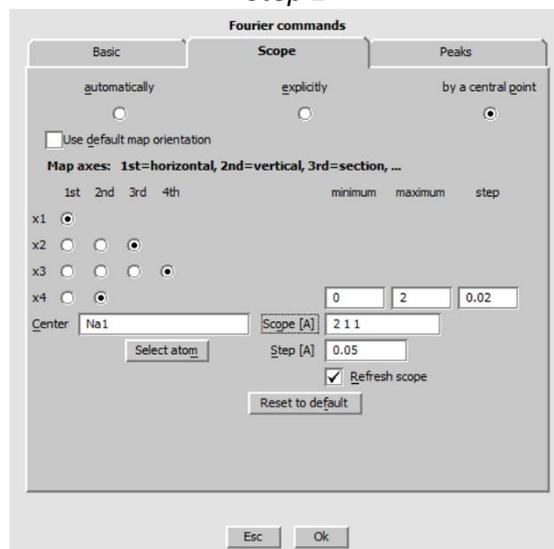
Change “Step [A]” from 0.02 to 0.05 to speed-up the calculation (Step2)

Step 1



OK; Yes+start

Step 2



### Notes

Fourier calculates a four-dimensional parallelepiped  $x_1$ – $x_4$ – $x_2$ – $x_3$  with dimensions 2-?-1-1 Å. In  $x_4$ , the calculation will run over two periods: from 0 to 2 with step 0.02. The step in the other directions will be 0.05 Å. The two-dimensional sections  $x_1$ - $x_4$  will be stacked along  $x_2$ ; the three-dimensional "sections"  $x_1$ - $x_4$ - $x_2$  will be stacked along  $x_3$ .

Start Contour

Press “New plot”

Select "General Contour procedure", "Use old maps" and "Draw maps as calculated"; OK  
(Step 3)

[On the screen: the first x1-x4 section]

Press "Sum on" and select summation over x2 and x3

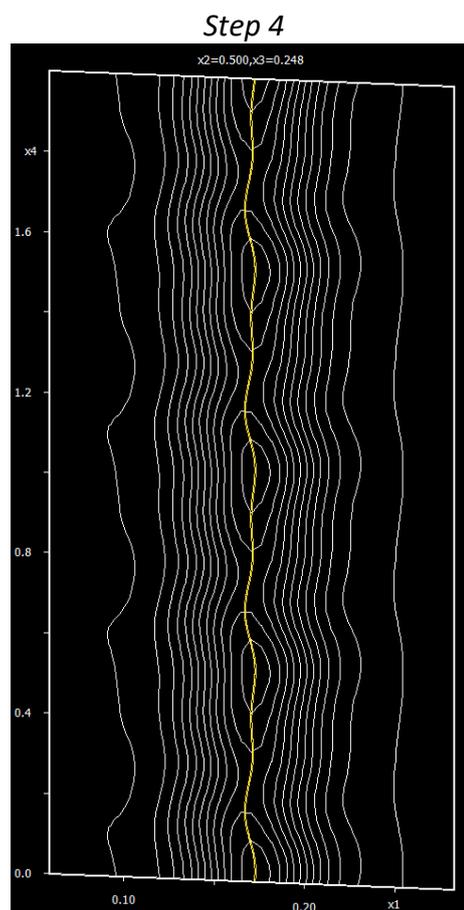
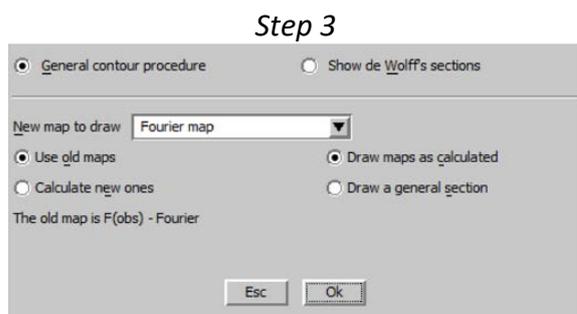
This merges all x1-x4 sections stacked along x2 and x3

[On the screen: merged section]

Press "Atom edit"

For "Atom name" type Na1; Add; OK

[On the screen: merged section with refined modulation function of Na1] (Step 4)



#### Notes

In your calculation, positions of atoms may be shifted (for instance y of Na2 from 0.5 to 0).

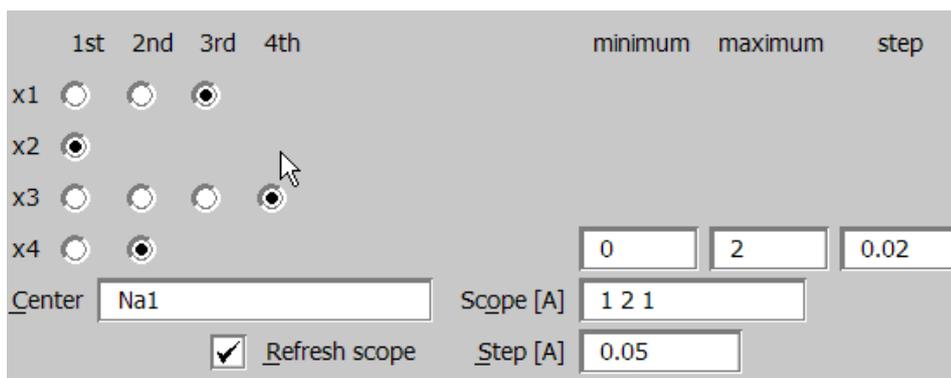
Press "New plot"

In the next dialogue select "General Contour procedure", "Calculate new ones" and "Draw maps as calculated"

[On the screen: Fourier commands, page Scope]

Change "Map axes" to plot sections x2-x4 instead of x1-x4: (Step 5)

## Step 5



### Notes

"Scope" has been refreshed automatically.

Fourier will calculate a four-dimensional parallelepiped  $x_2$ - $x_4$ - $x_1$ - $x_3$  with dimensions 2-?-1-1 Å. In  $x_4$ , the calculation will run over two periods: from 0 to 2 with step 0.02. The step in other directions will be 0.05 Å. The two-dimensional sections  $x_2$ - $x_4$  will be stacked along  $x_1$ ; the three-dimensional "sections"  $x_2$ - $x_4$ - $x_1$  will be stacked along  $x_3$ .

OK

[On the screen: the first  $x_2$ - $x_4$  section]

Press "Sum on" to merge the sections (select summation over  $x_1$  and  $x_3$ ) (Step 6)

[On the screen: merged sections  $x_2$ - $x_4$  with modulation curve of Na1]

Press "New plot"

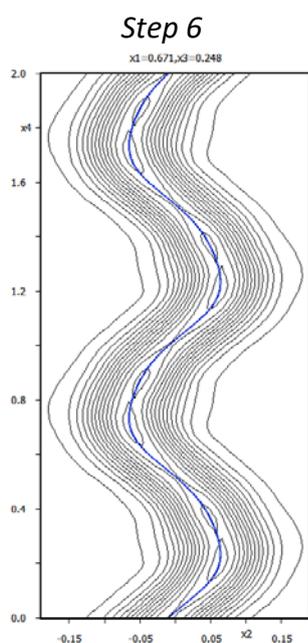
In the next dialogue select "General Contour procedure", "Calculate new ones" and "Draw maps as calculated"

[On the screen: Fourier commands, page Scope]

Switch to page "Basic"

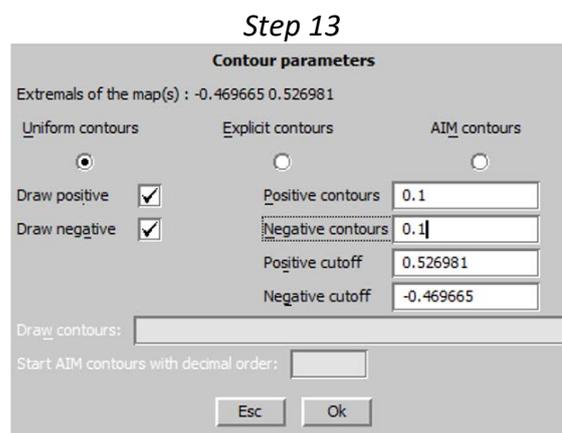
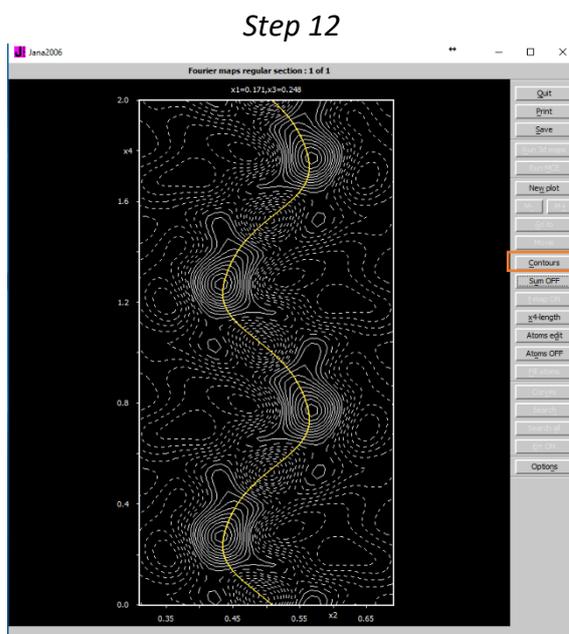
For "Map type" select "F(obs)-F(calc) - difference Fourier" (Step 7)

OK



Press "Sum on" and merge the sections (Step 8)

Press "Contours" and define step 0.1 for both positive and negative contours (Step 9)



[On the screen: merged difference section  $x_2-x_4$ ]

#### Notes

The difference peaks about  $0.5 e^-/A^3$  indicate modulation of ADP

### 3. De Wolff sections – automatic generation

The process described above could be repeated for other atoms of the structure but usually we can use the automatic procedure described here. Limitation of this automatic procedure is that all calculated sections have the same parameters (scope, width, summation ...)

Start Contour and press “New plot”

Select “Show de Wolff’s sections”

For “New map to draw” select “F(obs) – Fourier”

Define limits of  $x_4$ , primary and secondary scope, and interpolation step (Step 1)

Primary scope means the scope of the coordinate displayed in the plot; secondary scope means the scope of the other two coordinates. Sections will be automatically summed.

Press “Define atoms for de Wolff’s sections”

Using the List button, select all atoms, press “Select section for all three coordinates”, and press “Add”. (Step 2)

OK; OK

### Step 1

General contour procedure     Show de Wolff's sections

New map to draw:

	minimum	maximum	step	Primary	Secondary
x4	<input type="text" value="0"/>	<input type="text" value="2"/>	<input type="text" value="0.02"/>	<input type="text" value="2"/>	<input type="text" value="1"/>

Sum maps over secondary sections    Step [A]

Update existing sections

### Step 2

atdewolff 111 Na1 Na2 Na3 O1 O2 C1

Load      Add

Atoms

Calculate de Wolff's sections for:
  x1-x4     x2-x4     x3-x4

### Notes

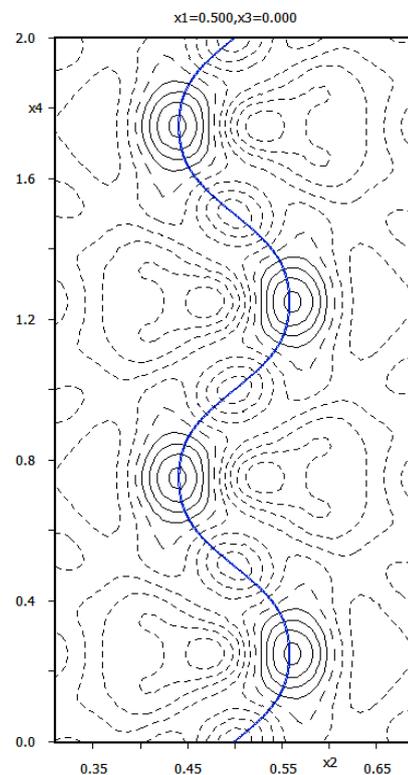
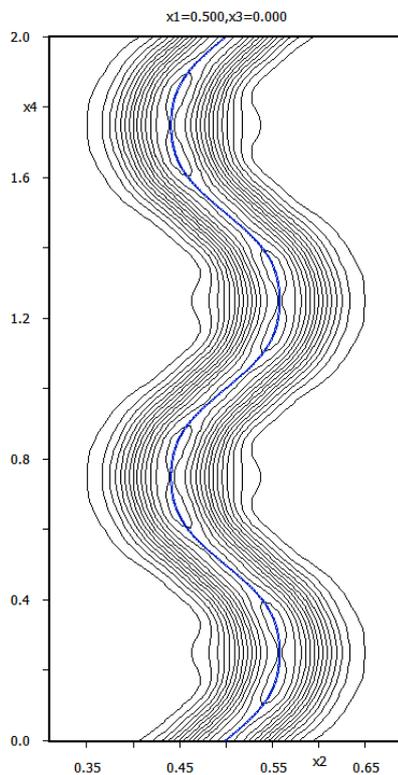
Contour calculates the de Wolff section as defined: for each atom, sections x1-x4, x2-x4 and x3-x4 will be calculated, with scope 2 1 1, 1 2 1 and 1 1 2, respectively, with step 0.02. The coordinate x4 will be calculated for two periods with step 0.02.

In Contour, press "W+" "W-" for displaying the sections.

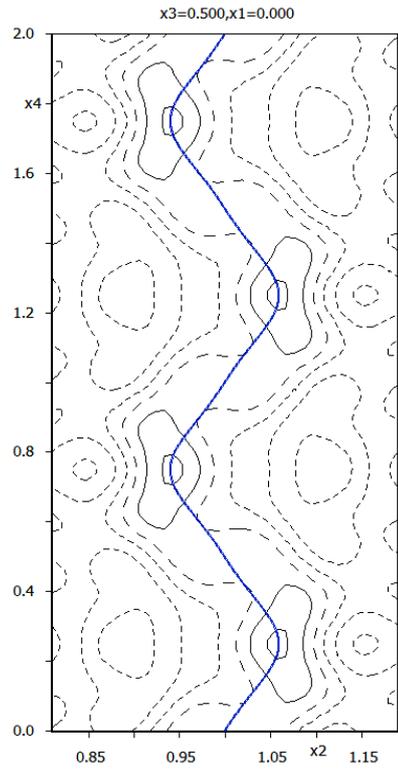
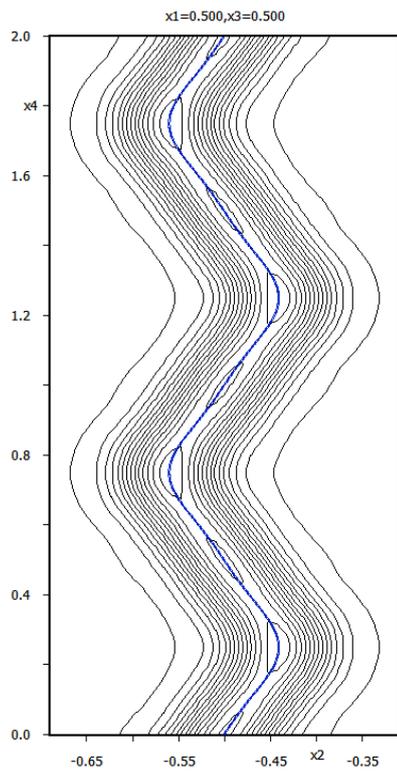
Repeat the same procedure for "F(obs)-F(calc) – difference Fourier" sections

### Notes

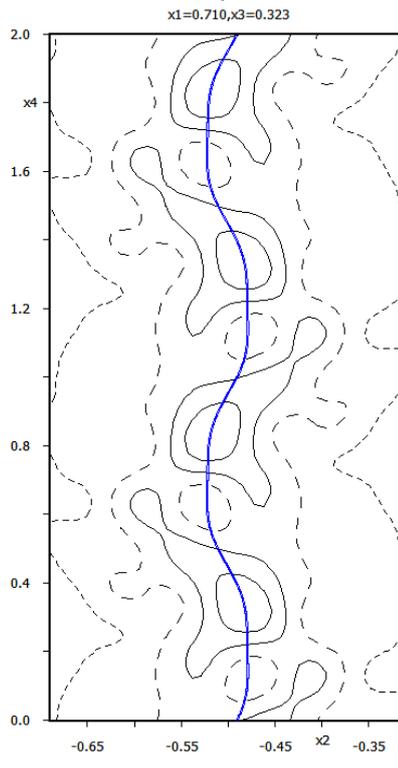
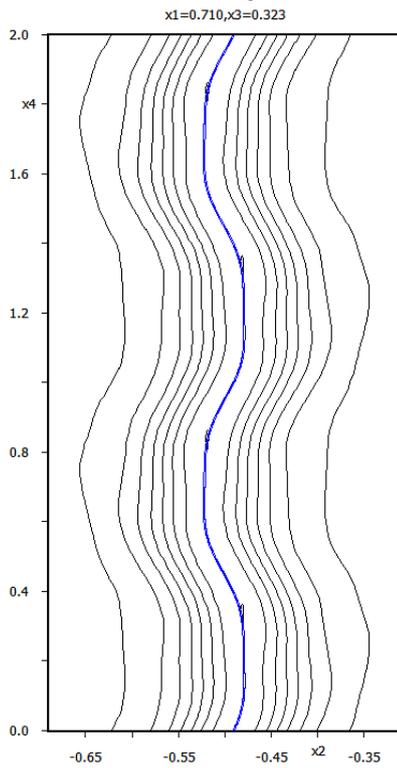
Selected sections are displayed here with the contour step 0.1):



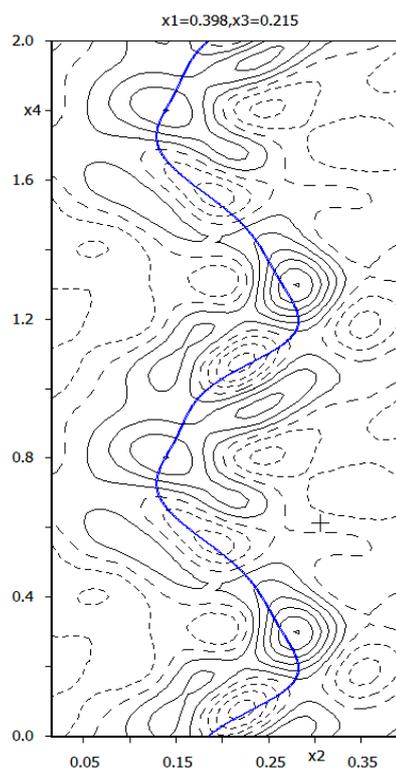
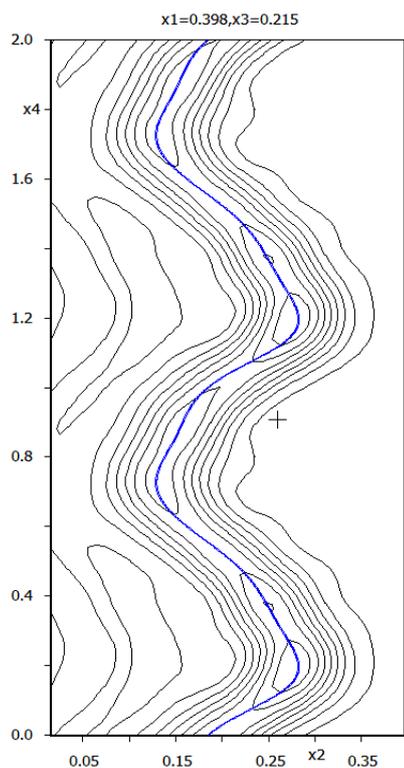
x2-x4 for Na2: observed and difference Fourier map



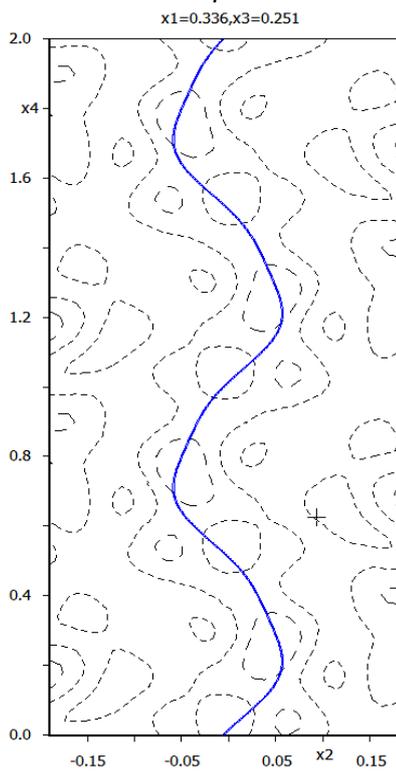
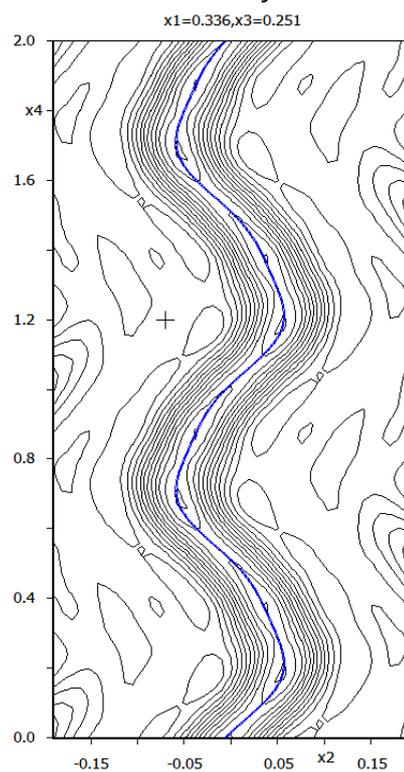
*x2-x4 for Na3: observed and difference Fourier map*



*x2-x4 for O1: observed and difference Fourier map*



*x2-x4 for O2: observed and difference Fourier map*



*x2-x4 for C1: observed and difference Fourier map*

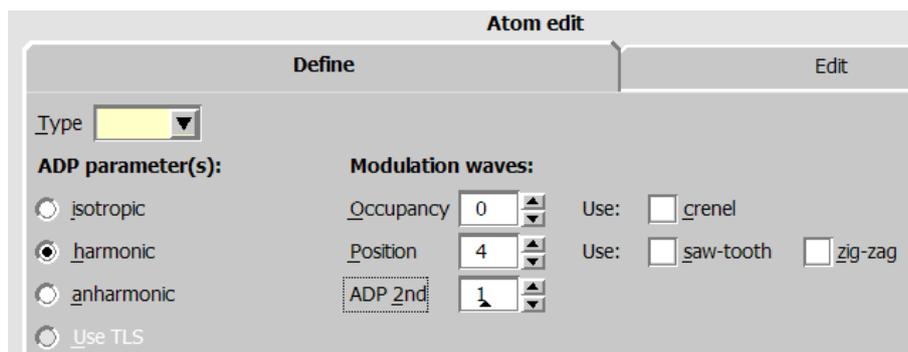
*For C1 no ADP modulation is indicated in the difference Fourier sections*

#### 4. Refinement of ADP modulations

Start "Edit Atoms"

Select all atoms except carbon and add one ADP modulation wave (Step 1)

### Step 1



#### Notes

The corresponding textbox has the label "ADP 2<sup>nd</sup>" which means we will setup modulation for the second order harmonic tensor ADP (ellipsoid)

Run refinement

$R_{obs}$  factors: 6%, 5%, 5%, 7%, 12%, 20%

Start "Edit/View → editing of M40 file".

#### Notes

This is the structure parameters file M40. Each atom has four modulation waves (number of waves and 24 parameters indicated in red) and – except carbon – one ADP modulation wave (number of ADP modulation waves and 12 parameters indicated in blue)

```

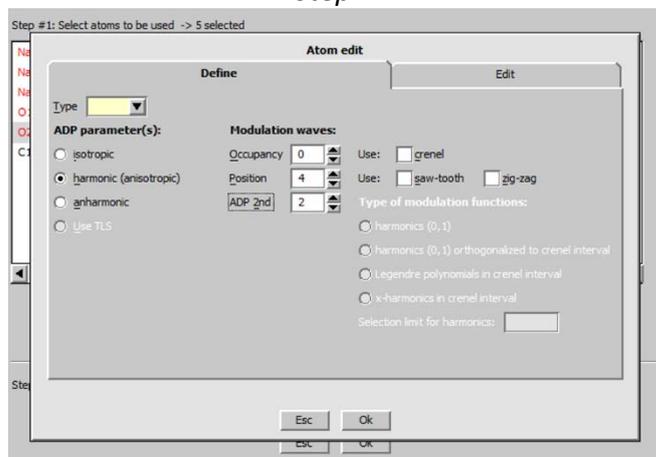
Na1      1  2      0.500000 0.670641 0.000000 0.247961      000 0  4  1
0.019755 0.023192 0.028421 0.000000 0.008258 0.000000      0101111010
0.000000 0.065455 0.000000 0.000000-0.005129 0.000000      010010
-0.001028 0.000000-0.001123 0.001502 0.000000 0.004475      101101
0.000000 0.001068 0.000000 0.000000-0.003381 0.000000      010010
0.001307 0.000000 0.000797 0.000771 0.000000 0.000106      101101
0.000000 0.000000 0.000000 0.000228 0.000000-0.001917      000101
0.000000 0.000000 0.000000 0.004284 0.000000 0.001486      000101
0.000000
  
```

Close the editor

Start "Edit Atoms"

Select all atoms except C1 and add another ADP modulation wave (Step 1)

### Step 1



## Repeat refinement

$R_{obs}$  factors: 5%, 4%, 4%, 5%, 9%, 14%

### Notes

According to de Wolff sections, O1 has the second smallest position modulations. Because ADP modulation usually corresponds to changes in environment of an atom due to position modulation, we should check whether ADP modulation of O1 is reasonable.

Remove ADP modulation of O1

Run refinement

Add one ADP modulation wave for O1

Run refinement

Add another ADP modulation wave for O1

Run refinement

### Notes

The first ADP modulation wave of O1 has improved fit significantly. For the second ADP wave the improvement was not so evident. Therefore, for O1 we shall use maximally two ADP waves.

For the remaining atoms we shall add ADP waves one-by-one to see where to stop.

Add the 3<sup>rd</sup> ADP modulation wave for Na1

Run Refinement

$R_{obs}$  factors: 4.5%, 3.8%, 3.5%, 5.3%, 8.8%, 14.2%

Add the 4<sup>th</sup> ADP modulation wave for Na1

Run Refinement

$R_{obs}$  factors: 4.5%, 3.8%, 3.5%, 5.2%, 8.6%, 14.3%

Remove the 4<sup>th</sup> ADP modulation wave for Na1

Run Refinement

Add the 3<sup>rd</sup> ADP modulation wave for Na2

Run Refinement

$R_{obs}$  factors: 4.5%, 3.8%, 3.5%, 5.3%, 8.8%, 14.2%

Remove the 3<sup>rd</sup> ADP modulation wave for Na2

Run Refinement

Add the 3<sup>rd</sup> ADP modulation wave for Na3

Run Refinement

$R_{obs}$  factors: 4.5%, 3.8%, 3.5%, 5.3%, 8.8%, 14.2%

Remove the 3<sup>rd</sup> ADP modulation wave for Na3

Run Refinement

Add the 3<sup>rd</sup> ADP modulation wave for O2

Run Refinement

$R_{obs}$  factors: 4.3%, 3.7%, 3.3%, 5.0%, 8.0%, 13.6%

Add the 4<sup>th</sup> ADP modulation wave for O2

Run Refinement

$R_{obs}$  factors: 4.2%, 3.8%, 3.2%, 4.6%, 8.0%, 12.0% (for 196 parameters)

*Finally, we shall optimize position modulation of carbon:*

Remove the 4<sup>th</sup> position modulation wave for C1

Run Refinement

*R<sub>obs</sub> factors: 4.2%, 3.8%, 3.2%, 4.7%, 8.1%, 12.0%*

Remove the 3<sup>rd</sup> position modulation wave for C1

Run Refinement

*R<sub>obs</sub> factors: 4.9%, 3.8%, 4.0%, 6.0%, 9.9%, 16.0%*

Return the 3<sup>rd</sup> position modulation wave for C1

Run Refinement

*R<sub>obs</sub> factors: 4.2%, 3.8%, 3.2%, 4.7%, 8.1%, 12.0% (for 192 parameters)*

Notes

*This is the final selection of modulation waves:*

Atom	Position waves	ADP waves
Na1	4	3
Na2	4	2
Na3	4	2
O1	4	2
O2	4	4
C1	3	0

**5. Extinction correction**

Start "Edit/View → View of Refine"

Press "GoTo" and select "Statistics Fo, sin(th)/lambda after refinement"

Notes

limits	10.4	13.6	17.1	22.0	30.3	44.2	73.5	965.1	unobs
number +	268	258	275	289	270	291	320	361	1895
-	313	320	305	291	310	288	259	219	3311
together	581	578	580	580	580	579	579	580	5206
av. wd F	4.6182	3.9657	2.9889	3.1684	4.2275	3.8626	3.0546	8.7431	1.0430
numerator +	372.8	440.8	390.4	433.6	381.7	374.7	454.5	1364.0	5674.4
-	-467.1	-451.3	-432.0	-399.5	-398.5	-363.8	-302.8	-1219.1	-7687.5
together	839.8	892.1	822.3	833.1	780.3	738.5	757.3	2583.1	13361.9
denominator	4992.4	6944.8	8847.7	11228.5	15085.1	21262.0	32687.9	97153.0	18962.2
R factor	16.82	12.85	9.29	7.42	5.17	3.47	2.32	2.66	70.47

*The shell of the strongest reflections has R factor 2.66% while the next strongest shell has 2.32%.*

Close the refinement listing

Start "Parameters → Extinction"

Select Isotropic, Type1, Gaussian; OK; Yes to rewrite changes

Run refinement

*R<sub>obs</sub> factors: 4.1%, 3.6%, 3.2%, 4.7%, 8.1%, 12.0% (for 193 parameters)*

Check refinement listing

Notes

limits	10.4	13.6	17.1	22.0	30.3	44.2	73.5	965.1	unobs
number +	268	262	276	294	275	291	316	361	1906
-	313	316	304	286	305	288	263	219	3300
together	581	578	580	580	580	579	579	580	5206
av. wd F	4.6520	3.9822	3.0041	3.2127	4.2791	4.0000	3.0451	7.3043	1.0465
numerator +	377.6	449.2	400.8	445.2	392.5	384.3	449.8	1574.0	5709.5
-	-464.3	-444.9	-421.8	-391.1	-390.6	-362.7	-310.5	-835.0	-7638.4
together	841.9	894.0	822.6	836.3	783.1	747.0	760.4	2409.0	13347.9
denominator	4992.4	6944.8	8847.7	11228.5	15085.1	21262.0	32687.9	97153.0	18962.2
R factor	16.86	12.87	9.30	7.45	5.19	3.51	2.33	2.48	70.39

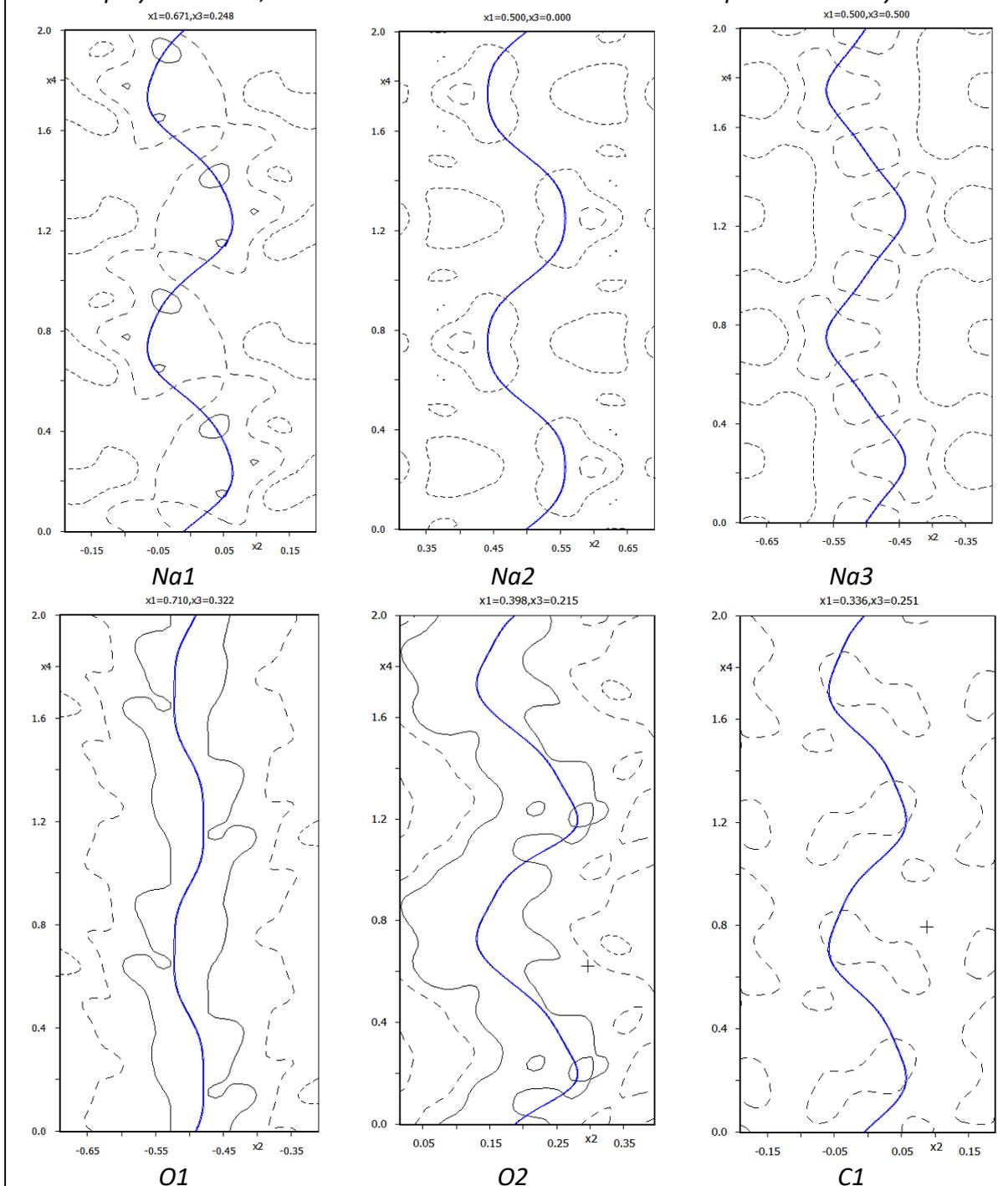
*The partial R factor for the strongest reflections is better (2.48%) but still slightly worse than the neighboring shell.*

## 6. Final check of Fourier sections

Using the same tool like before, plot de Wolff sections  $x_2$ - $x_4$  through the difference Fourier map for all atoms of the final structure model. The checkbox “update existing sections” must be selected.

### Notes

The following sections are displayed for the contour step 0.1. This must be set manually for each displayed section, otherwise Contour selects the contour step automatically.



Use "File → Structure → Save As" and create backup copy "naco\_final"

## V. Interpretation of results

### 1. Plotting of sodium carbonate with Diamond

#### Notes

*In this part names of atoms and position of the origin may differ from your results*

Start "Plot structure"

#### Notes

*In the following dialogue, we can plot either the average structure or the approximant structure. Average structure plot uses the reference positions of the basic structure and 3d symmetry. For approximant structure, Jana2006 expands the modulated structure to a user-defined area. Then the expanded structure is exported to the plotting software with P1 symmetry. In the plotting software (here Diamond), no symmetry operations are allowed including translations! The reason is that the plotting software cannot calculate corresponding modulation displacements.*

Select "Draw average structure"; start "Draw+continue"

[On the screen: Diamond]

Use Ctrl-A and Delete to remove an automatically created plot (if present)

Go to "Build → Fill → Super cell" and select "3x3x3" supercell

"Picture → Viewing direction → c"

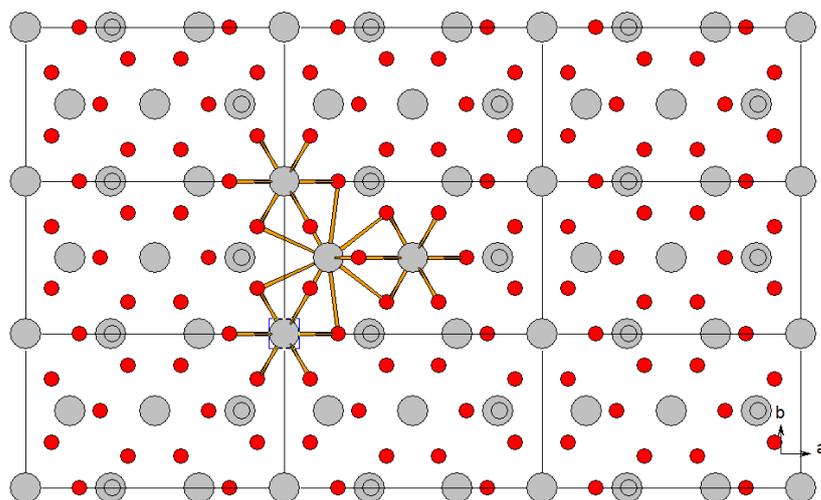


to plot unit cells

Go to "Build → Add cell edges" to define how many unit cells should be visible

"Objects → Coordinate system" to see axes

By selecting column of atoms and pressing  you can create the following figure:



*This plot allows for estimation which supercell we shall need for plotting of approximant structure. We shall use supercell 2 x 3 x 10*

Close Diamond without saving

[On the screen: basic window of Jana2006]

Start "Plot structure"

Select "Draw approximant structure" and define supercell 2 x 3 x 10 (Step 1)

### Step 1

Atom filter    Add Fourier peaks    Reset selection

0/0 ... number of excluded atoms/number of included peaks

Draw average structure

Draw supercell structure

Draw approximant structure

x from 0 to 2     step 0,1

y from 0 to 3     step 1

z from 0 to 10

Cutoff occupancy 0.5

tzero 0

Check short distances in the approximant

Min. distance

Keep atom names (duplicity could appear)

Change atom names to "atom\_type"+number

Draw+return    Quit    Draw+continue

### Notes

"Keep atom names" means that labels in Diamond will contain the original names from M40 followed by a sequence number".

Start "Draw + continue"

### [On the screen: Diamond]

Use  to add all atoms of the approximant to the plot. No operation creating new atomic positions is allowed

"Picture → Viewing direction → c"



to connect atoms

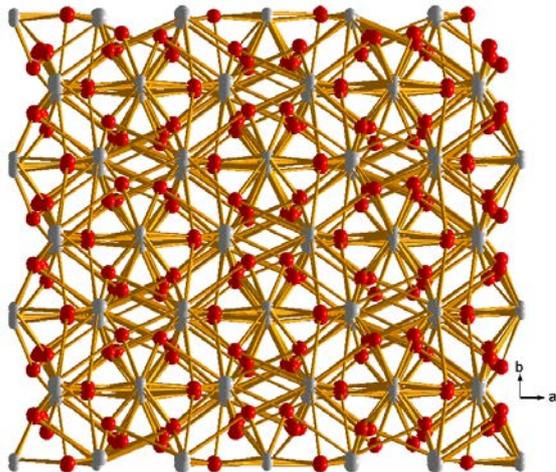
On the right sidebar switch to "Table of atom groups"

Right-click Na, press "Select atoms by group"

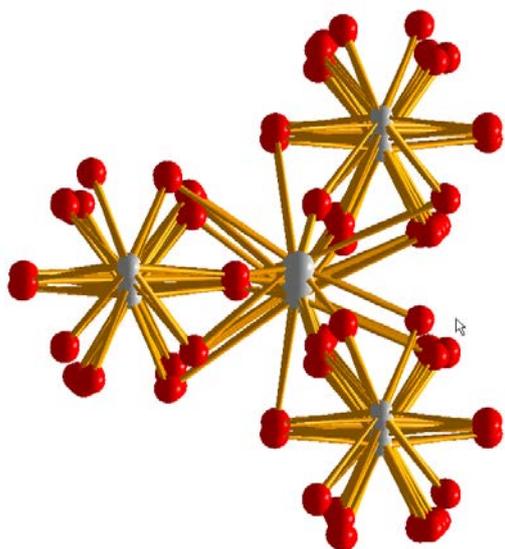
In the plot hit the right mouse button on some of the selected sodium atoms

From the context menu Select "Edit → Atom design"

Switch to the page "Radius" and define radius 0.2 Å



Using mouse and Delete (on the keyboard) and Ctrl-I (inverts selection) separate the following motif (three columns of sodium around the column of CO<sub>3</sub>):



(In case bonds obscure atoms too much, use Ctrl-A + Right click on a selected object + Edit → Atom design and change bond style from “thick” to “thin”)

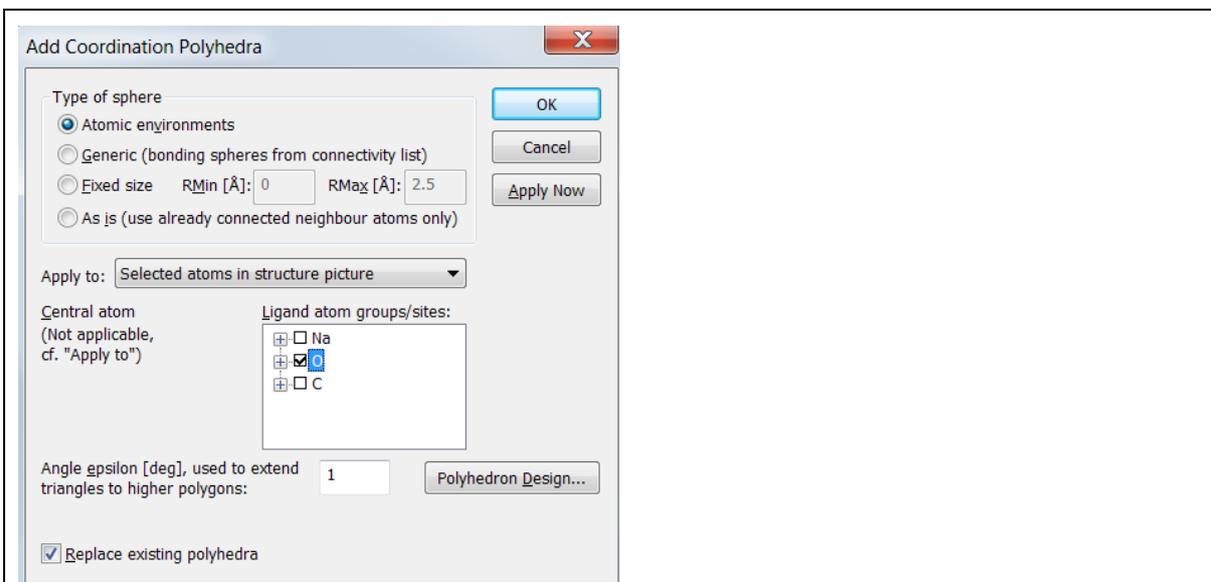
Note starting letters (Na1, Na2 or Na3) of labels of sodium atoms which are not in the middle of the plot

On the right sidebar switch to the table “Table of created atoms”

Order atoms by name and select the noted sodium atoms

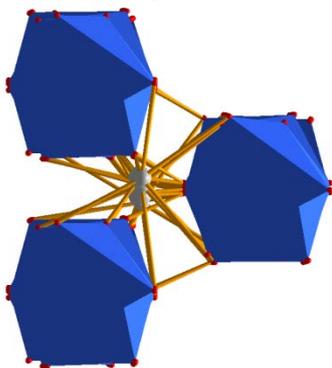
“Build → Polyhedra → Add coordination polyhedra”

Select oxygen for “Ligand atom groups”



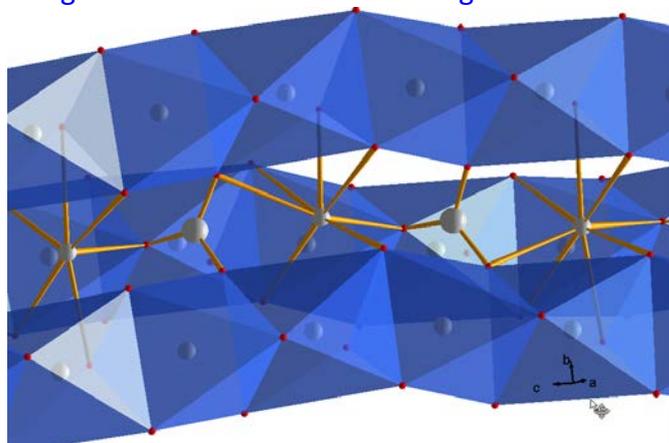
OK

With  make sure that Rendering and Lightning is activated  
The resulting plot will be:

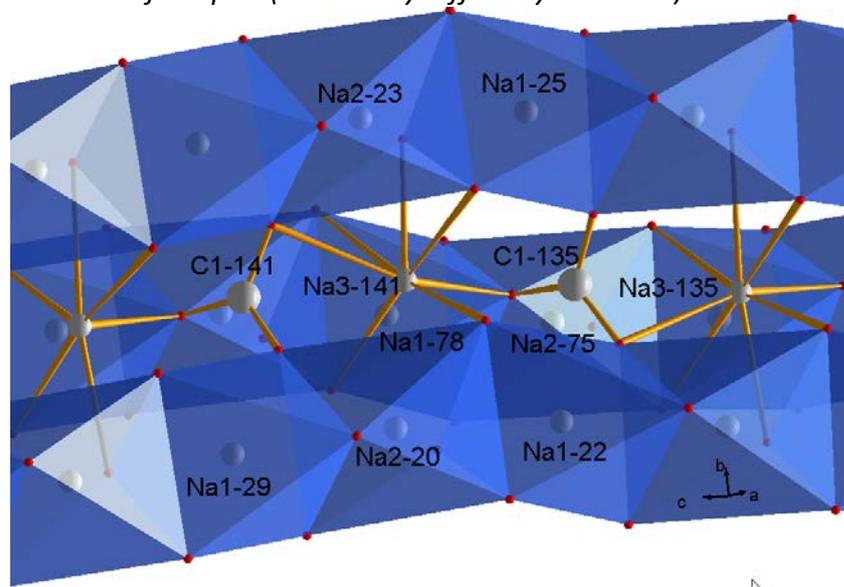


Press Ctrl-A to select all atoms  
Hit some of the selected objects with the right mouse button  
From the context menu select "Edit → Polyhedron design"  
Define transparency 0.4; OK

Using rotations   and zooming tool  create the following figure:



Select some sodium and carbon atoms  
 Hit one of them with the right mouse button  
 From the context menu select "Add → Atom labels"  
 For "Relative position" type "0 0 10". The last number will move the labels above the polyhedra  
 Correct positions of labels with mouse  
 This is the final plot (labels may differ in your result):



In the middle column the CO<sub>3</sub> groups alternate with Na atoms.

## 2. Properties of CO<sub>3</sub> anion

Start commands for Dist (click right mouse button on Dist icon)  
 In "Basic" page select "d(max) derived from atomic radii and typical distances"

### Notes

Jana uses typical distances from International Tables. When a typical distance is not available, atomic radius is used instead. The d(max) value is expanded by user defined %. Both typical distances and atomic radii can be changed in EditM50-Page Composition

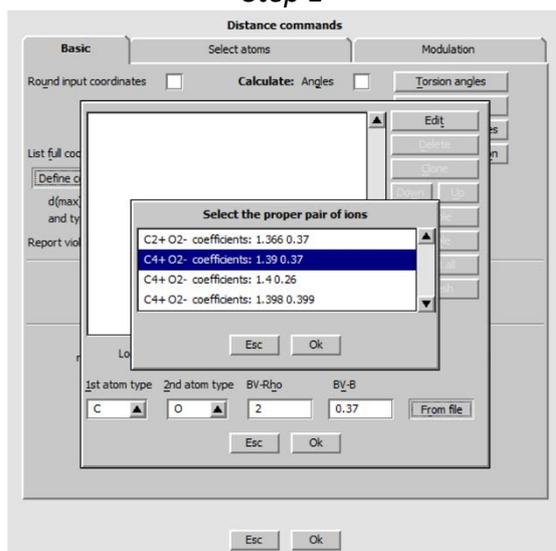
For "Listing form", select "Without symmetry codes"  
 Press "Define coefficients for bond valences"  
 [On the screen: dialogue for definition of bond valence constants]  
 Select "1<sup>st</sup> atom type" carbon, "2<sup>nd</sup> atom type" oxygen  
 Press "From file" and select constants given in the second line (Step 1)

### Notes

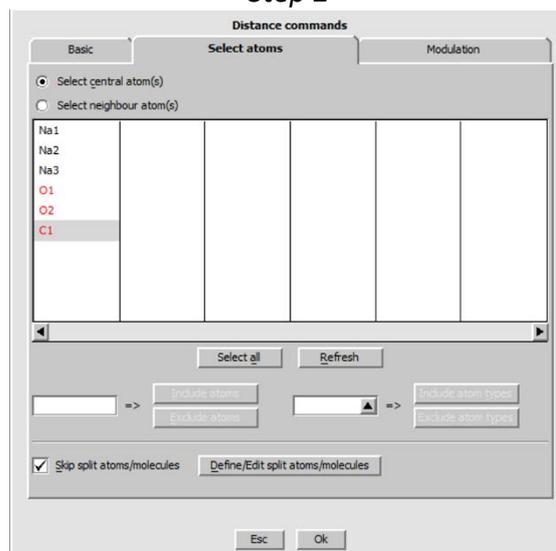
The list displays bond valence constants from various literature sources

Add; OK  
 [On the screen: Distance commands]  
 Switch to the page "Select atoms"  
 Press "Refresh"; for central atom select (with ctrl-left mouse button) C1  
 For neighbor atoms select O1, O2 (Step 2)

### Step 1



### Step 2

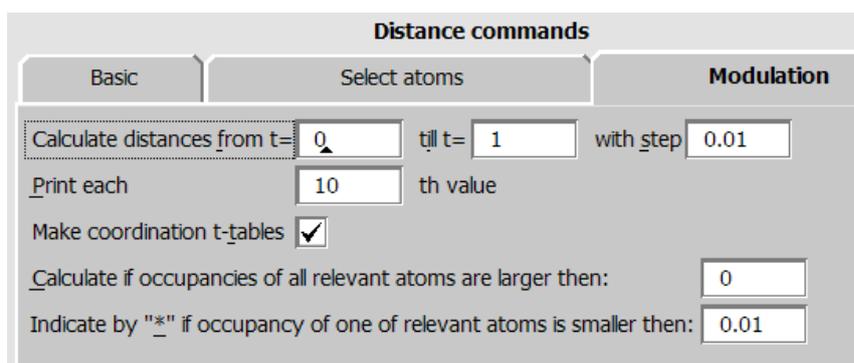


Switch to the page "Modulation"  
 Activate "Make coordination t-tables" (Step 3)

#### Notes

The default parameters for  $t$  have the following meaning: distances will be calculated for  $t$  between 0 and 1 with step 0.01, i.e. for 100 values of  $t$ . The 100 calculated distances will be used for calculation of  $d(\min)$ ,  $d(\max)$  and  $d(\text{ave})$  printed in the listing. These values will be followed by list of distances printed for each 10<sup>th</sup> value of  $t$ , i.e. for  $t$  between 0 and 1 with step 0.1

### Step 3



OK; YES+Start; YES to open listing  
 [On the screen: listing of Dist]  
 Use "Goto → List of distances"

#### Notes

Here the distances are shown as explained previously. The first distance (introduced with dotted line) is the distance between reference positions of the basic structure, which does not occur in the real modulated structure

Use "Goto → List of bond valences"

#### Notes

Here minimum, maximum and average BVS for carbon is printed  
At the bottom of the listing there is a Coordination table for carbon showing the three C-O distances for each step in t

Close listing of Dist

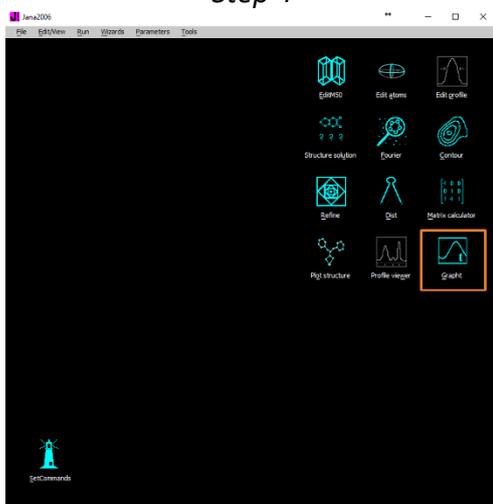
#### Notes

Similar information can be obtained from Grapht tool

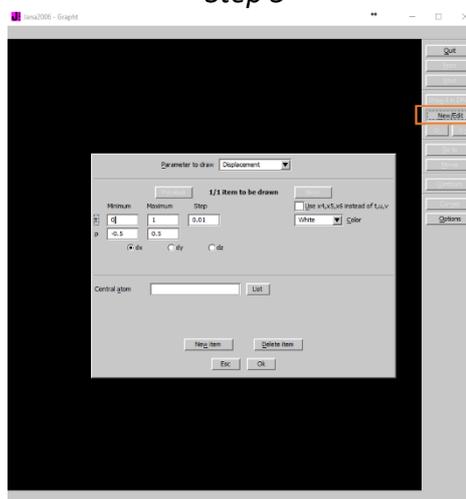
Start Grapht (Step 4)

Press "New/Edit" (Step 5)

Step 4



Step 5



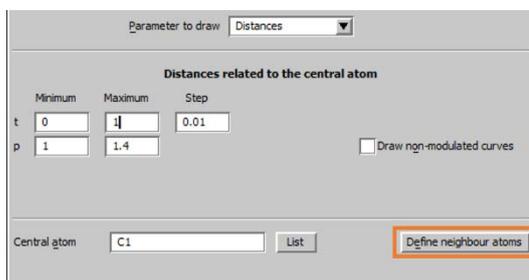
For "Parameter to draw" select "Distances" (Step 6)

For "p" type lower limit 1 and upper limit 1.4

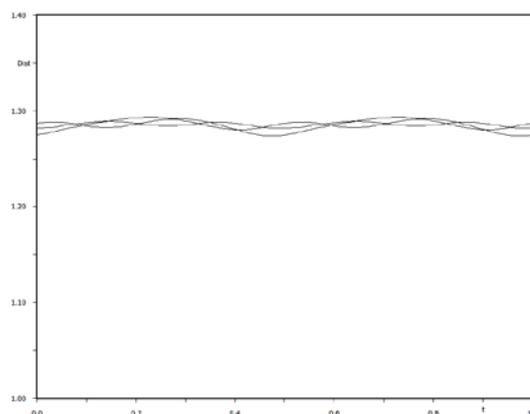
"p" stands for "parameter" to be drawn

For "Central atom" type C1

Step 6



[On the screen: Plot of three C-O distances as a function of t]



Press "Define neighbor atoms" and select O1, O2

OK; OK

## Notes

As we have already seen in *Dist* listing, C-O distances are almost constant over the whole interval of *t*

Press "New/Edit"

Change "Parameter to draw" to "Bond valence sum" (Step 7)

For "p" change lower limit to 3.5 and upper limit to 4.2

Press "Define bond valence coefficients"

OK; OK

### Step 7

Parameter to draw: Bond valence sum

Bond valence sum for the central atom

Minimum	Maximum	Step
0	1	0.01

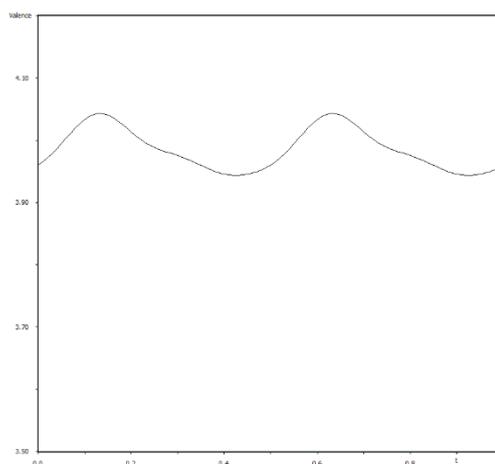
p: 3.5 to 4.2

Central atom: C1

Maximal distance: 3

Buttons: Define neighbour atoms, Define bond valence coefficients, Esc, Ok

[On the screen: Plot C1 Bond valence sum as a function of *t*]



## Notes

Using the mouse cursor, we can find the fluctuation of BVS is between 3.94 and 4.04  
Both *Graph* and *Dist* confirm the C-O bonds are constant. Now we shall check planarity of the CO<sub>3</sub> group:

Start "Edit Atoms"

Select atoms **only** O1, O2 and C1

Choose Action "Make symmetrically contiguous motif"

OK; YES to save changes

## Notes

With this procedure we transformed positions of C1, O1 and O2 to be connected without need of symmetry transformation

Start commands for *Dist*

In page "Basic" for "Listing form" check "With symmetry code" (Step 8)

In Page "Select atoms" make sure the central atoms is still carbon and the neighbor atoms are oxygens

OK; YES+Start; YES to open the listing

"Goto → List of distances"

## Step 9

Distance commands

Basic Select atoms Modulation

Round input coordinates  Calculate: Angles  Torsion angles

Best planes

Individual distances

Reference direction

List full coordination

Define coefficients for bond valences  d(min)

d(max) derived from atomic radii and typical distances  expanded by  %

Report violations of the Hirschfeld's condition if U(proj) >  % u.u.

Listing form

Without symmetry code  With symmetry code

Include peaks from Fourier calculation

none  maxima  minima  both

Esc OK

[On the screen: List of distances]

```
Distances concerning atom C1
=====
C1-O1      1.2792 (5)      2nd: O1      x, y, z
ave : 1.2859 (13)  min : 1.2819 (13)  max : 1.2892 (13)
C1-O2      1.2621 (3)      2nd: O2      x, y, z
ave : 1.2853 (17)  min : 1.2741 (17)  max : 1.2937 (17)
C1-O2      1.2621 (3)      2nd: O2#s4   x, -y, z
ave : 1.2854 (17)  min : 1.2741 (17)  max : 1.2937 (17)
-----
```

## Notes

There are three distances: C1-O1, C1-O2 and C1-O2. For the third distance, C1-O2, oxygen O2 must be transformed from the position given in M40 by the symmetry operation  $x, -y, z$ , which is encoded to the Jana symmetry code #s4 (i.e. the fourth symmetry operation). Other distances do not need a transformation because "Symmetry contiguous motif" has been created in the previous step

**Symmetry codes of may differ for various Superflip runs! (for example #s4t0,1,0)**

Close the listing of Dist

Start commands for Dist

In page "Basic" press the button "Best Planes"

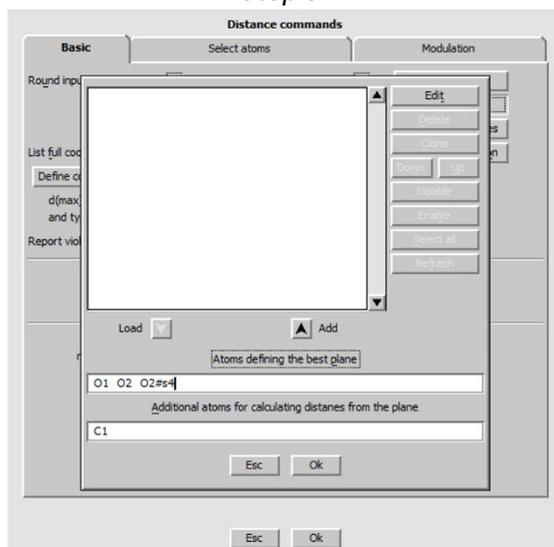
For "Atoms defining the best plane" type "O1 O2 O2#s4" (Use your symmetry code for O2)

For "Additional atoms" type C1 (Step 9)

Add; OK; OK; YES+Start; YES to open listing

"Goto → List of best planes"

## Step 9



[On the screen: List of best planes]

```
*****
* List of best planes *
*****
Equation of best plane through atoms : o1 o2 o2#s4
8.8895*x+0.0000*y-1.7967*z-1.3592 = 0   ChiQ = 0.000
(1)      (3)      (8)      (5)

Atom name :          o1          o2          o2#s4          c1
Distance from plane : 0.0000(5)  0.0000(4)  0.0000(4)  -0.6238(5)

t          A          B          C          D          Distances
0.000      8.9051     0.1888     -1.6340     -1.5447     0.000 0.000 0.000 -0.428
0.100      8.8973     0.0210     -1.8103     -1.3475     0.000 0.000 0.000 -0.606
0.200      8.8571     -0.1983     -1.9452     -1.1665     0.000 0.000 0.000 -0.821
0.300      8.8518     -0.2382     -1.9574     -1.1326     0.000 0.000 0.000 -0.860
0.400      8.8578     -0.1971     -1.9421     -1.1540     0.000 0.000 0.000 -0.821
0.500      8.8562     -0.1715     -1.9585     -1.1309     0.000 0.000 0.000 -0.798
0.600      8.8814     -0.0198     -1.8471     -1.3004     0.000 0.000 0.000 -0.648
0.700      8.9096     0.2006     -1.8926     -1.4271     0.000 0.000 0.000 -0.413
0.800      8.9120     0.2545     -1.5095     -1.6988     0.000 0.000 0.000 -0.354
0.900      8.9099     0.2157     -1.5686     -1.6278     0.000 0.000 0.000 -0.398
1.000      8.9051     0.1888     -1.6340     -1.5447     0.000 0.000 0.000 -0.428
```

### Notes

The listing shows that the distance of C1 from the plane of oxygens does not change with the t coordinate which means the planarity of CO<sub>3</sub> is not influenced by modulation. At the next step, we will visualize how atoms of CO<sub>3</sub> group move during modulation.

Run refinement (at least zero cycles) to get input M80 for Fourier calculation  
 Start Fourier commands, select "Map type" "F(obs) – Fourier"  
 In the page "Scope" select "automatically", "Use default map orientation"  
 OK; YES+Start; do not include new atoms; do not open listing  
 Start Contour; New Plot  
 Select "General Contour procedure", "Use old map", "Draw a general section"; OK (Step 10)  
 [On the screen: form for definition of the general section]  
 For the first atom type O1  
 For the second atom type O2  
 For the third atom type O2#s4 (Use your symmetry code for O2)

### Notes

The three atoms define the plane of the section through the electron density map. The dimensions of the plot are defined in Scope

For "Scope" type "4 4 0"  
 For "Interpolation step" type "0.02"

### Notes

This means the plot will be 4x4 Å. Number of parallel sections calculated by the program is 1+s3/is, where "s3" is the width of the section and "is" is the interpolation step. Here it means one section, because the third parameter is zero.

For "First point put to" type "1 1 0" (Step 11)

### Step 10

General contour procedure     Show de Wolff's sections

New map to draw:

Use old maps     Draw maps as calculated

Calculate new ones     Draw a general section

The old map is F(obs) - Fourier

### Step 11

	Atom	Coordinates	
1st	<input type="text" value="O1"/>	<input type="text" value="0.789857 0 0.677631"/>	Difference to 1st
2nd	<input type="text" value="O2"/>	<input type="text" value="0.601607 0.2062 0.785329"/>	<input type="text" value="-0.18825 0.2062 0.107698"/>
3rd	<input type="text" value="O2#s4"/>	<input type="text" value="0.601607 -0.2062 0.785329"/>	<input type="text" value="-0.18825 -0.2062 0.107698"/>

Scope		
Interpolation step	Scope of section	1st point put to
<input type="text" value="0.02"/>	<input type="text" value="4 4 0"/>	<input type="text" value="1 1 0"/> [Ang]

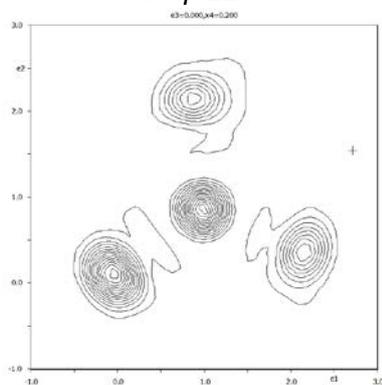
### Notes

The first point of the plot is O1. The horizontal axis of the plot will be O1-O2. The last atom O2#s4 will be above the horizontal axis.

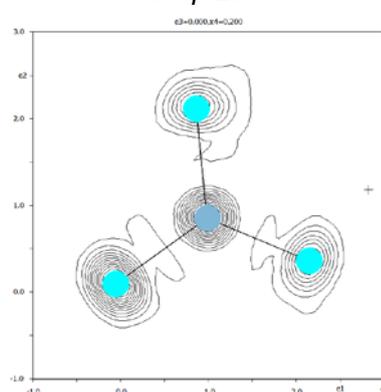
OK (Step 12)

Click the middle maximum and select all close atoms; OK (Step 13)

### Step 12



### Step 13



Press "Movie"; keep default parameters; OK

### Notes

The tool plots the successive sections calculated previously by Fourier for sequence of x4 values. Sampling in x4 can be changed in Fourier options, Page Scope.

ESC to break the movie

Press "t-map ON" and do the same animation for t-map.

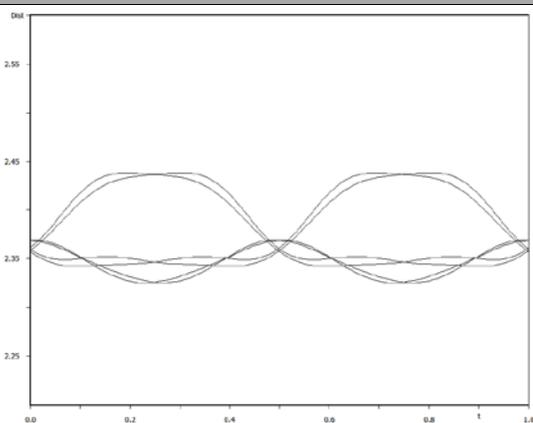
### Notes

For this case geometry of A3-A3 map is similar to that in R3-R3 map. Atoms of CO<sub>3</sub> are moving in phase and probably they could be described by rigid body. The position of one of oxygens is very stable comparing to the other atoms. This is the oxygen described with less ADP waves.

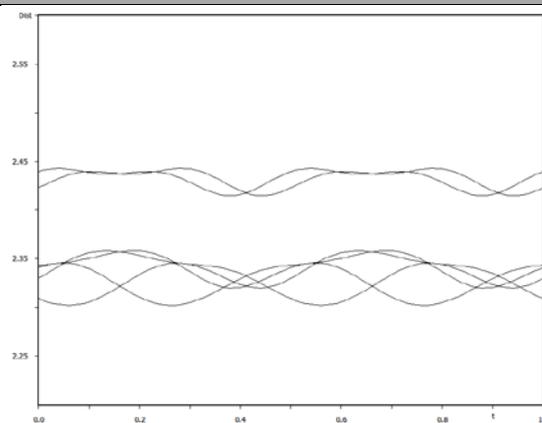
### 3. Sodium atoms

Using GraphT, plot Na-O distances for Na1, Na2 and Na3. In the GraphT dialogue select "Draw non-modulated curves" – they will appear in the plots like dashed lines indicating distances in the basic structure.

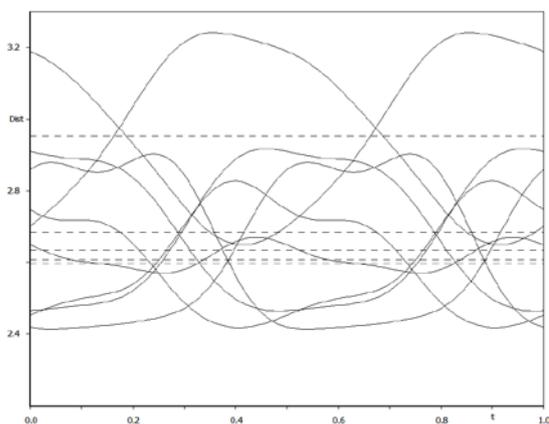
#### Notes



*Distances Na3-O*



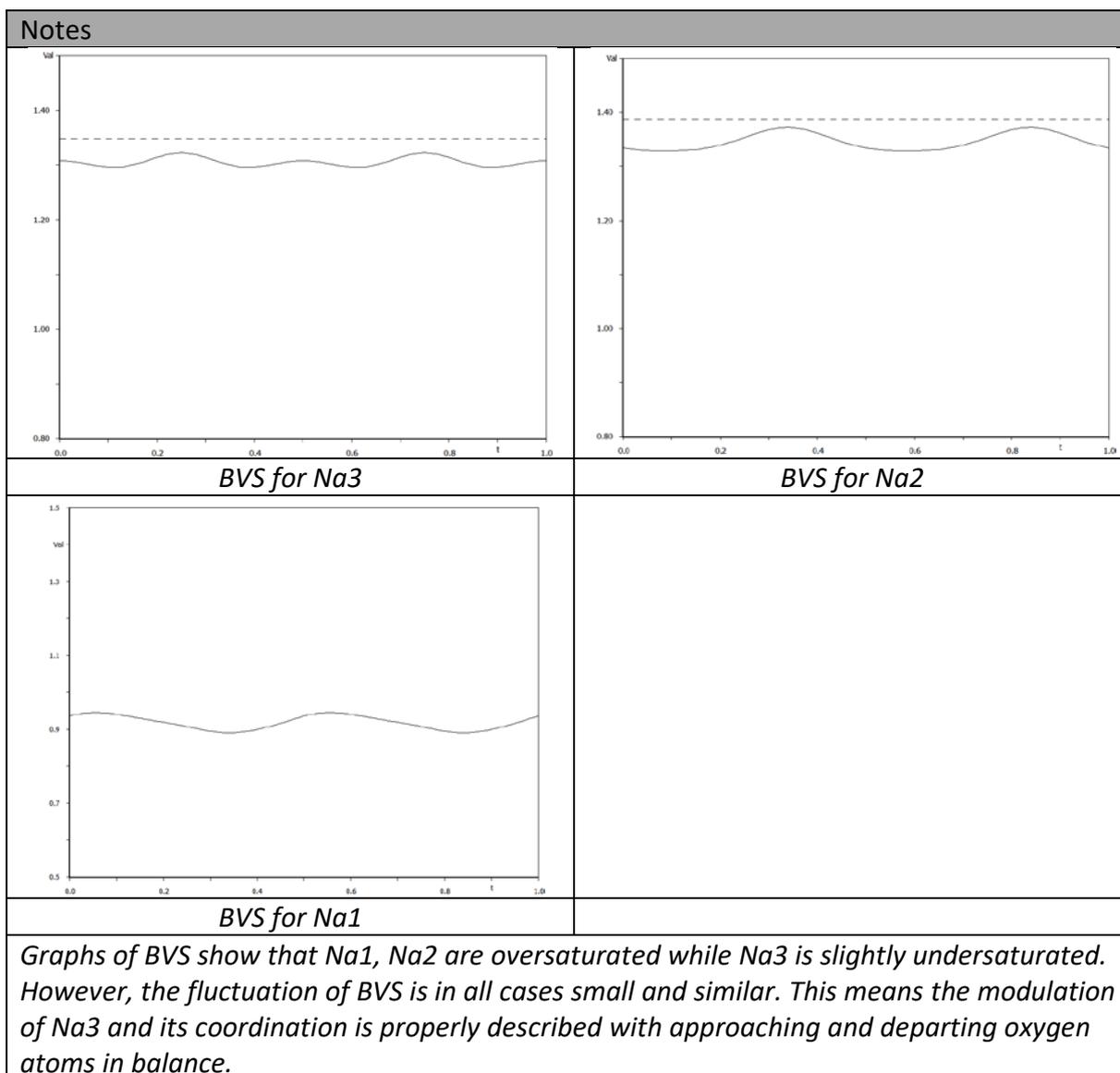
*Distances Na2-O*



*Distances Na1-O*

As it has been previously indicated by plot of the structure, Na1 which alternates with carbon in a column along *c*, has different coordination comparing with octahedrally coordinated Na2, Na3. Na1 has more neighbors with strongly varying distances which are all longer comparing with Na2 and Na3. Good test if this complicated model is reasonable provides plot of the bond valence sum.

Using Graph plot graphs of bond valence sums for Na1, Na2 and Na3 (do not forget to define coefficients for Na-O bond)



## References

---



# Example 5.3.1: CrPO data

CrysAlis data processing for the room temperature incommensurate phase of  $\text{Cr}_2\text{P}_2\text{O}_7$  measured with Nonius Kappa CCD diffractometer.

Revised: 07 September 2019

## $\text{Cr}_2\text{P}_2\text{O}_7$

Single crystal data measured with Nonius Kappa CCD four-cycle diffractometer

This example is based on the CrysAlis 171.40.53. CrysAlis is a program for control and data processing of Rigaku Oxford Diffraction (ROD) diffractometers. However, it can also read data from many other formats.

Data can be downloaded at [http://crysa.fzu.cz/jana/workshops/RT\\_data\\_Nonius.zip](http://crysa.fzu.cz/jana/workshops/RT_data_Nonius.zip) (for workshops, data should usually be available at flash disks)

Note: In the Example 5.3.2. (structure solution), we used different data set because of more pronounced disorder. This data set can be downloaded at

[http://crysa.fzu.cz/jana/workshops/CrPO\\_RT.zip](http://crysa.fzu.cz/jana/workshops/CrPO_RT.zip)

### 1. Starting CrysAlis

*For reading not-native data formats, CrysAlis first needs to open some existing structure just to show the CMD window. For this reason, we have created a folder "CrysAlis\_start" with a par file of some structure measured with ROD instrument.*

Start CrysAlis

In the dialogue that follows, use the button "Browse experiment", locate the folder "CrysAlis\_start" and select the file 2013\_E1\_2.par.

"Open selected"

For "Basic settings", select "Small molecule"; OK

OK for warning about par file

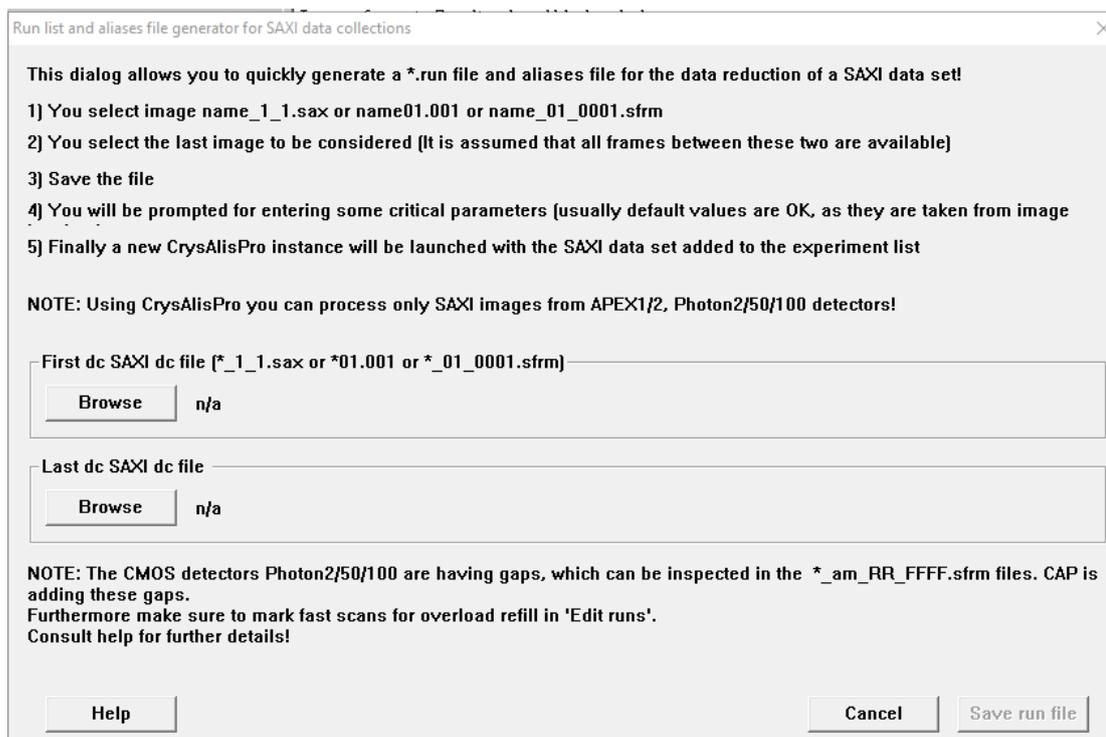
In the left toolbar, press button CMD

[On the screen: command shell]

Type the following command (case-independent): SAXI CREATERUNLIST

Press Enter

[On the screen: Run list and aliases generator for SAXI data collections]

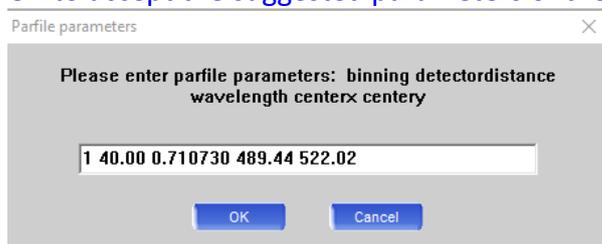


Browse for the first frame of the first run, i.e. CrPO\_RT\_01\_0001 in the folder RT\_data\_Nonius

Browse for the last frame of the last run, i.e. CrPO\_RT\_08\_0127

“Save run file”

OK to accept the suggested parameters of the experiment



[On the screen: Select experiment]

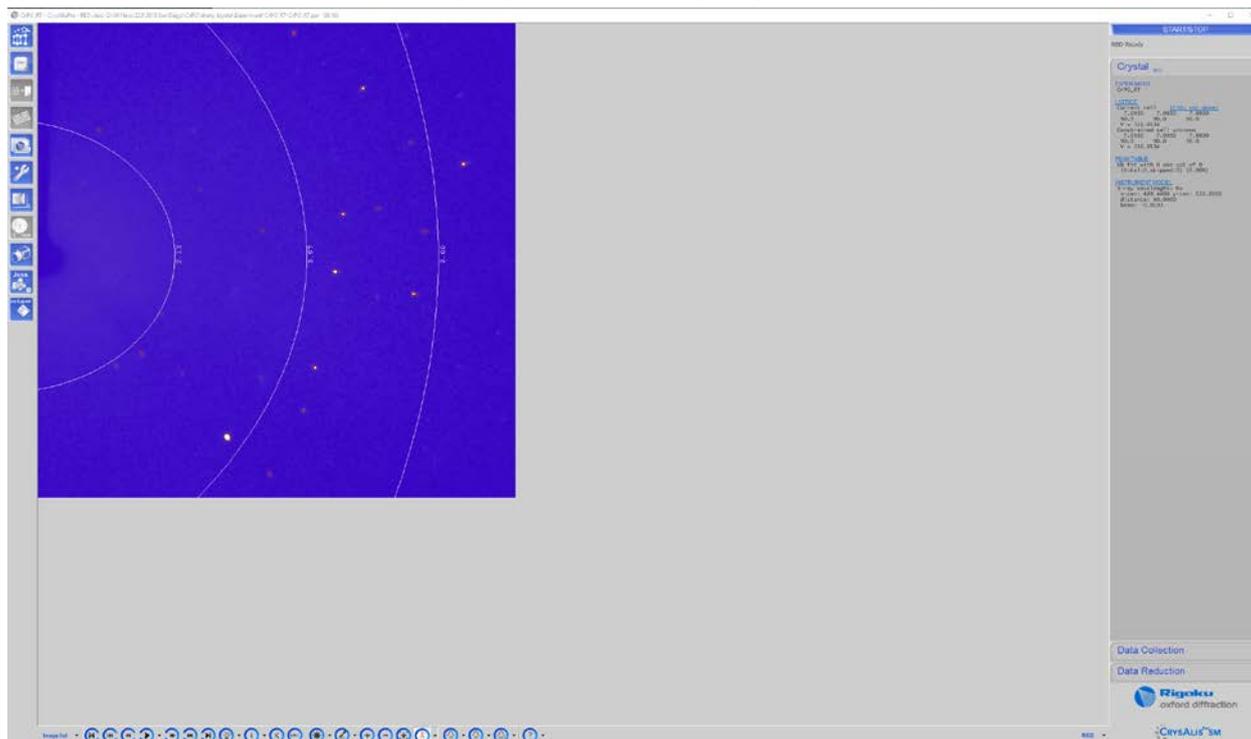
Highlight “CrPO\_RT”; Open selected

For “Basic settings”, select “Small molecule”; OK

At this point, CrysAlis opens the Nonius Kappa CCD experiment and displays the first frame

Use  at the bottom toolbar to decrease the image size

[On the screen: the basic window of CrysAlis with the first frame loaded]

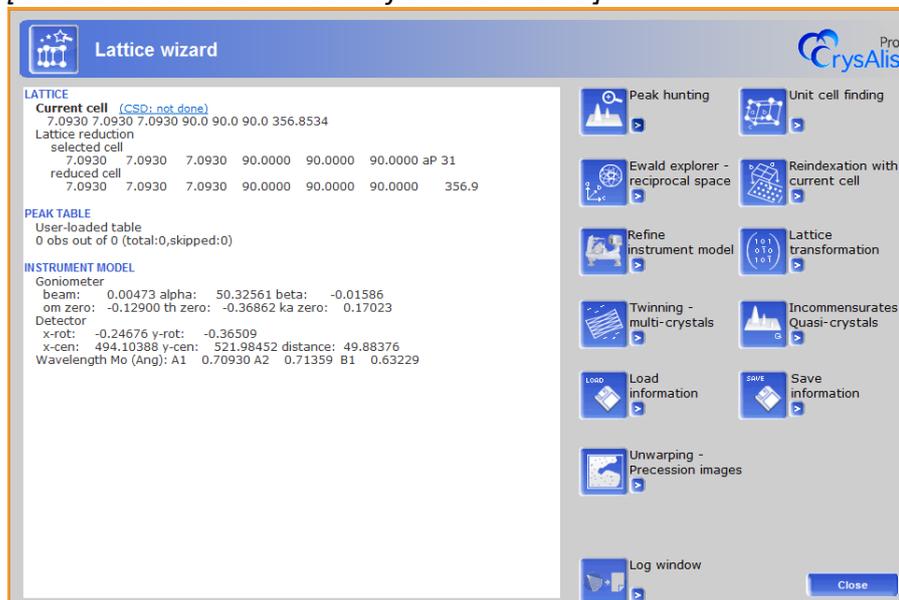


## 2. Determination of the unit cell



Start Lattice wizard using the button

[On the screen: the window of Lattice Wizard]



In this wizard, each button has a default function started by pressing the centre of the button and various optional functionalities, which are offered after pressing ">" part of the button

Start "Peak hunting" with default options

About 14000 peaks is found

Start "Unit cell finding" with default options

The program finds some unit cell and indexes about 35% of peaks

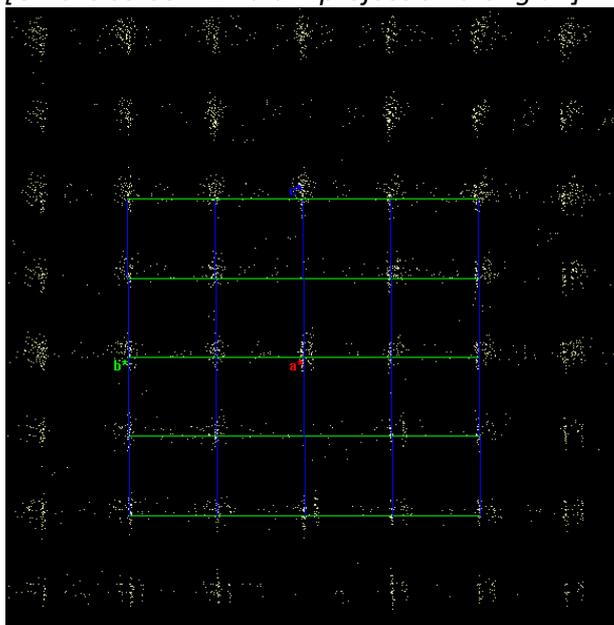


Start “Ewald Explorer” with default options

Use the buttons    to see projections of the found peaks along the unit cell axes.

Set projection along a\*

[On the screen: Ewald – projection along a\*]



Peak positions are located to clouds; this is typical for inexact instrument parameters.

Close “Ewald Explorer” and return to the Lattice wizard



Press  to refine instrument parameters

Repeat Unit cell finding

Repeat refinement of instrument parameters

Repeat Unit cell finding

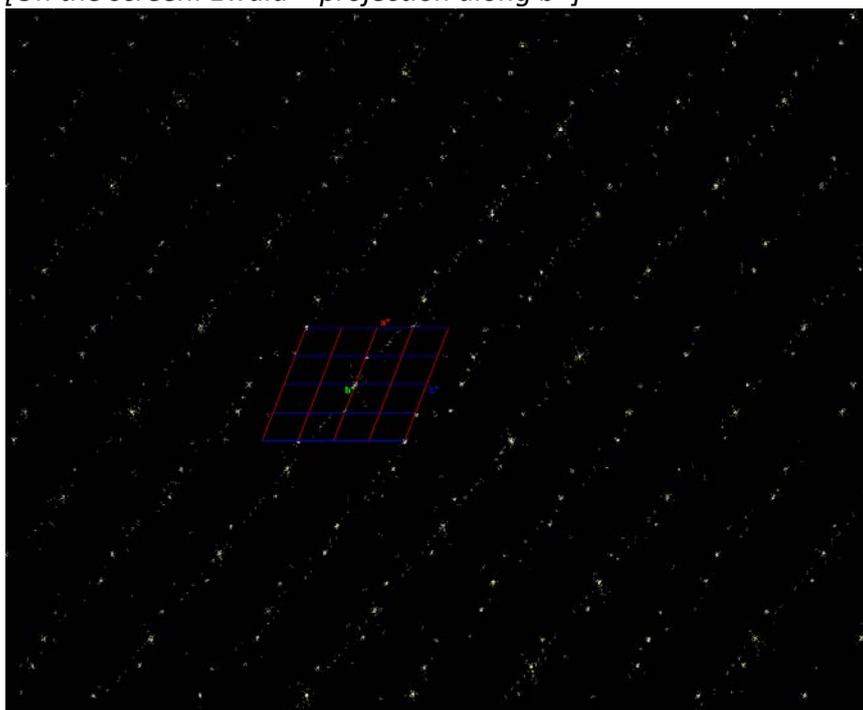
Repeat refinement of instrument parameters

The purpose of these steps is to include more indexed reflections to the refinement of

instrument parameters. With native ROD experiment, the parameters would be correct from the very beginning, but here we work with a not-native experiment and start from a rough estimation of the initial parameters as saved in the frame headers. At this step, the unit cell is not changing. Its size suggests this is a supercell trying to index main reflections as well as satellites

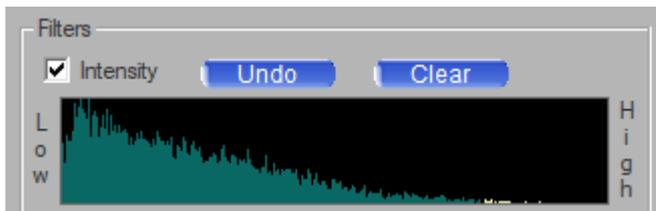


Start "Ewald Explorer"; select projection along  $b^*$   
 [On the screen: Ewald – projection along  $b^*$ ]

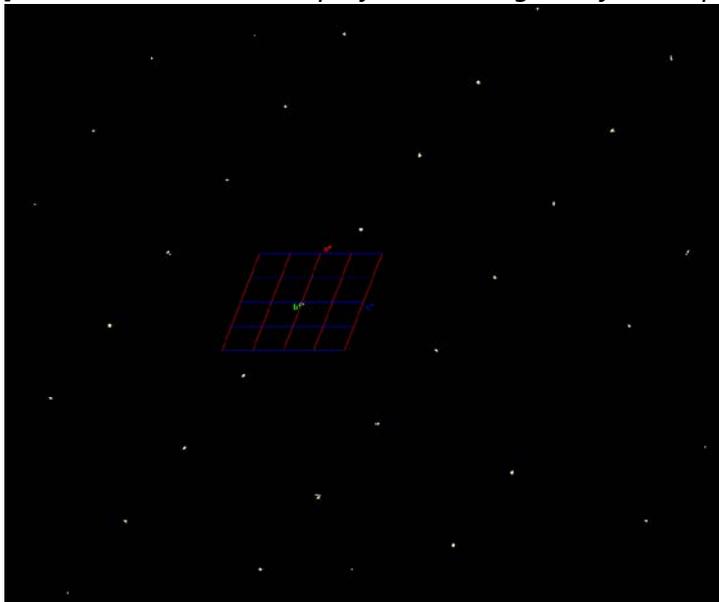


We can see set of strong points, which are probably main reflections, while the other points are satellites

In the right part of the Ewald explorer, switch to the page Filters  
 Activate the intensity filter and left only the strongest reflections.  
 [On the screen: Intensity filter]



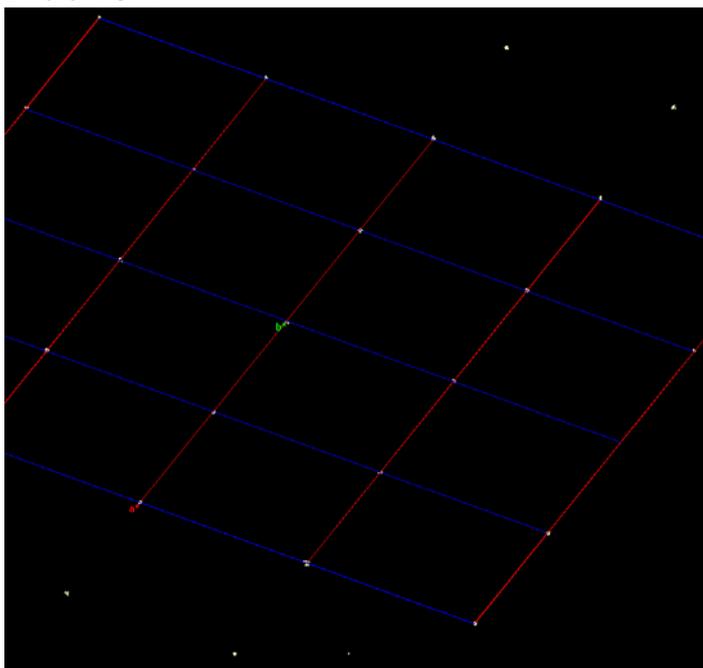
[On the screen: Ewald – projection along  $b^*$  – filtered peaks]



In the right part of the Ewald explorer, switch to the page Crystal  
 Click on “LATTICE” and select “Auto unit cell finding in shown peaks”  
 The resulting unit cell:

```
LATTICE (CSD: 0 +3L)
7.0446(7) 8.4242(7) 4.6372(4)
89.938(7) 108.625(8) 89.967(7)
V = 260.78(4) mC, index: 27.42%
Overlay off
```

Ewald view:

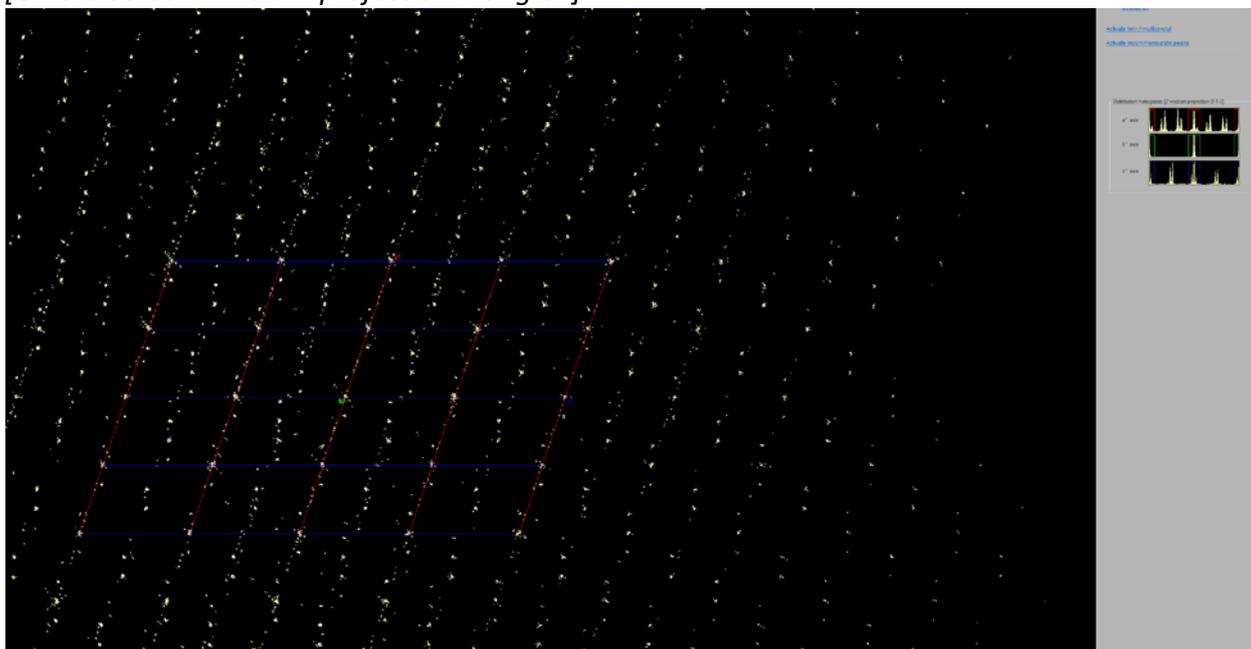


In the right part of the Ewald explorer, switch to the page Filters

Disable the intensity filter

Select view along  $b^*$

[On the screen: Ewald – projection along  $b^*$ ]



From this projection, it is clear that the additional spots cannot be indexed by any reasonable supercell because they are satellites.

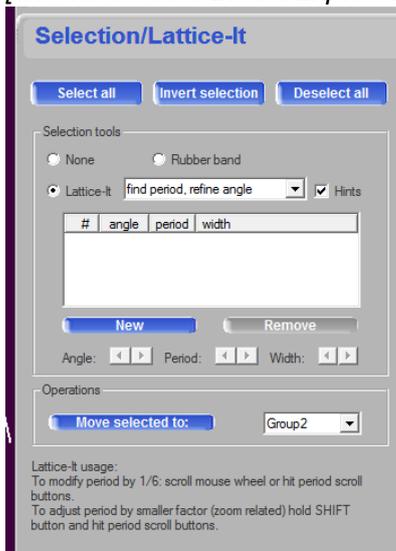
Set projection along  $a^*$

The peaks between the equidistant planes are evidently some spurious peaks arising e.g. from a small crystal attached on the main sample. We will now remove these peaks to get a clearer view

In the right panel, switch to the page “Selection/Lattice-It”

Activate the radio button “Lattice-It”

[On the screen: Ewald Explorer with activated function “Lattice-it”]



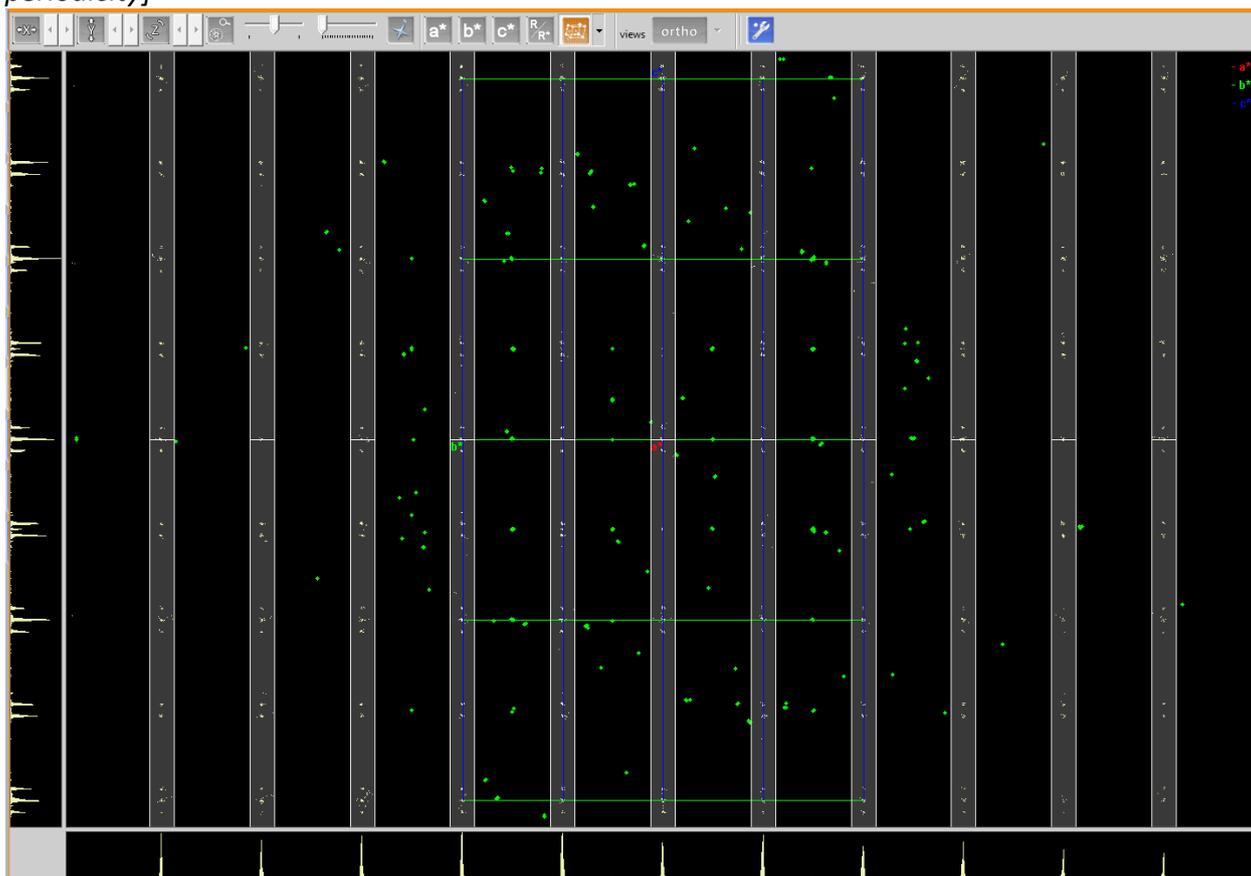
The cursor changes to a pair of white lines.

Orient these lines parallel with the horizontal rows of the peaks.

After some delay, the program automatically recognizes the periodicity.

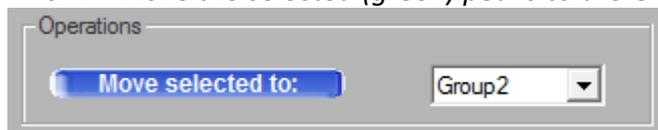
Click the left mouse button to fix the selection. The spurious peaks now become green.

[On the screen: Ewald Explorer with activated function "Lattice-it" and recognized periodicity]



In the right pane, press "Move selected to:"

This will move the selected (green) peaks to the Group2



At the bottom of the right panel, clear the checkbox of the group 2.

The spurious peaks now become invisible

At the right panel, switch to the page "Crystal"

Select view along  $b^*$

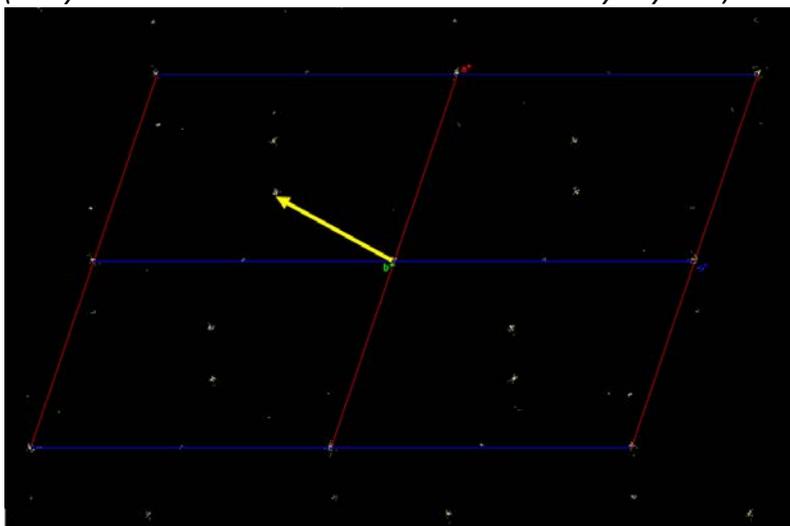
Now we have a clear figure suitable for determination of the  $q$ -vector

### 3. Determination of the $q$ -vector

For selection of the  $q$ -vector, we should consider the following:

- All satellites must have the same direction with respect to their parent main reflection, and this direction is defined by the  $q$ -vector
- First order satellites are usually stronger than the higher order ones
- The projection of peaks onto  $a^*$ ,  $b^*$  and  $c^*$  in the right panel suggests that the  $q$ -vector has zero beta component
- in order to be consistent with the workshop example 5.3.2, we would like the alpha component positive (towards the label  $a^*$ ) and the gamma component negative (opposite to the label  $c^*$ ). The labels  $a^*$  (red) and  $b^*$  (blue) are rather small, located at the end of the lattice vectors going through the origin.

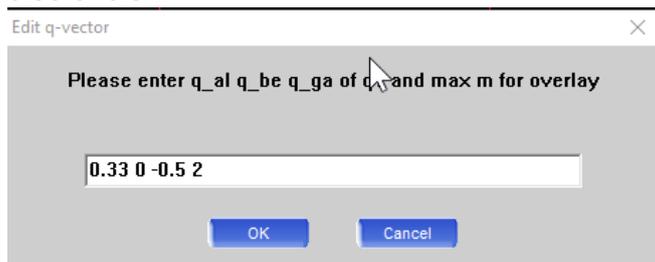
From these considerations we can suggest a q-vector like this:  
(the yellow arrow cannot has not been done by Crystals)



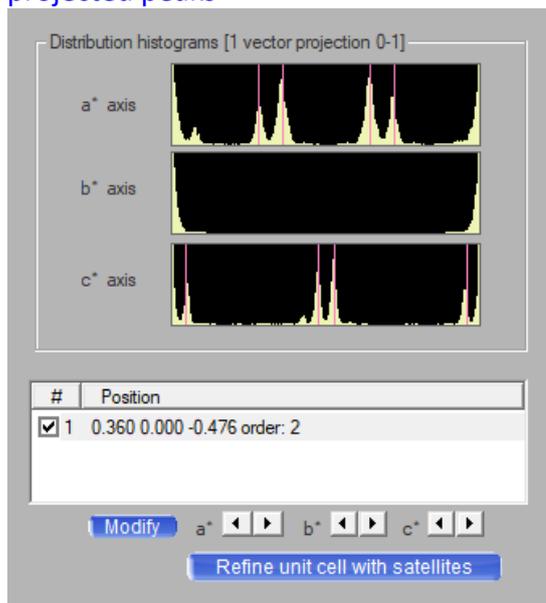
In the right panel, press “Activate incommensurate peaks” and select “Add 1d modulation vector (hklm)”

Activate the checkbox close to the q-vector and in the textbox that appears type estimated components of the q-vector and the maximal satellite index:

0.33 0 -0.5 2

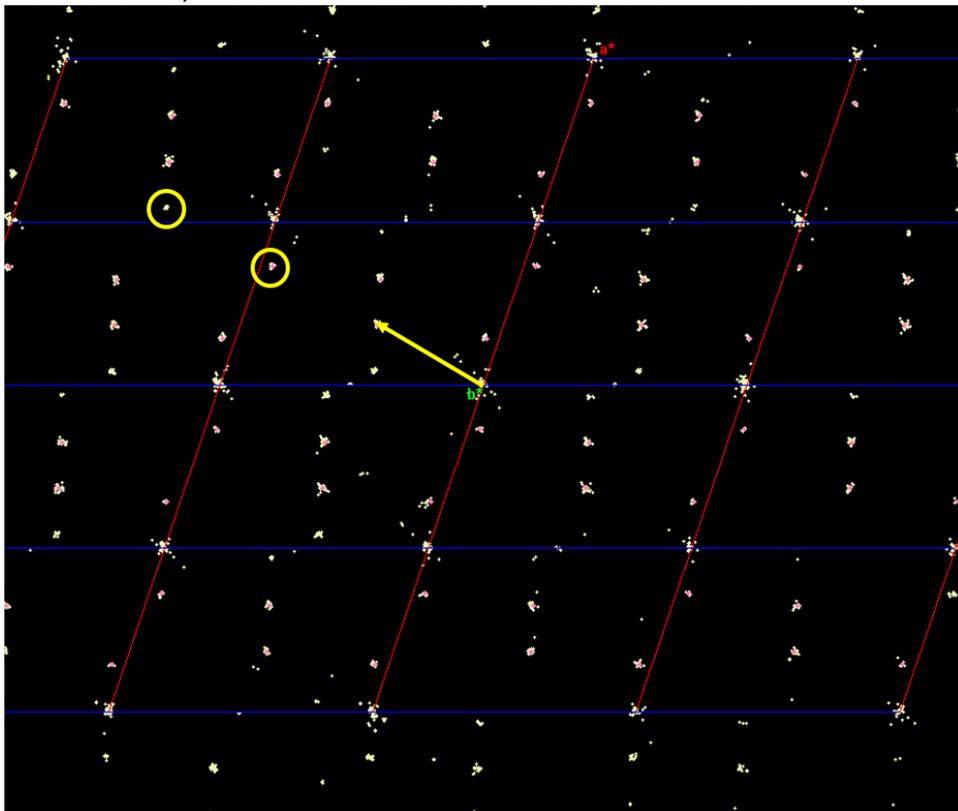


Play with the arrows close to “Modify” button until the satellite positions fit with the projected peaks



Toggle the checkbox close to the q-vector  1 0.362 -0.000 -0.465 order: 2 and check if the peak positions are properly described.

*In some areas, we can see that there are also the 3<sup>rd</sup> order satellites:*



Using the button “Modify” at the right panel, increase the satellite index to four.

*The reason for using the satellite index 4 is that when we can see the third order satellites by an eye there might be the fourth order satellites not found by the default peak search*

Please enter q\_al q\_be q\_ga of q1 and max m for overlay

OK Cancel

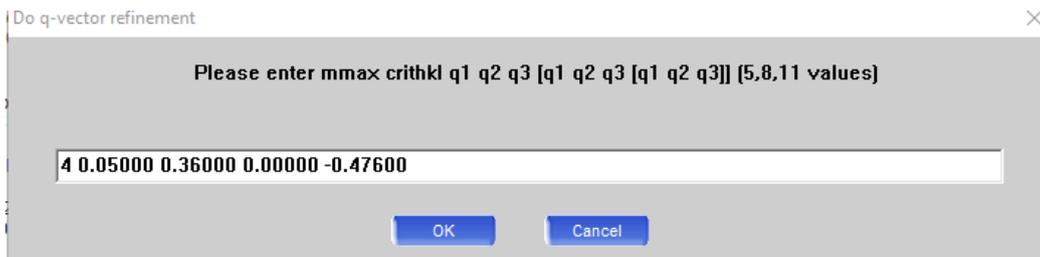
Check views along  $a^*$  and  $c^*$  to be sure that the satellites are described  
Close the window of the Ewald explorer

#### 4. Refinement of the q-vector

[On the screen: Lattice wizard]

Press the button “Incommensurates/Quasi-crystals”

In the displayed text box, define maximal satellite index (4) and the accuracy (0.05) defining the maximal tolerancy for an integer (for instance, 1.04 will be rounded to 1)



OK

The program refines the unit cell and  $q$ -vector an indexes 84% of the peaks. This is acceptable number because the indexing included also the previously suppressed spurious peaks.

#### LATTICE

##### Current cell (CSD: 0 +3L)

7.0437(7) 8.4230(7) 4.6365(4) 89.943(7) 108.629(9) 89.966(8) 260.67(4)

##### Constrained current cell

7.0410(8) 8.4224(8) 4.6383(5) 90.0 108.618(12) 90.0 260.67(5)

##### Lattice reduction

###### selected cell

7.0430 8.4219 4.6363 89.9456 108.6290 89.9674 mC 25

###### reduced cell

4.6363 5.4878 5.4909 100.1909 101.7790 101.8710 130.3

##### Incommensurate/quasi-crystal information

q(1): 0.3582(3) 0(4e-004) -4.746e-001(2)

#### PEAK TABLE

##### Peak hunting table

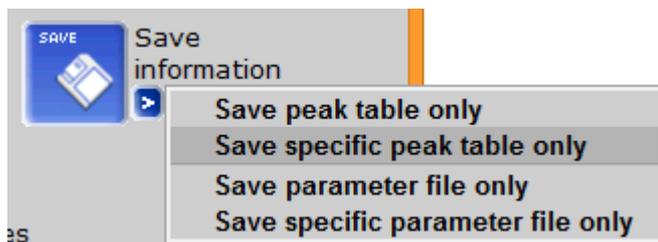
UB fit with 11971 obs out of 12889 (total:14364,skipped:1475) (92.88%)

3427 main refl.; 8544 q1 satellites

##### By order

8544 q1: (5215,2808,448,73)

Press the ">" part of the button "Save information" and select "Save specific peak table only". Make backup copy of the peak table under some name which cannot be overwritten by CrysAlis, e.g. "incommensurate"



Close the window of the Lattice Wizard

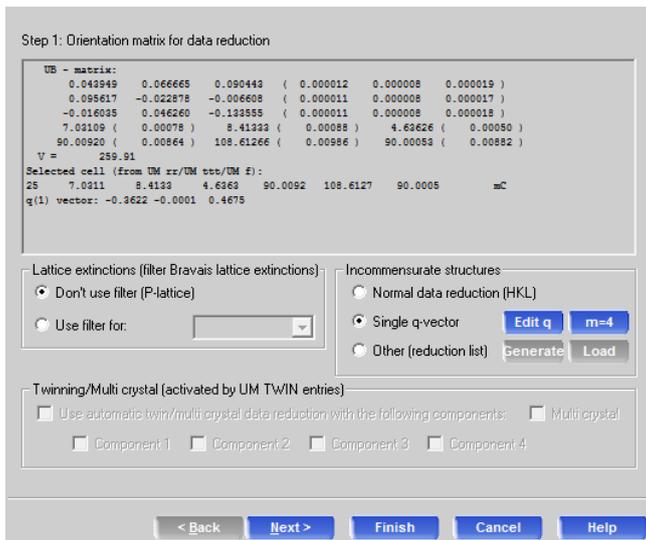
## 5. Data reduction

[On the screen: Basic window of CrysAlis]

In the right panel, press the button "Start-Stop"

In the next window, select "Data reduction with options"

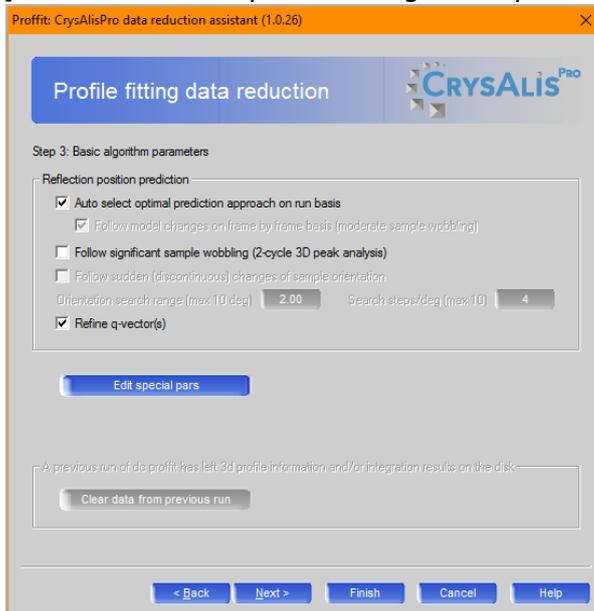
[On the screen: Step 1: Orientation matrix for data reduction]



Check the modulation vector (button “Edit q”) and maximal satellite index (button “m=”) The unit cell found previously is C-centered. Now we are having two options: “Use filter for C-lattice” or “Don’t use filter (P-lattice)”. Using the filter is good for cases with close diffraction spots because during the data processing, CrysAlis finds optimal positions for diffraction spots and it could skip from a systematically absent satellite position to an existing position. On the other hand, with less dense diffraction pattern, not using the filter gives us the complete information and we can verify the C centering. In our case, the filter for C-centering is not necessary.

NEXT; NEXT

[On the screen: Step 3: Basic algorithm parameters]



Uncheck “Follow significant sample wobbling” (we know that the sample was not wobbling) Note: In this case, no special parameters are necessary. For more complicated modulated structures, e.g. with short modulation vector, there are two typical parameters one should consider: (1) Disabling the option “Refine q-vectors(s)”; (2) “Overriding integration mask size” available through the button “Edit special parameters”; (2) “Skipping model refinement” available through the button “Edit special parameters” followed by Alt-E keyboard shortcut.

NEXT;

[On the screen: Step4: Background evaluation]

Keep all settings default; NEXT

The method "Average background" is faster and usually works well; the method "Smart background" is slower but sometimes gives better results

[On the screen: Step5: Outlier rejection]

Keep all settings default; NEXT

Outlier rejection based on monoclinic Laue symmetry does not mean that the program would create a false monoclinic data for non-monoclinic case. Although the algorithm behind is undescribed, we know from our experience that the process rejects only few reflections. The resulting data are unmerged.

[On the screen: Step6: Output]

Keep all settings default; FINISH

Data processing follows. At the first step, the program goes to the peaks positions predicted by the orientation matrix and makes profile analysis to get accurate peak positions and some other hidden information. The profile analysis is accompanied by the background subtraction. In the second step, the program makes data integration.

## 6. Output

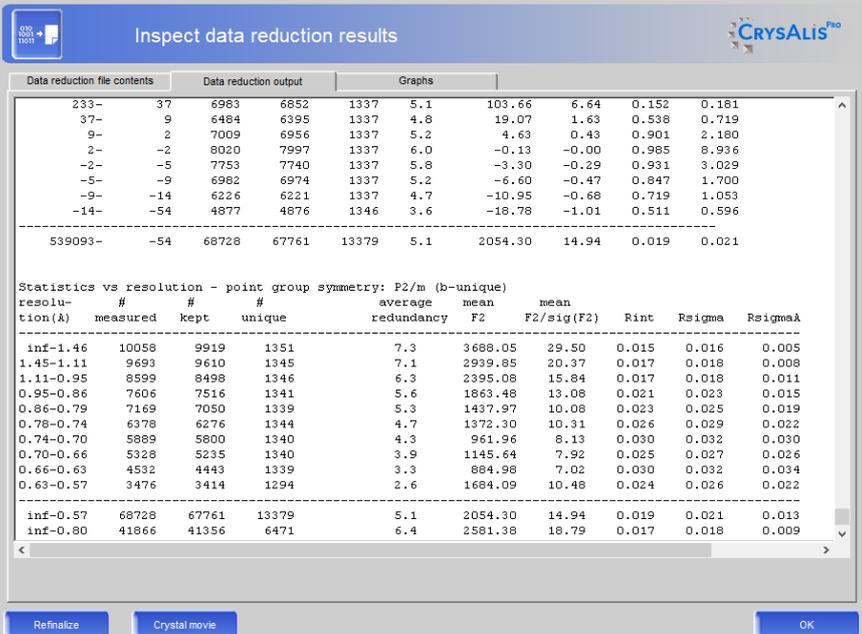
1) The resulting data are placed to the directory `struct\tmp`. For Jana2006 we need the files `CrPO_RT.cif_od` and `CrPO_RT.hkl`

2) In the left toolbar of CrysAlis, there is a button Jana. The button triggers the following actions: directory `struct\jana_CrPO_RT` is created; files `CrPO_RT.cif_od` and `CrPO_RT.hkl` are copied to this directory; Jana2006 is launched

3) In the left toolbar of CrysAlis, press the button 

[On the screen: Inspect data reduction results]

Go to the page "Data reduction output"



resolution (Å)	# measured	# kept	# unique	average redundancy	mean F2	mean F2/sig(F2)	Rint	Rsigma	RsigmaA
inf-1.46	10058	9919	1351	7.3	3688.05	29.50	0.015	0.016	0.005
1.45-1.11	9699	9610	1345	7.1	2939.85	20.37	0.017	0.018	0.008
1.11-0.95	8599	8498	1346	6.3	2395.08	15.84	0.017	0.018	0.011
0.95-0.86	7606	7516	1341	5.6	1863.48	13.08	0.021	0.023	0.015
0.86-0.79	7169	7050	1339	5.3	1437.97	10.08	0.023	0.025	0.019
0.78-0.74	6378	6276	1344	4.7	1372.30	10.31	0.026	0.029	0.022
0.74-0.70	5889	5800	1340	4.3	961.96	8.13	0.030	0.032	0.030
0.70-0.66	5328	5235	1340	3.9	1145.64	7.92	0.025	0.027	0.026
0.66-0.63	4532	4443	1339	3.3	884.98	7.02	0.030	0.032	0.034
0.63-0.57	3476	3414	1294	2.6	1684.09	10.48	0.024	0.026	0.022
inf-0.57	68728	67761	13379	5.1	2054.30	14.94	0.019	0.021	0.013
inf-0.80	41866	41356	6471	6.4	2581.38	18.79	0.017	0.018	0.009

This page shows the merging R values (Rint) sorted by intensity shells. When scrolled up, it

also shows the same information separately for satellites:

1. order satellite reflections

Statistics vs resolution - point group symmetry: P2/m (b-unique)

resolu- tion(Å)	# measured	# kept	# unique	average redundancy	mean F2	mean F2/sig(F2)	Rint	Rsigma	RsigmaA
inf-1.49	2271	2228	300	7.4	3623.56	48.34	0.019	0.023	0.007
1.49-1.13	2145	2117	301	7.0	3358.55	32.64	0.021	0.024	0.010
1.13-0.96	1938	1913	300	6.4	2965.10	29.75	0.022	0.026	0.013
0.96-0.87	1713	1677	300	5.6	2310.04	20.61	0.023	0.026	0.016
0.86-0.79	1611	1571	301	5.2	2087.42	18.73	0.022	0.023	0.019
0.79-0.74	1470	1435	302	4.8	1674.67	16.67	0.024	0.025	0.023
0.74-0.70	1358	1323	301	4.4	1844.32	15.73	0.024	0.025	0.023
0.70-0.67	1233	1201	301	4.0	1400.75	12.41	0.025	0.026	0.027
0.67-0.64	1004	973	300	3.2	1280.28	12.27	0.026	0.026	0.030
0.64-0.58	733	720	299	2.4	1253.45	11.85	0.025	0.029	0.031
inf-0.58	15476	15158	3005	5.0	2420.01	24.93	0.022	0.025	0.015
inf-0.80	9541	9372	1474	6.4	2966.77	31.54	0.021	0.024	0.012

2. order satellite reflections

Statistics vs resolution - point group symmetry: P2/m (b-unique)

resolu- tion(Å)	# measured	# kept	# unique	average redundancy	mean F2	mean F2/sig(F2)	Rint	Rsigma	RsigmaA
inf-1.50	2250	2229	299	7.5	479.52	16.48	0.034	0.036	0.026
1.49-1.13	2141	2132	300	7.1	434.75	12.07	0.039	0.045	0.038
1.12-0.96	1936	1925	300	6.4	340.78	9.07	0.051	0.056	0.054
0.96-0.86	1681	1667	300	5.6	330.66	7.57	0.055	0.061	0.061
0.86-0.79	1635	1619	300	5.4	220.11	5.38	0.074	0.078	0.088
0.79-0.74	1431	1403	299	4.7	257.16	5.55	0.070	0.068	0.085
0.74-0.70	1335	1318	299	4.4	253.28	5.51	0.074	0.082	0.091
0.70-0.67	1185	1172	299	3.9	196.83	4.22	0.094	0.106	0.114
0.67-0.64	1022	1003	299	3.4	144.38	3.49	0.114	0.121	0.147
0.64-0.58	770	761	303	2.5	176.35	3.86	0.105	0.109	0.129
inf-0.58	15386	15229	2998	5.1	312.80	8.38	0.056	0.065	0.061
inf-0.80	9555	9484	1481	6.4	371.40	10.60	0.045	0.051	0.046

3. order satellite reflections

Statistics vs resolution - point group symmetry: P2/m (b-unique)

resolu- tion(Å)	# measured	# kept	# unique	average redundancy	mean F2	mean F2/sig(F2)	Rint	Rsigma	RsigmaA
inf-1.49	2203	2200	295	7.5	46.50	4.02	0.127	0.166	0.143
1.49-1.13	2133	2126	296	7.2	52.31	2.91	0.143	0.184	0.180
1.13-0.97	1919	1912	297	6.4	38.10	1.98	0.214	0.284	0.270
0.97-0.87	1660	1650	295	5.6	32.89	1.51	0.244	0.325	0.326
0.87-0.80	1590	1578	296	5.3	30.38	1.30	0.260	0.334	0.359
0.80-0.75	1408	1396	297	4.7	33.22	1.43	0.285	0.365	0.370
0.75-0.70	1281	1273	296	4.3	19.90	0.73	0.357	0.481	0.479
0.70-0.67	1167	1158	295	3.9	24.66	0.94	0.336	0.440	0.468
0.67-0.64	1050	1041	296	3.5	22.55	0.83	0.344	0.434	0.487
0.64-0.57	784	777	295	2.6	23.46	0.90	0.343	0.393	0.502
inf-0.57	15195	15111	2958	5.1	35.11	1.92	0.233	0.326	0.310
inf-0.80	9475	9436	1473	6.4	41.03	2.47	0.186	0.252	0.238

4. order satellite reflections

Statistics vs resolution - point group symmetry: P2/m (b-unique)

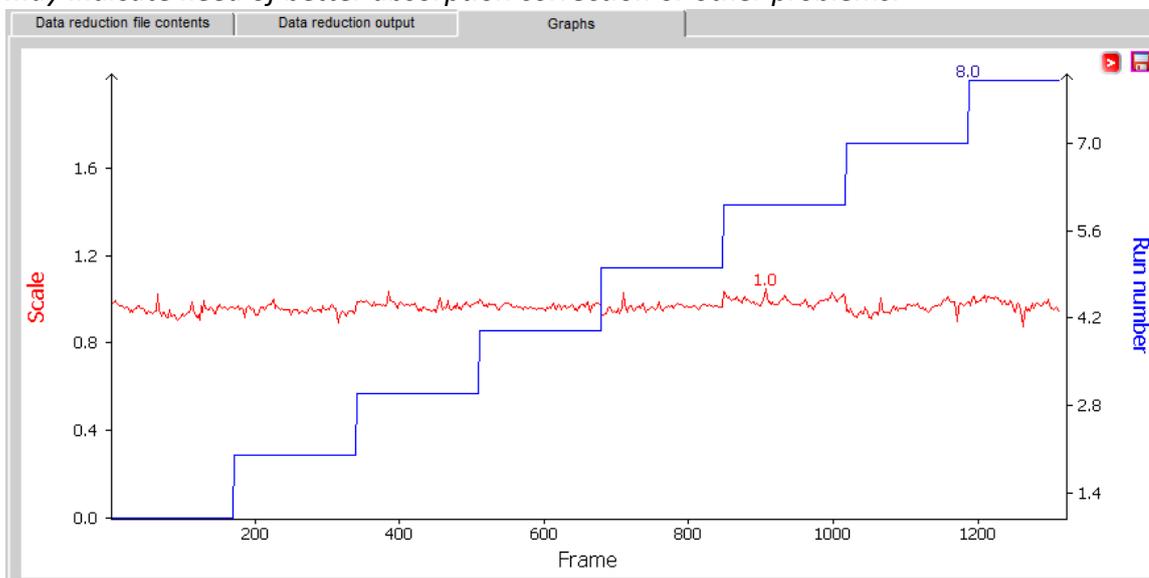
resolu- tion(Å)	# measured	# kept	# unique	average redundancy	mean F2	mean F2/sig(F2)	Rint	Rsigma	RsigmaA
inf-1.50	2195	2192	294	7.5	18.36	1.92	0.242	0.279	0.298
1.49-1.13	2074	2064	292	7.1	16.33	1.31	0.324	0.402	0.422
1.13-0.97	1873	1868	291	6.4	11.90	0.77	0.397	0.528	0.541
0.97-0.87	1659	1651	291	5.7	10.67	0.62	0.440	0.585	0.602
0.87-0.81	1576	1567	291	5.4	5.17	0.26	0.517	0.719	0.729
0.80-0.75	1371	1364	292	4.7	4.60	0.23	0.561	0.762	0.781
0.75-0.71	1295	1286	291	4.4	2.36	0.13	0.610	0.866	0.853
0.71-0.67	1123	1114	292	3.8	0.29	0.01	0.658	0.967	0.935
0.67-0.64	1006	1000	291	3.4	-1.72	-0.09	0.681	1.006	0.966
0.64-0.58	777	773	291	2.7	-4.46	-0.20	0.675	0.962	1.074
inf-0.58	14949	14879	2916	5.1	8.49	0.67	0.459	0.659	0.638
inf-0.80	9452	9416	1474	6.4	12.96	1.04	0.373	0.492	0.500

The  $R_{int}$  is calculated together for observed and unobserved reflections. After reading data

into Jana2006,  $R_{int}$  can be seen separately for observed and unobserved reflections.

[Go to the page "Graphs"](#)

The most important is the graph from the frame scaling. Too large fluctuation of this graph may indicate need of better absorption correction or other problems.



#### 4) Note about the absorption correction

The data were automatically corrected using the empirical absorption correction, in CrysAlis called ABSPACK. At the bottom of the "Inspect data reduction results", there is the button "Abs display" for indexing of the crystal shape for better absorption correction. However, photos of the crystal shape are only available for native ROD experiments. For our case, the absorption correction of ABSPACK using the spherical harmonic functions is sufficient.



# Example 5.3.2: CrPO

Solution of the room temperature incommensurate phase of  $\text{Cr}_2\text{P}_2\text{O}_7$ .

Revised: 08 March 2019

## $\text{Cr}_2\text{P}_2\text{O}_7$

Single crystal data measured with Nonius Kappa CCD diffractometer

Input folders:

- 1) APEX data from Nonius (small disorder)
- 2) CrysAlis data from Nonius (small disorder)
- 3) CrysAlis data from Kuma (large disorder)

The sample measured with Nonius has been processed with both APEX and CrysAlis. For CrysAlis data reduction, see Example 5.3.1. This sample has small disorder and its data are not suitable for those wanting to solve the advanced part of this example (disorder of crenel functions)

The sample measured with KUMA has more pronounced disorder, and the workshop example is based on it.

**For this example, we recommend using data in the folder “CrysAlis data from Kuma (large disorder)”**

Frame scaling, absorption correction: done with software of the diffractometer

### 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: for jobname type crpo

### 2. *Import Wizard for data processed by CrysAlis*

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction – CCD”; use “Browse” to locate hkl file; NEXT

In “Define basic input file” select “Input from cif\_od file”; OK

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

For absorption correction select “None or done before importing”; NEXT

FINISH

[On the screen: Data repository]

OK; YES to accept the data set

### 3. *Import Wizard for data processed by APEX*

Select “Known diffractometer formats”; NEXT

Select “Bruker – CCD”; use “Browse” to locate hkl file

[On the screen: selection of the diffractometer format and hkl file]

NEXT

[On the screen: information from the p4p file]

The hkl file in this format always has six indexes (two of them not used in our example)

NEXT

Change "Target dimension" to 4

To have the same q-vector as expected in this manual, we need to invert its components

Press "Define transformation matrix"

In the row M, change "1" for "-1"; OK

NEXT

For absorption correction select "None or done before importing"; NEXT

FINISH

[On the screen: Data repository]

OK; YES to accept the data set

#### 4. Symmetry Wizard

Use default tolerances for crystal system recognition  
Select monoclinic Laue symmetry  
Select C centering  
Select space group C2/m  
Select superspace group C2/m(a0g)0s  
Accept the superspace group in the original cell

#### 5. Creating refinement reflection file

Follow default steps of the wizard

#### 6. Structure solution wizard

Type the formula Cr<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, two formula units  
Select "Superflip" and "Peaks from Jana2006 but first run Fourier"  
"Run solution"  
*Superflip converges with R around 19% and confirms the selected superspace group*  
Close the listing of Superflip  
Press "Accept last solution"

#### 7. Investigation of charge flipping results

Start EditM50, page Composition; press "Formula from M40"  
*The formula based on structure model for Z=2 is Cr<sub>2</sub>P<sub>2</sub>O<sub>8</sub>, i.e. one oxygen more*  
Start Options for Dist; for "Listing form" select "With symmetry codes"; In "expanded by" textbox, type 15%;  
Run Dist and open listing  
In the listing make sure that the atoms P1, O1, O2 and O3 make symmetrically contiguous motif, i.e. that O1, O2 and O3 listed in coordination of P1 have one of their symmetry codes equal to "x,y,z".  
*In this example, oxygens are NOT in correct symmetry positions and transformation is necessary. This will facilitate making connections between modulation function of the PO<sub>4</sub> anion later in this cookbook.*  
Start "Edit atoms"  
Select P1, O1, O2, O3  
"Action → Make symmetrically contiguous motifs"  
Repeat calculation of distances with symmetry codes.  
*The listing of Dist should look as follows:*

```
Distances concerning atom P1
=====
P1-O1      1.5561(4)                2nd: O1                x,y,z
ave : 1.5575(4)  min : 1.5561(4)  max : 1.5588(4)
P1-O2      1.5039(2)                2nd: O2                x,y,z
ave : 1.525542(10)  min : 1.49223(2)  max : 1.57991(2)
P1-O2      1.5039(2)                2nd: O2#s4t0,1,0      x,-y+1,z
ave : 1.526194(11)  min : 1.49223(2)  max : 1.57991(2)
P1-O3      1.6491(2)                2nd: O3                x,y,z
ave : 1.6607(4)  min : 1.5371(5)  max : 1.7813(5)
P1-O3      1.6491(2)                2nd: O3#s3t0,1,3     -x,-y+1,-z+3
ave : 1.6582(4)  min : 1.5079(5)  max : 1.7911(5)
-----
```

***The symmetry codes of transformed atoms may be different because Superflip solutions are never exactly the same!***

*In the next step, we will visualize electron density prepared by Superflip*

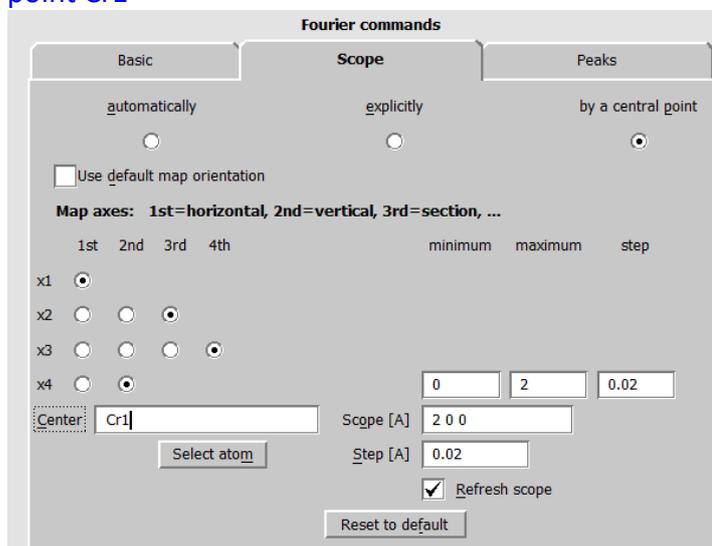
Start Contour and New plot

Select "General Contour procedure"

Select "Calculate new ones"; OK (if the option is not active, Contour has no old map and it will calculate a new map by default)

In Fourier option, page Basic, select "Map type" = "F(obs) – Fourier"

In page Scope, select "by central point", set calculation of the x1-x4 section with the central point Cr1



OK;

[On the screen: Contour window with plot of x1-x4 section through position of Cr1]

Press "Atoms edit" and add Cr1 to the list of atoms to be plotted

This was example how to setup de Wolff section manually. For making more de Wolff sections, we can use an automatic tool:

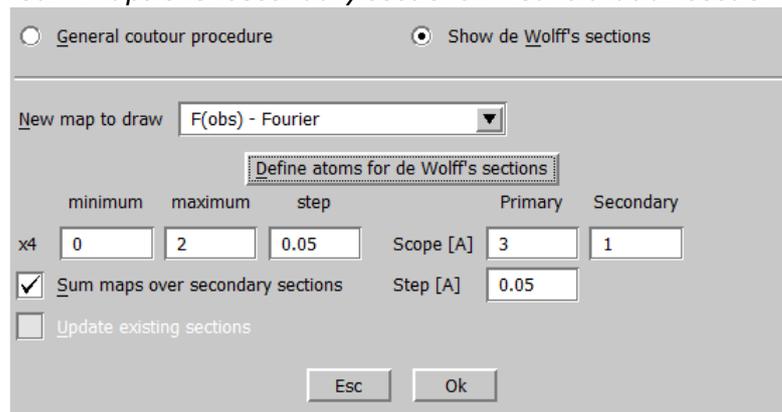
Start Contour, "New plot"

Select "Show de Wolff's sections"; change Step[A] to 0.05; change primary and secondary scope to 3 and 1

Primary scope defines length in Å of the visible axis of the plot (x1, x2 or x4)

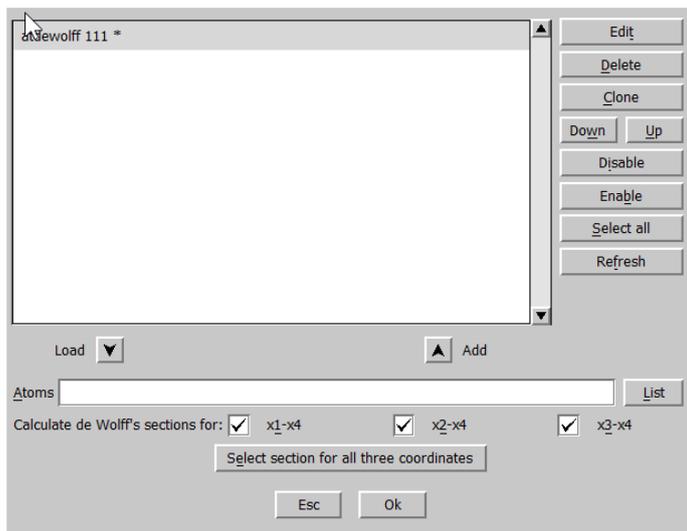
Secondary scope defines length in Å of the other axes of the plot (x2,x3; x1,x3 or x1,x2)

"Sum maps over secondary sections" means that all sections will be merged to one section.



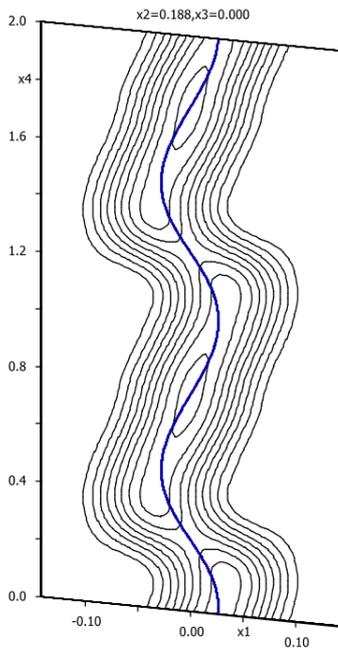
Press "Define atoms for de Wolff's sections"

Check x1-x4,x2-x4 and x3-x4 boxes; For Atoms type "\*"; Add

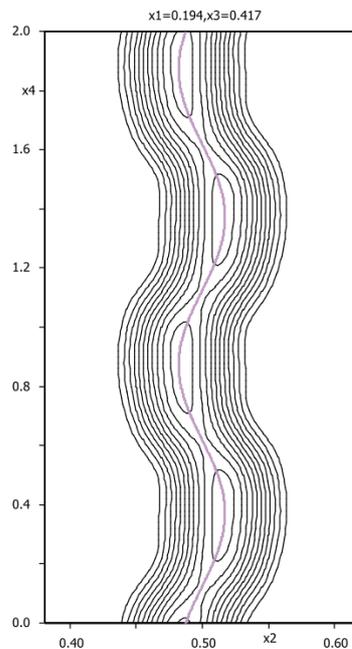


OK; OK to run the tool

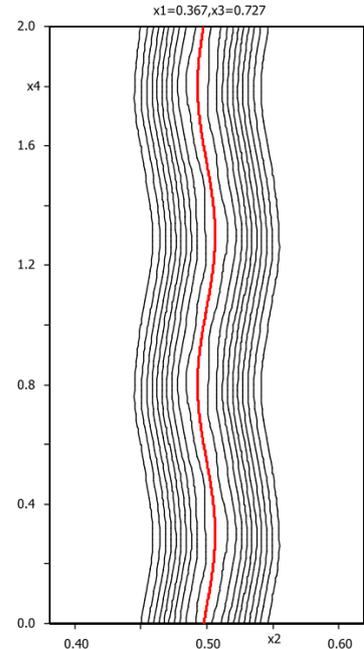
Use "W+" and "W-" to see the resulting plots



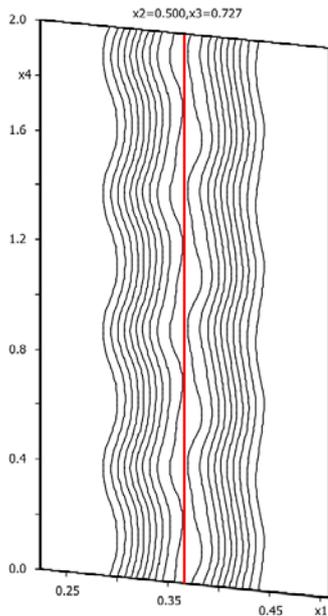
Cr1: section x1-x4



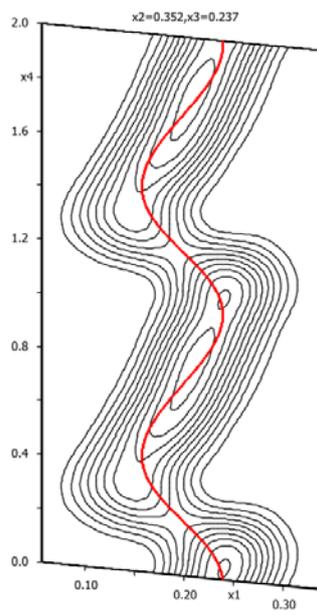
P1: section x2-x4



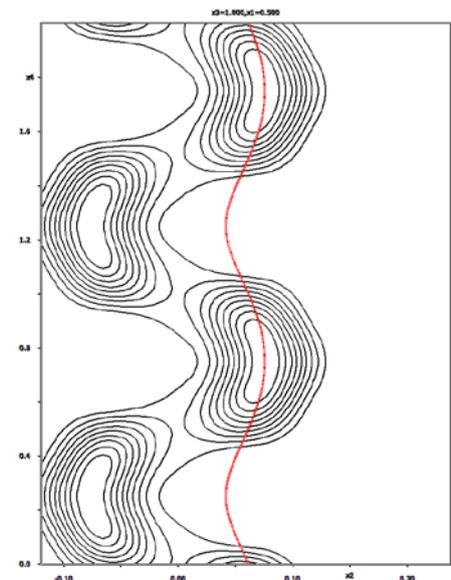
O1: section x2-x4



O1: section x1-x4



O2: section x1-x4



O3: section x2-x4

From the plots we can conclude:

**(Positions of the centers depend on the Superflip solution and may be different, note your values! For instance, Cr may have the centre of its modulation function at 0.25)**

Cr1 needs a saw-tooth function with center at 0.75 and width 1

P1 needs more modulation waves

O1 seems to be properly described in x2-x4 section but not in x1-x4

O2 needs saw-tooth function with center 0.75 and width 1

O3 needs a crenel function with centre 0.75 and width 0.5; the remaining maxima could be described with modulation function related by symmetry operation  $-x, -y+1, -z+3$ , i.e.

**#s3t1,0,2 in Jana encoding (This can be found from the Dist listing. Again – this operation depends on the Superflip solution!)**

For making your results similar to the results presented here, rename (if necessary) oxygen atoms to be O2 with saw-tooth and O3 with crenel (Edit atoms – rename selected atoms manually)

The saw-tooth shape of modulation function can be modeled by three ways:

1) As a discontinuous positional modulation named in Jana2006 saw-tooth positional modulation

2) As a discontinuous occupational function called crenel function combined with modulation described with Legendre polynomials

3) As a discontinuous occupational function called crenel function combined with modulation described with so-called  $x$ -harmonics.

The first method is obsolete. Here we will use the second method, i.e. crenel function (a straight line along  $x_4$ ) rotated to the saw-tooth direction by Legendre position modulation.

(For more details, see *Z.Kristallogr.* 2016, 231(5), 301-312)

## 8. Setting crenel functions

Use “File → Structure → Save As” and create backup copy “crpo\_superflip”

Do not continue with the new structure

Start “Edit atoms”

Double-click Cr1

[On the screen: Atom Edit tool]

In page “Define” activate “crenel” and define  $\delta=1$  and  $x_4=0.75$ ;

Leave refinement boxes clear (we don't want refinement of  $x_4$  or  $\delta$ , as  $x_4$  is fixed to 0.75 by symmetry and the atom seems to be present for all  $x_4$  values); OK

Refinement keys of  $\delta$  and  $x_4$  are not automatic

Select “Legendre polynomials in crenel interval”;

OK

Repeat the process for O2 (here  $\delta=1$ ,  $x_4=0.75$ )

Repeat the process for O3 (here  $\delta=0.5$  and  $x_4=0.75$ )

your value of  $x_4$  may be 0.25, depending on the Superflip solution

Leave “Edit atoms”, YES to save changes

After activation of Legendre polynomials, the keys “Legendre” will appear in M40 file.

Start EditM50, page Composition; press “Formula from M40”

The program now prints correct composition for  $Z=2$ : Cr<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. Number of oxygens has been reduced from 8 to 7 by using crenel function with  $\delta=0.5$  for O3

Start Contour, “New plot”

Select “Show de Wolff's sections”

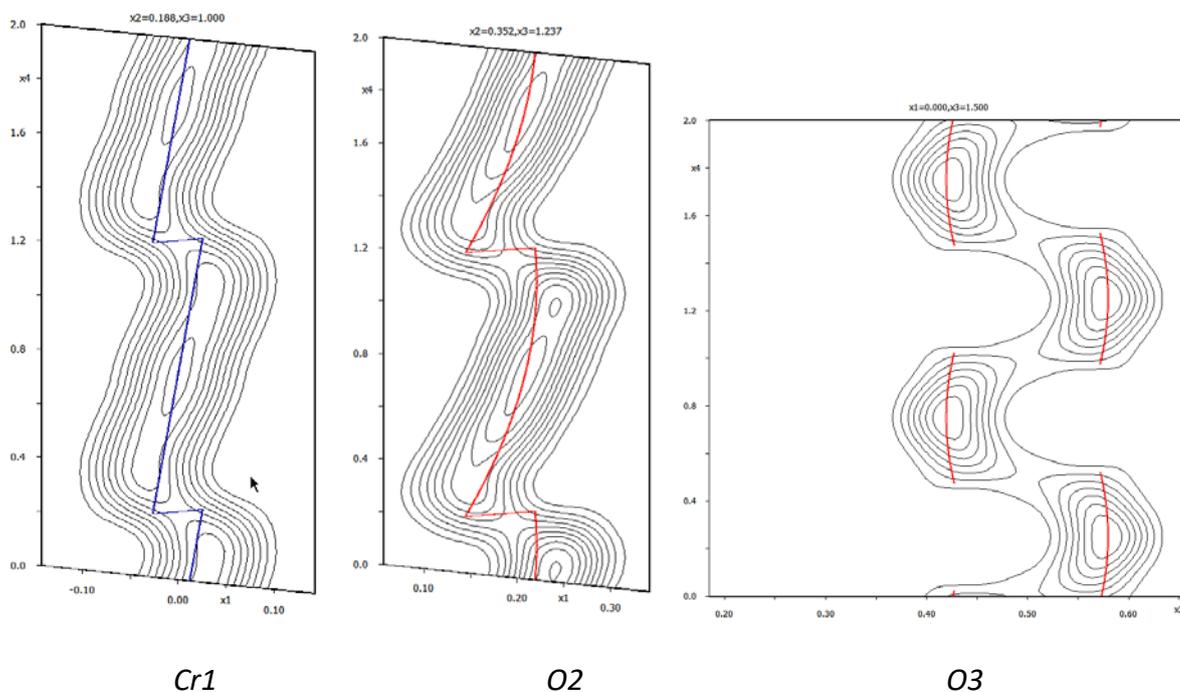
Keep clear “Update existing sections” because we want to see the previous Fourier maps with new modulation functions

Plot again the de Wolff sections for all atoms

The electron density will be still the one from Superflip because we did not refine the structure. The displayed modulation functions will have a shape calculated from the centre, width and previous harmonic waves found in the Superflip electron density. In case some crenel modulation function would not fit with the corresponding maximum, check its centre. The most probable reason is that the actual position of the centre differs of the value given in this cookbook, because Superflip put the origin to a different equivalent point. In such

case, read the backup (File – Structure – Copy in) and repeat the process with correct origin position.

The coefficients of Legendre polynomials are calculated such that the resulting modulation function fits best with the original modulation function. However, the first modulation wave expressed by Legendre polynomials has only the linear (coefficients 1-3) and quadratic (coefficients 4-6) part so the shape cannot fit exactly.



For O3 we can also display the modulation function related by symmetry operation  $O3\#s3t1,0,2$  (or your actual symmetry operation available from the list of Dist). To display such plot, use the following steps:

Press the Contour button "From list"

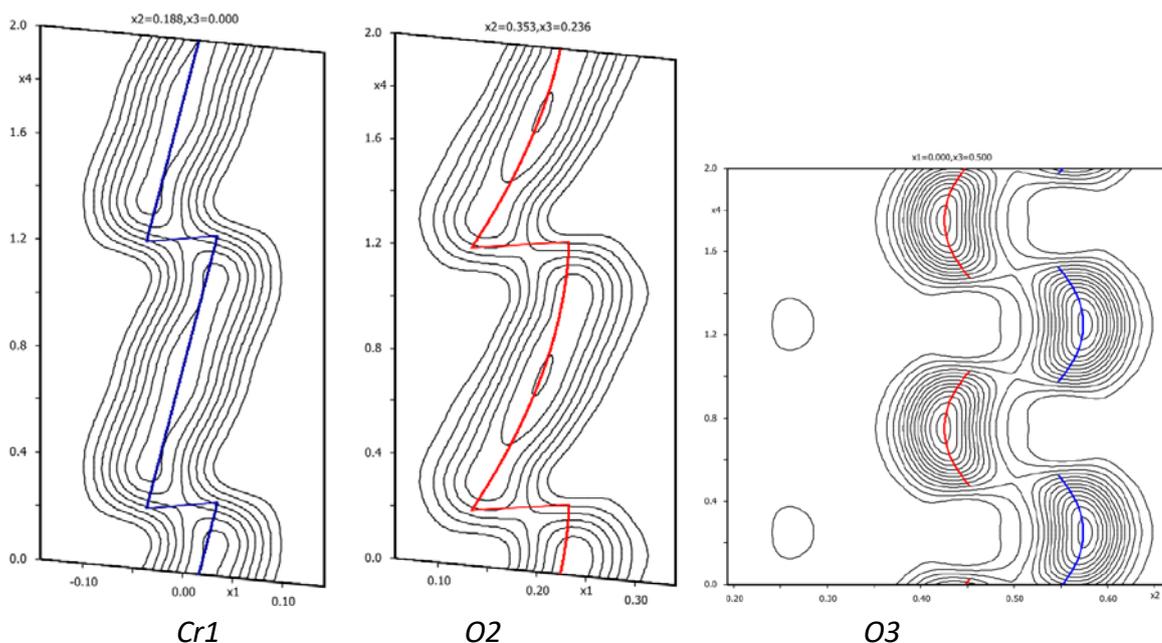
Select the section  $O3\_x2-x4$ ; OK

Press Atom edit and add  $O3\#s3t1,0,2$ ; OK

Run refinement

Refinement converges with Robs factors 23%, 14%, 22%, 53%, 61% and 116%

Run Contour and plot again the three sections:



Start Edit atoms and change ADP of all atoms to “harmonic”

Repeat refinement

Refinement converges with Robs factors 21%, 9%, 24%, 52%, 61% and 109%

Start Edit atoms and add one position modulation wave for each atom

Repeat refinement

Refinement converges with Robs factors 12%, 5%, 14%, 21%, 54% and 92% for 68 parameters

Make backup copy “crpo\_initial\_crenel”

### 9. Setting up a constraint for discontinuity points of O2 and O3

The shape of the PO4 tetrahedron cannot be changed too much by modulation because it would contradict the chemistry. Thus the discontinuity points of crenel functions of oxygen atoms O2 and O3 must have the same  $t$  coordinate.

Start “Graph”

Press “New/Edit”

For “Parameter to draw” select “Distances”

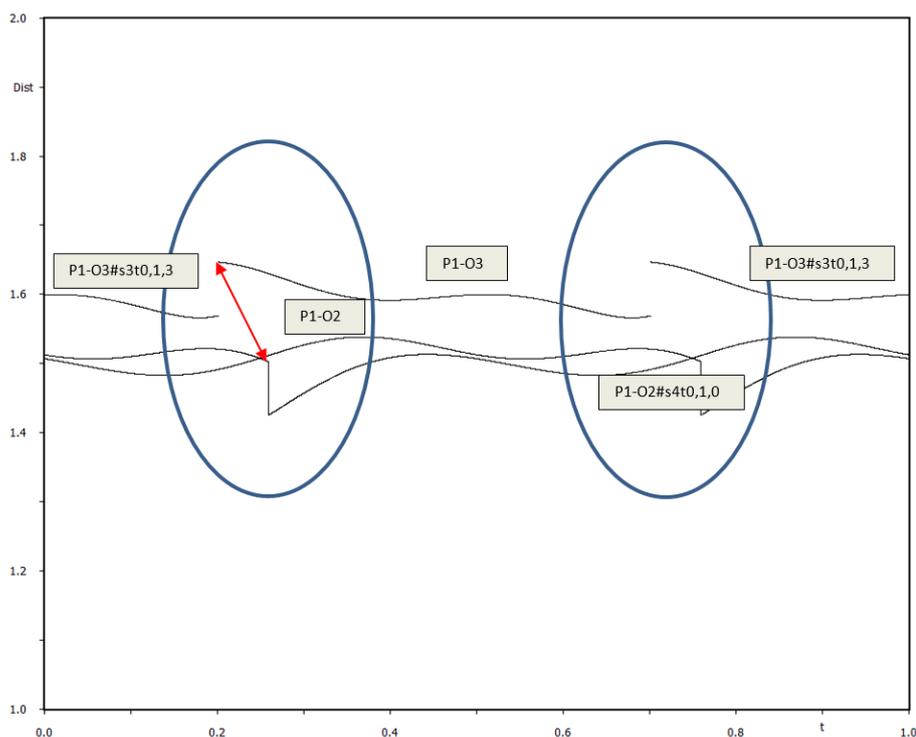
For “Central atom” type P1

Step in  $t$  0.001; For “ $p$ ” type “1.2” and “1.8”;

“ $p$ ” determines the lower and upper limits of the visualized parameter

Press “Define neighbor atoms” and select only O2 and O3

OK



The plot shows distances P1-O2, P1-O2#s4t0,1,0, P1-O3 and P1-O3#s3t0,1,3 as a function of  $t$  and it is obvious that discontinuities occur for slightly different values of  $t$ . However, the discontinuous changes of oxygen positions must occur at the same  $t$  value, because  $PO_4$  cannot be so much distorted.

The centre  $x_{40}$  of the crenel function of O3 must be fixed at 0.75 (or equivalent value following from your structure solution), because this atom is in a special position; for different center, there would be an overlap with symmetry related O3 leading to a disordered structure. The  $t$ -coordinate of this centre is  $t_{40}[O3]$ .

For O3  $\delta=0.5$ , therefore one of the two discontinuity points is  $t_{40}[O3]+0.25$

For O2  $\delta=1.0$  and one of the two discontinuity points is  $t_{40}[O2]-0.50$

The following equation will align the two discontinuity points:

$$t_{40}[O3]+0.25 = t_{40}[O2]-0.50 \Rightarrow t_{40}[O2] = t_{40}[O3]+0.75 \Rightarrow t_{40}[O2] = t_{40}[O3]-0.25$$

(The symbol  $t_{40}$  means  $x_{40}$  transformed to  $t$  coordinate.) In the last step the equivalent translation has been applied to get  $t_{40}[O2]$  from the interval (0,1).

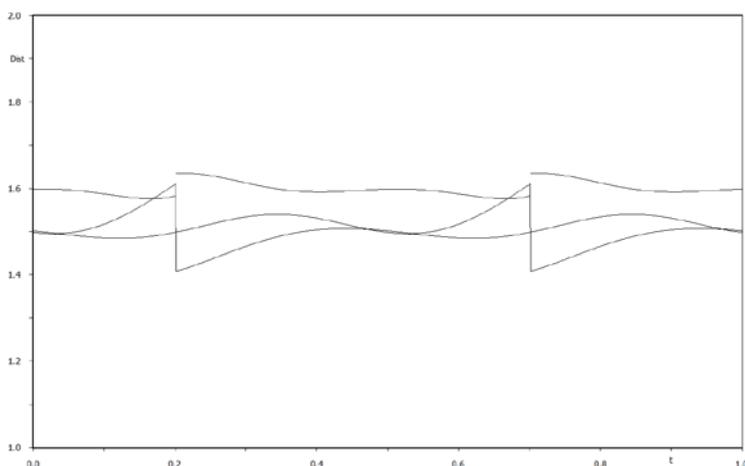
Start Refinement options, page "Various"

Press "Equations" and add equation  $t_{40}[O2]=t_{40}[O3]-0.25$

Add; OK; OK; YES+Start

Refinement converges with similar Robs factors like in the previous refinement. If large changes occur, this is probably due to mistake in sign. In such case, recover the files (Tools – Recover), edit the equation and try again.

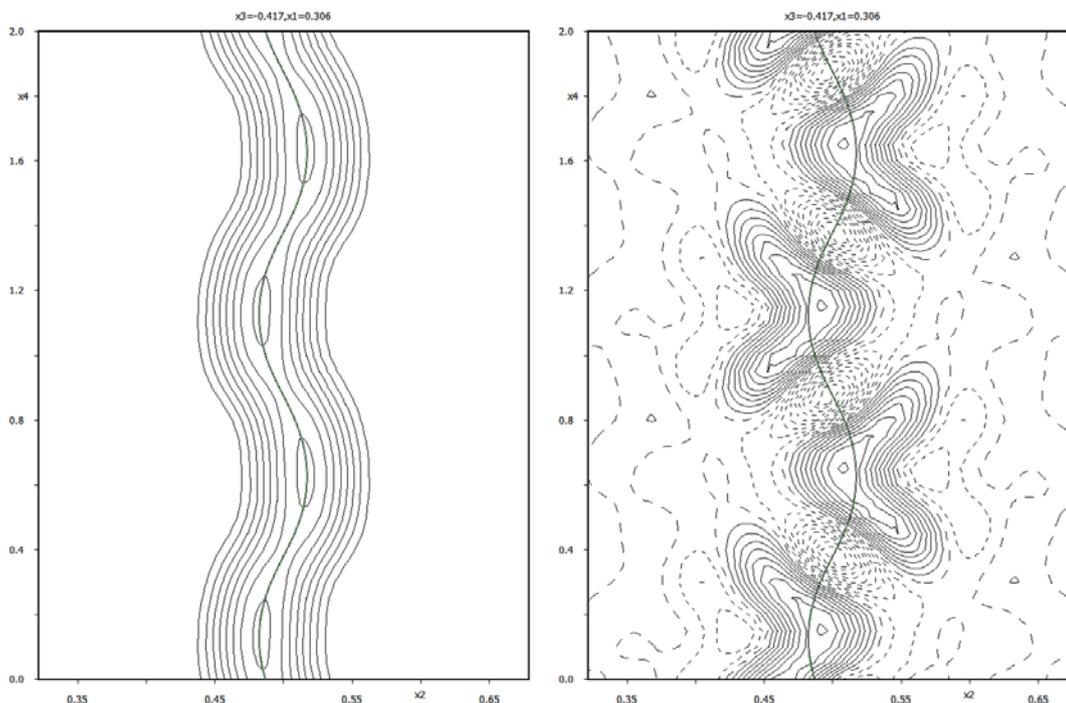
Start "Graph" and repeat the same plot like before



The discontinuity points for O2 and O3 now occur at exactly the same value of t  
 Make backup copy "crpo\_aligned"

### 10. Crenel function for phosphorus

Start Contour and plot the observed Fourier section x2-x4 for P1 using the scope 0 2 0. Plot similar section for the difference Fourier map.



Although P1 seems to be correctly described with harmonic functions, the difference Fourier reveals fluctuation of density along the modulation function. For this reason, we shall describe P1 similarly like in case of O3: with two symmetry equivalent crenel functions of the width 0.5

Quit Contour

Start "Edit atoms"

For P1 activate crenel; define x40=0.86 (replace with your value as follows from the Fourier map) and delta=0.5; activate Legendre polynomials;

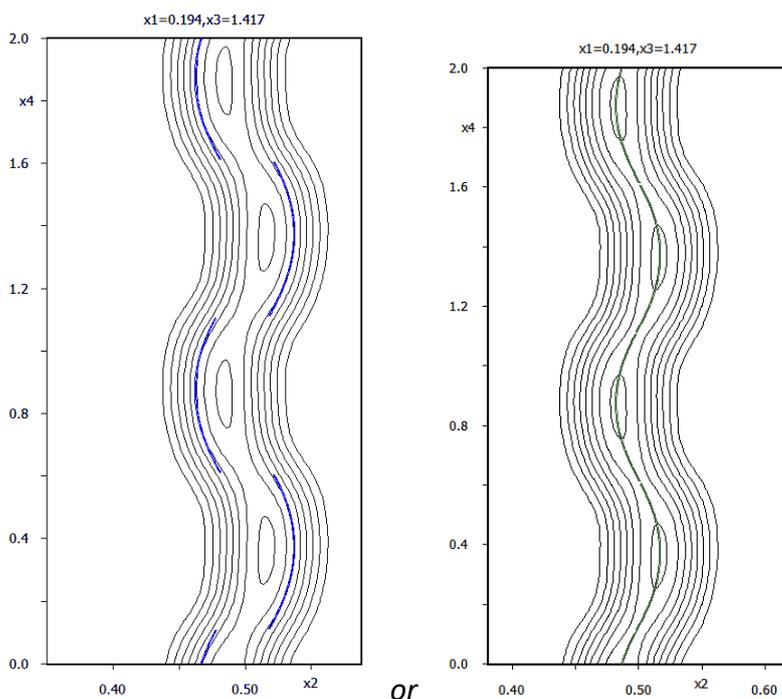
Return to Edit page

Note that y has been shifted slightly from the specil position (this has been done automatically by activation of Legendre); change site occupancy from 0.5 to 1 (we are now

out of the special position, and the occupancy is reduced by the crenel function)  
Close "Edit atoms"; check formula in EditM50 (should be still Cr2 P2 O7 for Z=2)  
Start Contour; use old maps

In "Atoms edit" of Contour add P1 and the symmetry equivalent P1#s4

In this case, the proper symmetry code does not appear in the Dist listing because the crenel width 0.5 makes both P1 positions exclusive. To see the code, the crenel width must be edited to be above 0.5. This generates a disorder from t values where both crenel functions co-exist, and the corresponding distance with symmetry code will appear in the Dist listing. After noting the code, do not forget to return the crenel width back to 0.5.



The left image occurs when we shift  $y[P1]$  from the special position more than necessary. The right image shows the situation when  $y[P1]$  was adjusted automatically during the conversion of the harmonic modulation function to Legendre polynomials. Both starting points are sufficient for successful refinement.

Quit Contour

Start Refinement option, page "Various", button "Equations"

Define equation  $t40[P1] = t40[O3]$

This bounds discontinuity points of P1 with O3.  $\frac{1}{2}$  shift may be needed depending on the Superflip solution.

Run refinement

Refinement converges with Robs factors 11%, 5%, 11%, 15%, 54% and 106% (77 parameters), i.e. better fit for 1<sup>st</sup> and 2<sup>nd</sup> order satellites

If the initial changes of parameters are large, the previously defined equation is probably incorrect. In such case, recover files (Tools – Recover files), edit the equation and try again.

Make backup copy (rewrite crpo\_aligned)

## 11. More modulation waves

At this point all atoms have two position modulation waves and no modulation of ADP. We will add position and ADP modulation waves until they improve R factors. Normally this

would be result of trials and errors, here the process will be simplified.

Oxygen O1 is only slightly modulated and does not need more waves.

Set three position modulation waves for Cr1, P1, O2 and O3

Refine

Refinement converges with Robs factors 9%, 5%, 11%, 8%, 56% and 76%

Add the first ADP modulation wave for Cr1, P1, O2 and O3

Start Refinement options, change number of refinement cycles to 100 and set damping factor 0.4

Refine

Refinement converges with Robs factors 7%, 4%, 7%, 13%, 37% and 56%

Set two ADP modulation waves for Cr1, P1, O2 and O3

Refine

Refinement converges with Robs factors 6%, 3%, 6%, 11%, 23% and 39%

Add another position modulation wave only for Cr1

Refine

Refinement converges with Robs factors 5%, 3%, 4%, 5%, 13% and 31%

Add another ADP modulation wave only for Cr1

Refine

Refinement converges with Robs factors 5%, 3%, 4%, 7%, 18% and 38%

Refine isotropic extinction (Parameters → Extinction)

Refinement converges with Robs factors 4%, 3%, 4%, 6%, 18% and 36% with 177 refined parameters.

Make backup copy: crpo\_simple

```
R factors : [4235=2722+1513/177], Damping factor: 0.4000
GOF(obs)= 3.43 GOF(all)= 2.90
R(obs)= 4.19 wR(obs)= 6.46 R(all)= 6.02 wR(all)= 6.90
R factors for main reflections : [491=488+3]
R(obs)= 2.63 wR(obs)= 4.37 R(all)= 2.65 wR(all)= 4.38
R factors for satellites +(1) : [904=856+48]
R(obs)= 3.91 wR(obs)= 5.27 R(all)= 4.10 wR(all)= 5.31
R factors for satellites +(2) : [989=780+209]
R(obs)= 6.44 wR(obs)= 7.24 R(all)= 8.12 wR(all)= 7.53
R factors for satellites +(3) : [900=410+490]
R(obs)= 17.60 wR(obs)= 23.01 R(all)= 31.47 wR(all)= 25.10
R factors for satellites +(4) : [951=188+763]
R(obs)= 36.05 wR(obs)= 40.71 R(all)= 73.92 wR(all)= 46.67
Last wR(all): 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90
Maximum change/s.u. : 0.0318 for GIso
```

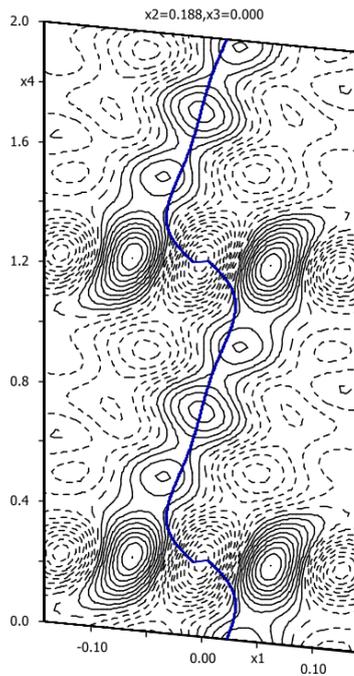
The result is looking well except the poor fit of the 3<sup>rd</sup> and 4<sup>th</sup> order satellites: is it caused by structure model or weak satellite intensity? For 3<sup>rd</sup> order satellites there is still 50 % of reflections above the observability limit. GOF > 4 also suggests the model could be improved. Another problem are warnings about ADP of P1 and O3, which are not positive definite for some regions of t.

Start “Edit/View → View of Reflection report”

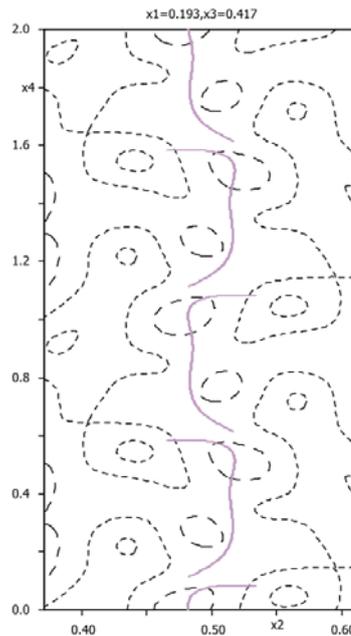
Press "GoTo" and move to "Summary after averaging"

Here we can see  $R_{int}$  for the 3<sup>rd</sup> order observed satellites (11%) and for the 4<sup>th</sup> order observed satellites (19%). This also suggests the quality of high order satellites is sufficient for a model improvement.

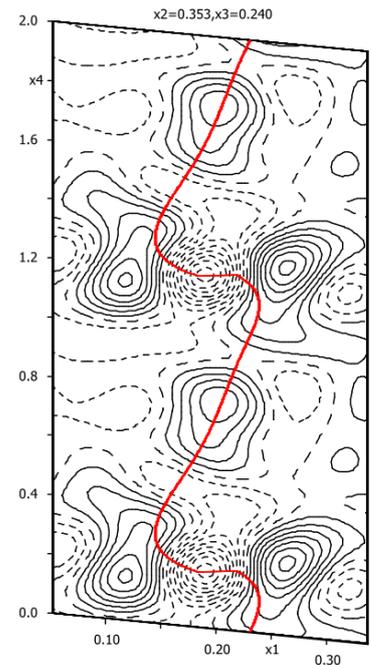
Start Contour and plot the following difference Fourier sections:  $x_1$ - $x_4$  for Cr1,  $x_2$ - $x_4$  for P1,  $x_1$ - $x_4$  for O2 and  $x_2$ - $x_4$  for O3. For plotting use always the contour step 0.2. You can also plot the section automatically by the "Show de Wolff's section", in such case contour step is set automatically but size of difference maxima is shown under the mouse cursor.



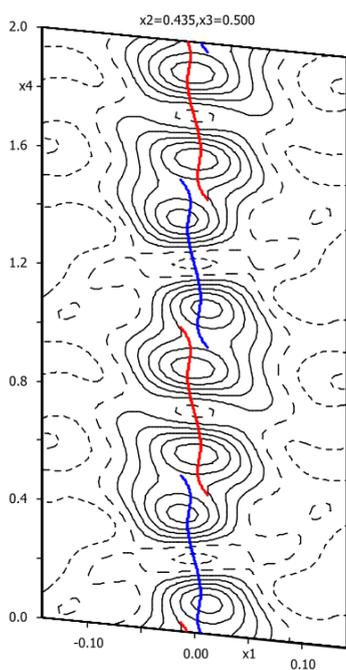
Cr1:  $x_1$ - $x_4$



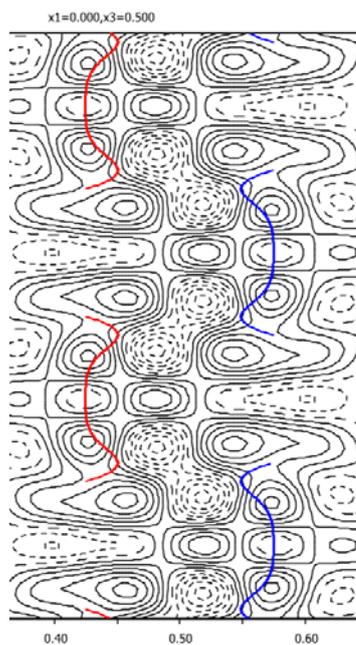
P1:  $x_2$ - $x_4$



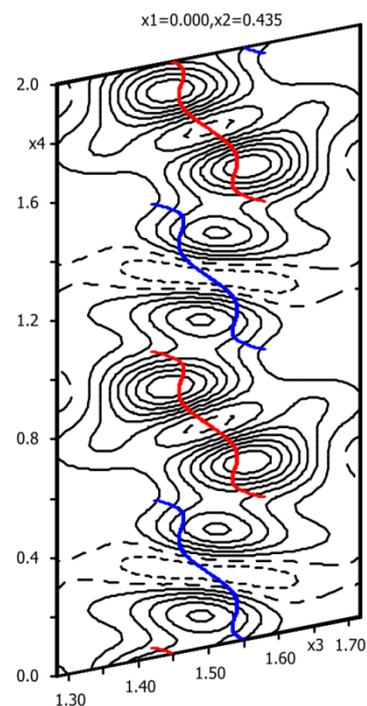
O2:  $x_1$ - $x_4$



O3: x1-x4



O3: x2-x4



O3: x3-x4

## 12. Disordered structure

The difference Fourier sections for Cr1, O2 and O3 indicate a disorder close to the discontinuity points of crenel function. At this part, we shall create a structure model with initial modulation functions describing the disorder.

For each of the atoms delta will be shortened and additional atoms with small complementary delta will be placed to the difference maxima found in the Contour sections. The resulting structure model must keep formula unchanged. The delta of all disordered atoms will be kept the same.

The atoms Cr1 and O3 have to be duplicated and the atoms O2 triplicated (because of lower symmetry). Then the atomic parameters of the original and split atoms must be modified to account for the disordered model as found from difference Fourier maps.

Start "Edit atoms"

Select Cr1, O2 and O3; Press "Action" → Select "Split atom";

Choose 0 for relative occupancy of split atom;

Check the manually defined shift of atoms equal 0 0 0;

Uncheck "Reset ADP to isotropic";

Uncheck "Generate restrict command for refine";

Press "Apply->Go to next";

Repeat this procedure for O2 and O3;

Select the atoms O2' and repeat the split procedure once more to create O2'';

OK; Yes to the question about rewriting;

The new positions will describe disorder at the discontinuity area. For Cr1' and O3' two

positions are generated by symmetry; for O2 we have introduced both positions.

Start "Edit atoms"

Select Cr1', O2', O2'', O3'

Change number of their position and ADP modulation waves to zero

Change ADP to isotropic

OK; Refresh

*In the following, the suggested coordinate changes may not be applicable to your solution.*

*In such case, plot again the Contour sections and note proper values.*

For Cr1' change x to 0.06 and site occupancy to 0.5

For O2' change x to 0.12 and site occupancy to 0.5

For O2'' change x to 0.26 and site occupancy to 0.5

For O3' change z to 1.44 and site occupancy to 0.5

*New positions can be found on the above shown difference sections.*

Start Refinement option, page "Various"

Press "Equations" and define the following equations:

$t40[Cr1'] = t40[Cr1] + 0.5$

*This puts the additional atom Cr1' to proper position along x4 related to Cr1*

$\delta[Cr1'] = 1 - \delta[Cr1]$

*This defines delta of the additional atom like complementary to the original atom*

$t40[O2'] = t40[O3] + 0.25$

*This puts the additional atom O2' to proper position along x4 related to O3.*

$t40[O2'] = t40[O2] - 0.5$  but we can substitute for  $t40[O2]$  from already defined equation

$t40[O2] = t40[O3] + 0.75$

$\delta[O2'] = \delta[Cr1']$

*We want delta the same for all additional atoms*

$t40[O2''] = t40[O3] + 0.25$

$\delta[O2''] = \delta[Cr1']$

$\delta[O2] = 1 - \delta[Cr1']$

$t40[O3'] = t40[O3] + 0.25$

$\delta[O3'] = \delta[Cr1']$

$\delta[O3] = 0.5 - \delta[Cr1']$

*After applying these equations all delta intervals will depend on delta of Cr1 and the total occupation of atoms will be the same like in the simple model.*

In page Basic **set zero refinement cycles**

Run refinement

*The refinement applies the equations and calculates structure factors*

*Because  $\delta[Cr1]$  is one all delta parameters of additional atoms are zero and R values are as before: 4%, 3%, 4%, 5%, 14% and 23% for 177 refined parameters*

Start EditM50, page "Composition", and press "Formula from M40"

This shows correctly Cr2 P2 O7

*We want to assign some non-zero delta for additional atoms and view modulation functions but with the original electron density*

Start "Edit atoms" and change delta of Cr1 from 1 to 0.9

*In refinement we have still zero cycles*

Run refinement

*This recalculates delta based on equations and creates new (unwanted) input for Fourier*

Start "File → Structure → Save As" and create copy "tmp"

Do not continue with the new structure

Change delta of Cr1 back to 1

Run refinement (with zero cycles)

*This creates good input for Fourier*

Start "File → Structure → Copy in" and copy to the current structure only M40 from the previously created backup copy "tmp"

*Now we have old input for Fourier and new input for plotting modulation functions*

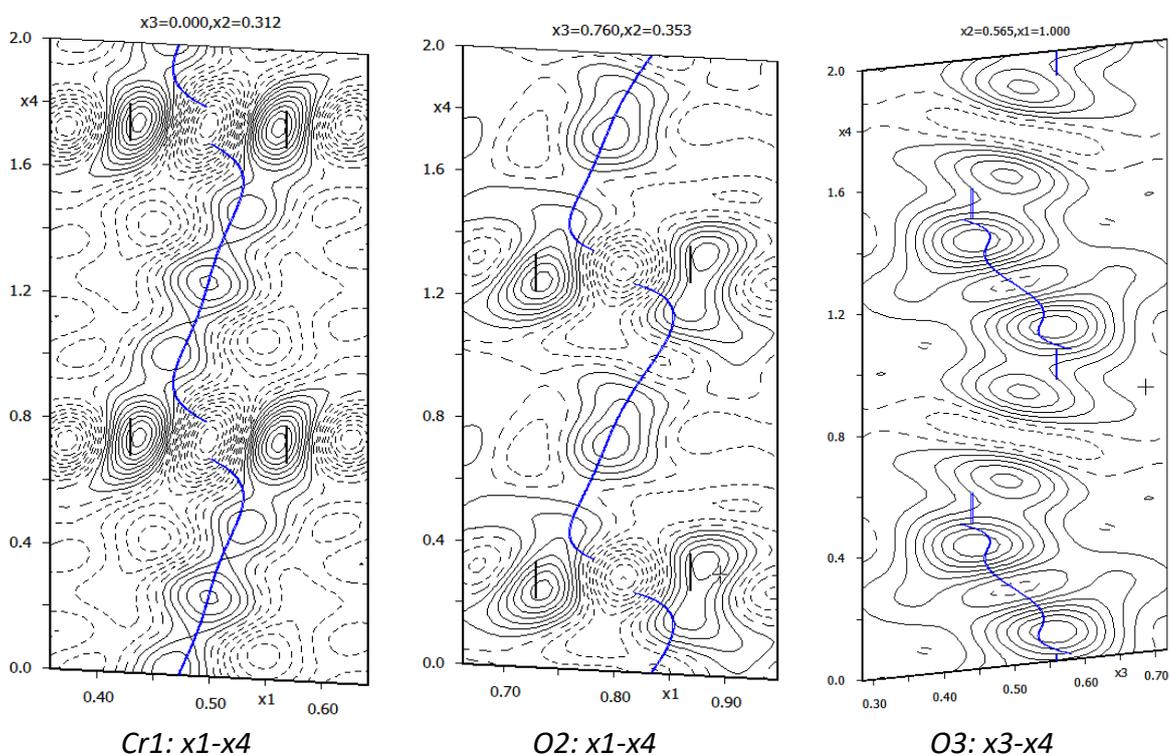
Start Contour

For Cr1 plot x1-x4 difference section and visualize Cr1, Cr1', Cr1'#s2t0,0,2

*Your symmetry codes may be different*

For O2 plot x1-x4 difference section and visualize O2, O2' and O2''

For O3 plot x3-x4 difference section and visualize O3, O3' and O3'#s2t0,1,3



Make backup copy: crpo\_disorder\_initial

### 13. Refinement of disordered model

*Refinement of the disordered model must be started from very small delta for additional disordered atoms. The purpose of this refinement is not to obtain proper geometry of the disordered atoms because the corresponding scattering power is very small: for O3 and delta=0.1 the disordered atom would have  $0.1 \cdot 0.5 \cdot 8$  electrons, which is less than 0.5 of hydrogen.*

Start "Edit Atoms"

Change delta of Cr1 to 0.98 and leave it fixed

Run zero refinement cycles

*This will create  $\delta=0.02$  for additional atoms*

Test Formula (EditM50 – must be Cr2 P2 O7)

Start Refinement options, set 100 refinement cycles with damping 0.4

Uncheck “Disable atoms having too large isotropic ADP”

Run refinement until convergence

*The simple model without disorder converged with Robs factors 4%, 3%, 4%, 6%, 18% and 36% for 177 refined parameters.*

*Now we have obtained Robs factors 3%, 2%, 2%, 4%, 9% and 18% for 193 refined parameters. This means the fit has been considerably improved for higher satellites, and we can try to refine delta.*

Start “Edit atoms” and activate refinement of delta for Cr1

Run refinement

*Refinement converges with Robs factors 3%, 2%, 2%, 4%, 9% and 18% for 194 refined parameters. Delta of additional atoms refines to 0.093.*

Start “Edit atoms” and add one position modulation wave to all additional atoms (Cr1', O2', O2'' and O3').

Run refinement

*If refinement is unstable, press “Parameters” and switch on the Marquart technique.*

*Refinement converges with Robs factors 2.4%, 1.9%, 2.0%, 3.5%, 7.3% and 12.1% for 218 refined parameters. GOF = 2.0. Delta of additional atoms refines to 0.11.*

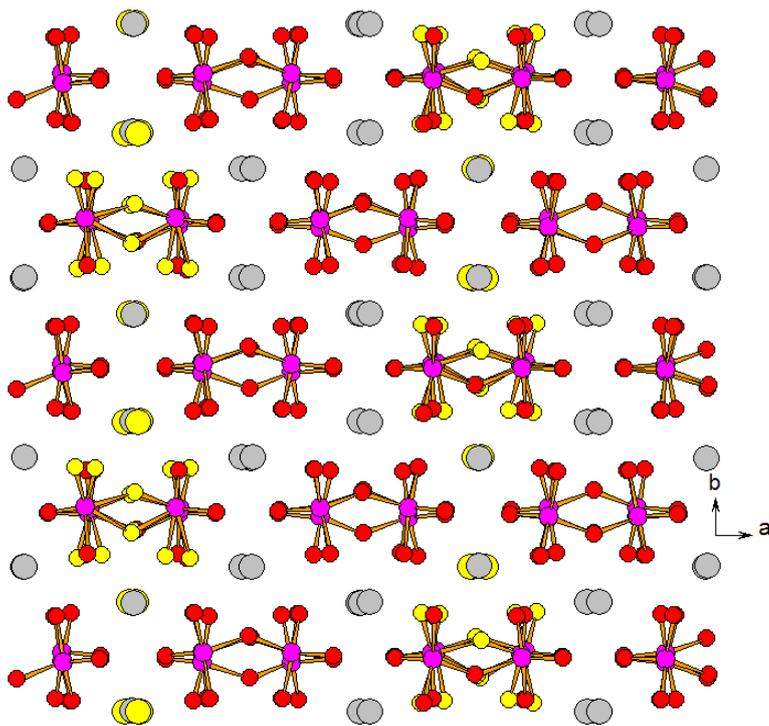
Make backup copy: crpo\_disorder\_final

### **Conclusions**

*The disordered model does not provide proper geometry of disordered atoms. However, we can draw an approximant structure in large area and try to determine in which places of the real space the structure becomes disordered.*

Plot the structure expanded to 3x3x3 cells

Indicate the atoms with ' and '' in yellow



*In view along c we can distinguish columns without disorder and columns with disorder*

Using Graph, we can visualize  $U(\min)$  to see for which  $t$  values it becomes negative (leading to the serious warning during refinement)

**We can see this occurs close to the disordered area**



# Example 5.4: Fresnoite

Solution of (3+2)-dimensional incommensurately modulated structure.

## Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>

Single crystal data measured with Oxford Diffraction four-cycle diffractometer

Input files: fresnoite.hkl, fresnoite.cif\_od

Frame scaling, absorption correction: done with software of the diffractometer

### 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click fresnoite

### 2. *Import Wizard*

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction – CCD”; NEXT

In “Define basic input file” select “Input from cif\_od file”; OK

Change all q-vector components to 0.302 keeping the original sign; NEXT

Leave all settings unchanged; NEXT

For absorption correction select “None or done before importing”; NEXT

FINISH

*[On the screen: Data repository]*

OK; YES to accept the data set

### 3. *Symmetry Wizard*

Use default tolerances for crystal system recognition

Select tetragonal Laue symmetry 4/mmm

Press Show/modify X centering

*[On the screen: select individual centering vectors]*

Select centering vectors: (0 0 0 0) and (0 0 1/2 1/2 1/2); OK; Next

Select space group X4/mbm and note the non-centrosymmetric possibilities

Accept the superspace group in the original cell

*For five-dimensional structures the wizard does not offer selection of superspace group. It will be done later manually.*

### 4. *Creating refinement reflection file*

Follow default steps of the reflection wizard

The program discards 54372 reflections, 455 observed, Rint=3.28%

### 5. *Structure solution wizard*

ESC

## 6. **Solution of average structure – centrosymmetric solution**

*Superflip for five-dimensional structure returns five-dimensional electron density map. However, Jana2006 would not evaluate initial modulation functions from this map and we would get average structure. For this reason solution will be done separately for average structure*

Start “Tools → Transformation → Go to average 3d structure”

For name use “ave\_centro”

Follow steps of the Reflection wizard

Continue with the new structure

Start “Run → Solution”

For Formula type “Ba Ti Si O”

Select “Superflip” and “Peaks from Jana2006”

Select “Use a specific random seed” and type “111” for random seed

*With this option result of charge flipping will be the same in most computers and origin position and special atomic position will be equivalent with this cookbook. For normal work Random seed should not be fixed.*

OK

*Superflip converges with R around 18% and confirms the selected space group*

Accept the result

Start EditM50 and check formula for Z=4: Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>4</sub> (should be Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>8</sub>)

Run Refinement

*Refinement converges with Robs=14%*

Using “Edit Atoms”: check Uiso of O1 is it rather high ~ 0.13 Å<sup>2</sup>; Esc

Plot the average structure; Check that the O1 atom is in a close contact with Ba1 ~ 1.16 Å

Run “Edit atom” and delete the atom O1

Run refinement

*Refinement converges with Robs=13%*

Run difference Fourier

Add difference maxima Max1, Max2, Max3 as oxygens

Run refinement

*Refinement converges with Robs=12%*

In EditM50 check formula: Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>8</sub>

Run difference Fourier; Add difference maxima Max1 as a new oxygen atom

Run refinement

Check formula: Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>16</sub>

In EditM40 allow refinement of atomic occupancies – “ai” parameter – of all oxygen atoms;

*Refinement converges with Robs=9.1%*

Check formula: Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>9.2</sub>

Using “Edit atoms” change all ADP to harmonic

Run refinement

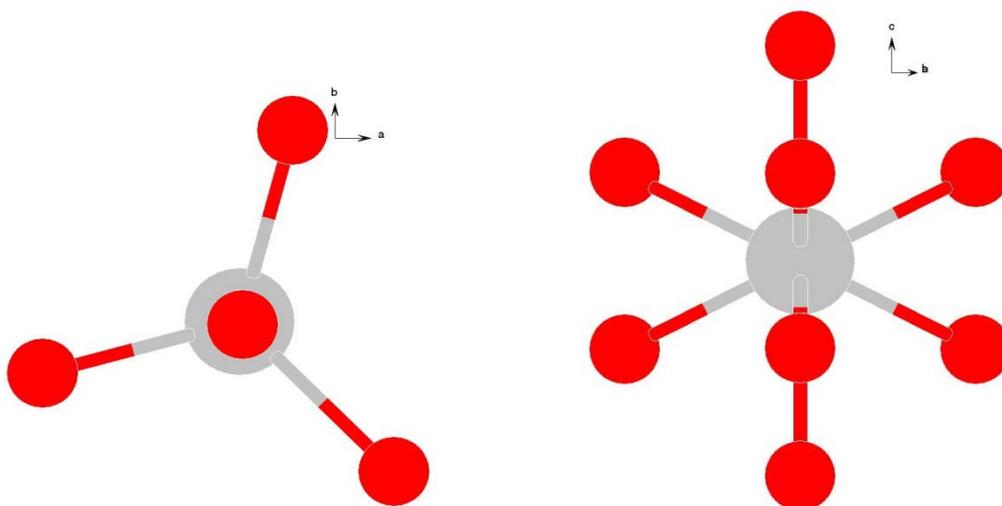
*Refinement converges with Robs=5.9%*

Check formula: Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>10.1</sub>

Plot average structure; make Si-O coordination; draw the projection along [0,0,1] and along [1,-1,0]

*Jana2006 sends to Diamond expanded structure in P1 symmetry. This is because of centering X which Diamond cannot use. In the plot the silicon atom is surrounded by eight*

partially occupied oxygen atoms. This can be either reality which would be described by crenel functions or wrong symmetry for average structure.



The figures indicate a disorder of  $\text{SiO}_4$  groups by the mirror perpendicular to the  $c$  axis. The disorder can be described alternatively by the two fold axis perpendicular to  $c$  and  $a+c$ . The disorder in the average structure can be produced either by the fact the structure is not centrosymmetric or by modulation. First we shall test non-centrosymmetric description.

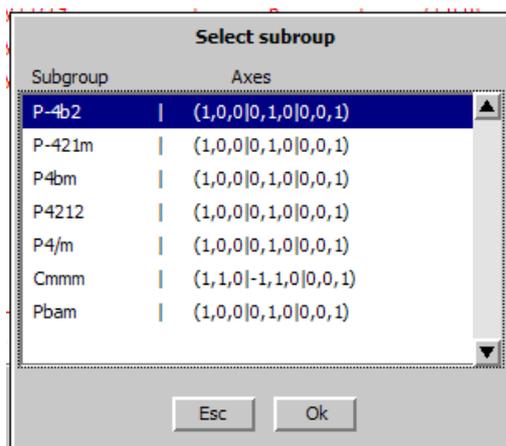
#### 7. Solution of average structure – non-centrosymmetric solution

In order to see all highest non-isomorphic subgroups we shall create a testing structure:

Start “File → Structure → save as” and create a testing structure named “ave-test”.

EditM50: change symmetry from X4/mbm to P4/mbm; Accept changes without re-creation of the diffraction file;

Start “Tools → Transformations → Go to subgroup structure”; Press the button “Select non-isomorphic subgroup:”



The highest subgroups not giving a split model for  $\text{SiO}_4$  group are  $P-42_1m$  and  $P4bm$ . Now we have to check if basic positions  $(x,y,z)$  of atoms Si1, O1, O2 and O4 belong to a unique tetrahedron.

Return to the structure “ave-centro”; Set distance commands: in the “Basic” define calculation of angles and the listing form “with symmetry codes”.

Run dist; Open the listing:

Si1-O1	1.670 (14)	2nd: O1	x, y, z
O1-Si1-O1	44.3 (16)	3rd: O1#s4t1,0,0	-x+1, -y, -z
O1-Si1-O2	66.7 (12)	3rd: O2	x, y, z
O1-Si1-O2	111.0 (12)	3rd: O2#s10	x, y, -z
O1-Si1-O4	105.5 (9)	3rd: O4	x, y, z
O1-Si1-O4	105.5 (9)	3rd: O4#s6	-y+1/2, -x+1/2, z
O1-Si1-O4	124.9 (7)	3rd: O4#s10	x, y, -z
O1-Si1-O4	124.9 (7)	3rd: O4#s16	-y+1/2, -x+1/2, -z
Si1-O1	1.670 (14)	2nd: O1#s4t1,0,0	-x+1, -y, -z
O1-Si1-O2	111.0 (12)	3rd: O2	x, y, z
O1-Si1-O2	66.7 (12)	3rd: O2#s10	x, y, -z
O1-Si1-O4	124.9 (7)	3rd: O4	x, y, z
O1-Si1-O4	124.9 (7)	3rd: O4#s6	-y+1/2, -x+1/2, z
O1-Si1-O4	105.5 (9)	3rd: O4#s10	x, y, -z
O1-Si1-O4	105.5 (9)	3rd: O4#s16	-y+1/2, -x+1/2, -z
Calculating of distances, angles, torsion angles and best planes structure :			
Si1-O2	1.55 (2)	2nd: O2	x, y, z
O2-Si1-O2	177.6 (7)	3rd: O2#s10	x, y, -z
O2-Si1-O4	66.7 (8)	3rd: O4	x, y, z
O2-Si1-O4	66.7 (8)	3rd: O4#s6	-y+1/2, -x+1/2, z
O2-Si1-O4	114.5 (8)	3rd: O4#s10	x, y, -z
O2-Si1-O4	114.5 (8)	3rd: O4#s16	-y+1/2, -x+1/2, -z
Si1-O2	1.55 (2)	2nd: O2#s10	x, y, -z
O2-Si1-O4	114.5 (8)	3rd: O4	x, y, z
O2-Si1-O4	114.5 (8)	3rd: O4#s6	-y+1/2, -x+1/2, z
O2-Si1-O4	66.7 (8)	3rd: O4#s10	x, y, -z
O2-Si1-O4	66.7 (8)	3rd: O4#s16	-y+1/2, -x+1/2, -z
Si1-O4	1.576 (16)	2nd: O4	x, y, z
O4-Si1-O4	105.1 (8)	3rd: O4#s6	-y+1/2, -x+1/2, z
O4-Si1-O4	47.8 (9)	3rd: O4#s10	x, y, -z
O4-Si1-O4	126.1 (8)	3rd: O4#s16	-y+1/2, -x+1/2, -z
Si1-O4	1.576 (16)	2nd: O4#s6	-y+1/2, -x+1/2, z
O4-Si1-O4	126.1 (8)	3rd: O4#s10	x, y, -z
O4-Si1-O4	47.8 (9)	3rd: O4#s16	-y+1/2, -x+1/2, -z
Si1-O4	1.576 (16)	2nd: O4#s10	x, y, -z
O4-Si1-O4	105.1 (8)	3rd: O4#s16	-y+1/2, -x+1/2, -z
Si1-O4	1.576 (16)	2nd: O4#s16	-y+1/2, -x+1/2, -z

The blue lines indicate the bond distances and red lines bond angles of the basic  $\text{SiO}_4$  group. From the symmetric codes we can see that only the atom O2 should be transformed by the symmetry operation #s10 i.e. by x,y,-z

Start "Edit atoms": select the atom O2 and transform it by x,y,-z

Before testing of non-centrosymmetric space groups we have to reset the occupancies to their the values corresponding the  $\text{SiO}_4$  split. This means that their full values are to be reduced by 1/2. The atom O3 is coordinating Ti and it can also be shown that it has to represent a split position.

Start "Edit atoms" set "ai" for O1, O2, O3 and O4 to 0.25, 0.5, 0.25 and 1, respectively.

In the next step we shall test non-centrosymmetric space group  $X-42_1m$

Start "Tools → Transformation → Go to subgroup structure"

[On the screen: Define subgroup]

The button for selecting non-isomorphic subgroup is missing because of non-standard

*centering*

Select symmetry operator for the screw axis  $2_1$  and rotation axis -4 of the space group  $X-42_1m$

Press "Complete subgroup"

*The subgroup should be  $X-42_1m$  without changing axes*

Next; Next

*[On the screen: select one representative of the 2<sup>nd</sup> coset]*

Select inversion as operator for expansion to the subgroup; Next

Deselect "Make as twinned structure"

Type name of the structure (for instance "ave\_-421m"); Next

Follow steps of the Reflection wizard

Continue with the new structure

Check formula – still Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>16</sub> for Z=4

"Edit atoms": delete atoms O<sub>1\_2</sub>, O<sub>2\_2</sub> and O<sub>4\_2</sub> and reduce the occupancy of O<sub>3</sub> to 0.25.

Check formula – still Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>8</sub> for Z=4

In "Refine commands" set damping factor to 0.5

Run Refinement

*Refinement converges with R<sub>obs</sub>=8.3%*

*In the next step we shall test non-centrosymmetric space group  $X4bm$*

Start "File → Structure → Open" and return to the centrosymmetric average structure ("ave\_centro")

Start "Tools → Transformation → Go to subgroup structure"

*[On the screen: Define subgroup]*

*The button for selecting subgroup is missing because of non-standard centering*

Select symmetry operator for glide plane b and rotation axis 4 of the space group  $X4bm$

Press "Complete subgroup"

*The subgroup should be  $X4bm$  without changing axes*

Next; Next

*[On the screen: select one representative of the 2<sup>nd</sup> coset]*

Select inversion like operator for expansion to the subgroup; Next

Deselect "Make as twinned structure"

Type name of the structure (for instance "ave\_4bm"); Next

Follow steps of the Reflection wizard

Continue with the new structure

Check formula – still Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>16</sub> for Z=4

"Edit atoms": delete atoms O<sub>1\_2</sub>, O<sub>2\_2</sub>, O<sub>3\_2</sub> and O<sub>4\_2</sub>.

Check formula – still Ba<sub>2</sub> Ti Si<sub>2</sub> O<sub>8</sub> for Z=4

Run Refinement

*Refinement converges with R<sub>obs</sub>=2.27%*

"Edit atoms": rename oxygens to O<sub>1</sub>, O<sub>2</sub>, O<sub>3</sub>, O<sub>4</sub> using "Rename selected atoms to atom

"File → Structure → Save As": ave\_final

## **8. Back to the modulated structure**

"File → Structure → Open": open "fresnoite"

EditM50:

In "Composition page" type formula Ba Ti Si O and formula units 4

In "Symmetry" page change symmetry to X4bm  
 OK to confirm centering  
 OK for the first translation part  
 OK for the second translation part  
 Close Editm50  
 Re-create refinement reflection file  
 "File → Structure → Copy in": import **only** M40 from the average structure "ave\_final"  
 Run refinement  
 Refinement confirms R value for the average structure:

```
R factors : [6599=4677+1922/37], Damping factor: 1.0000
GOF(obs)= 22.66 GOF(all)= 19.14
R(obs)= 40.27 Rw(obs)= 61.44 R(all)= 43.31 Rw(all)= 61.61
R factors for main reflections : [796=789+7]
R(obs)= 2.27 Rw(obs)= 3.82 R(all)= 2.29 Rw(all)= 3.83
R factors for satellites of order 1 : [2858=2499+359]
R(obs)=100.00 Rw(obs)=100.00 R(all)=100.00 Rw(all)=100.00
R factors for satellites of order 2 : [2945=1389+1556]
R(obs)=100.00 Rw(obs)=100.00 R(all)=100.00 Rw(all)=100.00
Last Rw(all): 61.91 61.61 61.61 61.61
Maximum change/s.u. : 0.0058 for U11[O4]
```

### 9. Superspace symmetry

In the previous paragraph the program asked for completion of the translation part of superspace symmetry operators. For the present case two symmetry operators should be completed:

Complete translational part for the operator:

-x2 x1 x3 -x5 x4	
Rotation	Translation
0 -1 0 0 0	0
1 0 0 0 0	0
0 0 1 0 0	0
0 0 0 0 -1	<input type="text" value="0"/>
0 0 0 1 0	<input type="text" value="0"/>

Ok

and

Complete translational part for the operator:

-x1+1/2 x2+1/2 x3 x5 x4	
Rotation	Translation
-1 0 0 0 0	1/2
0 1 0 0 0	1/2
0 0 1 0 0	0
0 0 0 0 1	<input type="text" value="0"/>
0 0 0 1 0	<input type="text" value="0"/>

Ok

Each translation part has two elements which can be either 0 or 1/2. Thus we have sixteen combinations: 0 0 + 0 0, 0 0 + 1/2 0, 0 0 + 0 1/2, 0 0 + 1/2 1/2 ... However, the translation part can be combined with the X centering (0 0 1/2 1/2 1/2) which makes equivalent for instance the pairs 0 0 + 1/2 1/2 and 1/2 1/2 + 0 0. Moreover, some combinations are forbidden because they lead to inconsistent translation (0 0 0 1/2 1/2).

Finally we have only two independent possibilities:

0 0 + 1/2 1/2

0 0 + 0 0

Start EditM50

Go to page "Symmetry"

Focus the textbox "Space group" and press TAB. The program offers the first symmetry operator needing to complete.

At the first attempt try combination 0 0 for the first operator and 1/2 0 for the second one.

*The program will not allow it.*

Then try the combination 0 0 + 0 0. Close EditM50 and re-create refinement reflection file.

From the screen output of the symmetry wizard note number of rejected reflections: 54372 rejected reflections from which 455 is observed with the largest  $I/\sigma(I)$  around 15

Return to EditM50

TAB in the textbox "Space group"

For translation parts use combination 0 0 + 1/2 1/2

Re-create refinement reflection file

*From the screen output of the symmetry wizard note number of rejected reflections: 55353 rejected reflections from which 463 is observed with the largest  $I/\sigma(I)$  around 15*

*This means: the translation part 1/2 1/2 of the second operator leads to 1000 more forbidden reflections but the number and sigma level of the observed forbidden reflections remains almost the same like with the translation part 0 0. This confirms the presence of the translation part 1/2 1/2 for the second symmetry operator.*

## 10. Refinement of modulated structure – position modulation

Make backup copy: "fresnoite\_backup"

Start "Parameters → Options"

Press "Define wave vectors"

For the third wave define 1 1

*This means modulation wave vector given by a sum of the q vectors*

For the fourth wave define -1 1

*This means modulation wave vector given by a difference of the q vectors*

"Edit atoms": set two position modulation waves for all atoms

*This means one harmonic wave along the first wave vector ( $q_1$ ) and one harmonic wave along the second wave vector ( $q_2$ )*

Run refinement

*Refinement converges with the following  $R_{obs}$  values for all reflections, main reflections, 1<sup>st</sup> and 2<sup>nd</sup> order satellites: 10%, 3%, 13%, 51%*

*By second order satellites are considered reflections described by combination of  $q_1$  and  $q_2$ :  $q_1 + q_2$  or  $-q_1 + q_2$ .*

"Edit atoms": add another two position modulation waves for all atoms

*This mean one harmonic wave along the first wave vector combination ( $q_1+q_2$ ) and one harmonic wave along the second wave vector combination ( $-q_1+q_2$ )*

Run refinement

*Refinement converges with the following  $R_{obs}$  values for all reflections, main reflections, 1<sup>st</sup> and 2<sup>nd</sup> order satellites: 4%, 2%, 7%, 6%*

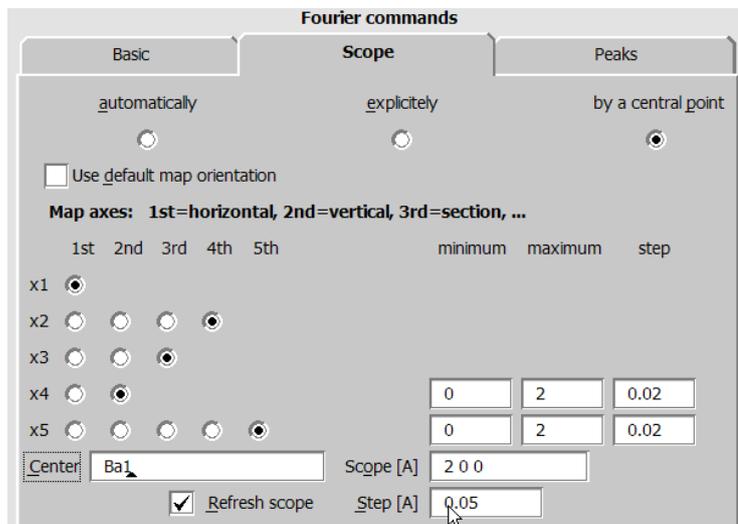
## 11. Contour sections and ADP modulation

“Start Contour → New plot → Calculate new ones”

Select observed Fourier

For “Scope” define Ba1 as central atom

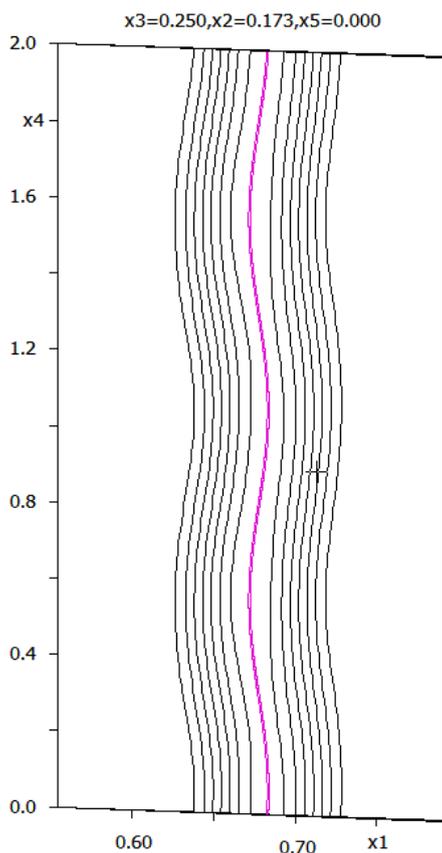
For map axes select x1, x4, x3, x2, x5 with limits as shown below



*This will plot section x1-x4 but the shape of atomic domain will be function of x5*

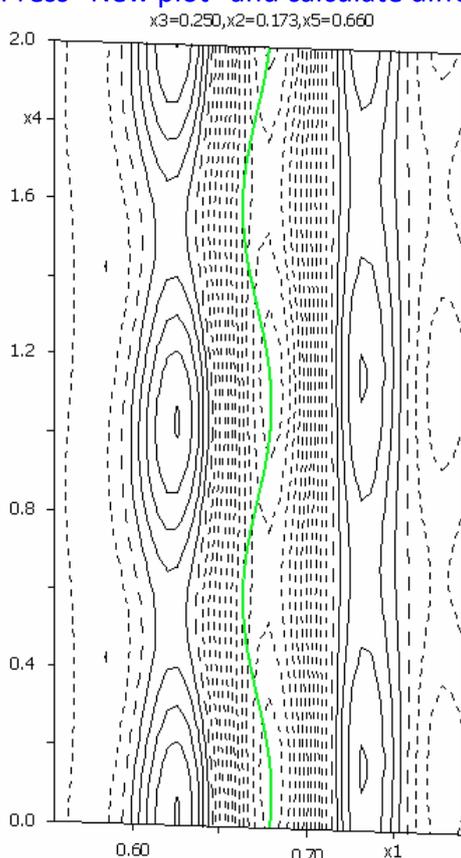
OK to calculate Fourier map

In Contour press “Atoms edit” and add Ba1



Press “Movie” to see the changes of this figure with x5

Press “New plot” and calculate difference Fourier map for the same section



The difference maxima around Ba1 are very strong indicating ADP modulation

“Edit atoms”: set two ADP modulation waves for Ba1

Run refinement

Refinement converges with the following Robs values for all reflections, main reflections, 1<sup>st</sup> and 2<sup>nd</sup> order satellites: 3%, 2%, 4%, 6% for 121 parameters

## 12. Refinement of inversion twin

As the structure is non-centrosymmetric we cannot be sure that the proper absolute configuration has been reached. To prove the correct configuration we shall refine so called Flack's parameter which means the volume fraction of twins related by the inversion centre.

“Start EditM50” to the page cell, define the twinning operation by inversion centre

Run “Parameters→ Twin fraction” and allow refinement of the twin ratio.

Run refinement

Refinement converges with the following Robs values for all reflections, main reflections, 1<sup>st</sup> and 2<sup>nd</sup> order satellites: 2.1%, 1.5%, 2.6%, 5.5% for 122 parameters.

Run “Parameters→ Twin fraction” to see the refined volume fraction ~ 0.915. Which means the absolute configuration is opposite to that we got when going from the centrosymmetric to non-centrosymmetric description.

Make backup copy: “fresnoite\_final”

## 13. Inverted barium position – false minimum

Barium is located in a special position  $x, x-1/2, 1/4$ . Application of a two-fold axis creates a position  $-x, -x+1/2, 1/4$ , which becomes – after application of the three-dimensional part of

*the X centering  $0\ 0\ 1/2\ 1/2\ 1/2$  – equivalent to the inverted position  $-x, -x+1/2, -1/4$ . Thus in average structure position of barium can be inverted. In modulated structure inversion of barium yields different modulation functions because of the 4<sup>th</sup> and 5<sup>th</sup> component of the centering vector.*

*Refinement of fresnoite tends to be trapped in a false minimum because of very good fit of main reflections and relatively weak satellites. Inversion of the position of barium helps to leave the false minimum.*

Start “Edit Atoms”, select Ba1

“Action → Transform selected atoms” and apply inversion -x1,-x2,-x3,-x4,-x5

Save the result, leave “Edit atoms”

Run refinement

*Refinement converges with the following Robs values for all reflections, main reflections, 1<sup>st</sup> and 2<sup>nd</sup> order satellites: 7.6%, 2.7%, 15.6%, 14.2%. This means that the structure can reach a false minimum but also stable minimum.*

# Example 5.5.1: Melilite data

Data processing of a (3+2)-dimensional incommensurately modulated structure with overlaps of satellites, using Crysalis.

Revised: 07 September 2019

## Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>

Single crystal data measured with Oxford Diffraction four-cycle diffractometer

Input files: directory Melilite available at <http://crysa.fzu.cz/jana/workshops/Melilite.zip>

(for workshops, data should be available at flash disks)

This example is based on the Crysalis 171.40.53. Crysalis is a program for control and data processing of Oxford Diffraction diffractometers.

### 1. Getting the input data (if not available in workshop materials)

Start your browser

Connect to <http://crysa.fzu.cz/jana/workshops/Melilite.zip> and download the archive

Unpack the archive

It will create directory Melilite

### 2. Starting Crysalis

Start Crysalis

In a dialogue that follows locate the file run.par

Crysalis opens the experiment.

Use  to decrease the image size

### 3. Determination of the unit cell

Start Lattice wizard using the button



[On the screen: the window of Lattice Wizard]

Start "Peak hunting" with default options

About 30000 peaks have been found

Start "Unit cell finding" with default options

The program finds a unit cell 7.84 7.84 5.02 90 90 90 and indexes about 70% of peaks

#### LATTICE

Current cell (CSD: not done)

7.8437(3) 7.8451(2) 5.01487(15) 90.005(2) 90.005(3) 90.005(3) 308.587(17)

Constrained current cell

7.8448(2) 7.8448(2) 5.01429(18) 90.0 90.0 90.0 308.587(17)

Lattice reduction

selected cell

7.8437 7.8451 5.0149 90.0053 90.0049 90.0054 tP 21

reduced cell

5.0149 7.8437 7.8451 90.0054 90.0053 90.0049 308.6

#### PEAK TABLE

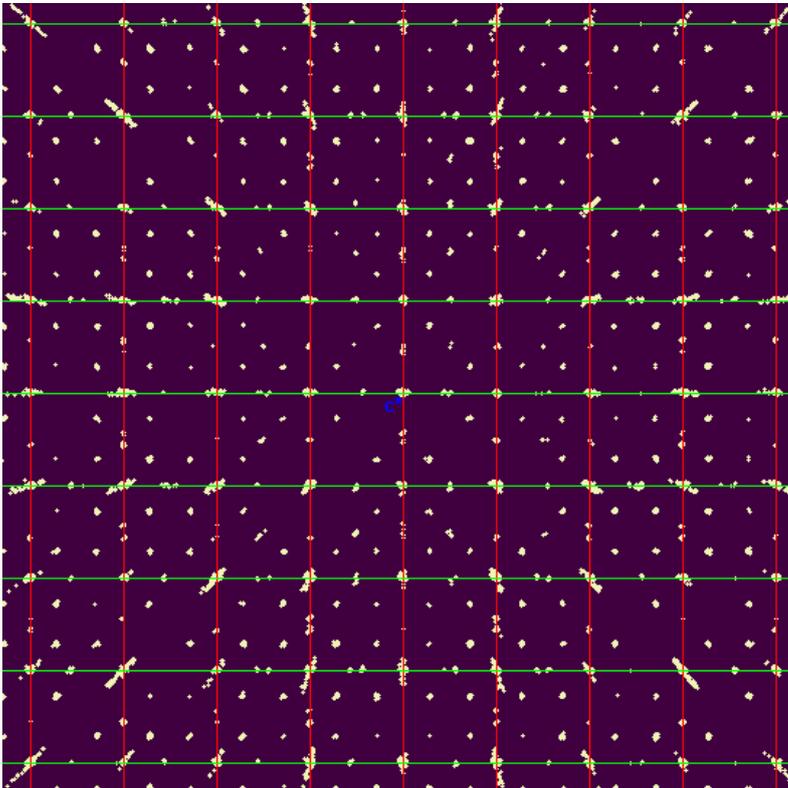
Peak hunting table

UB fit with 21276 obs out of 30622 (total:30622,skipped:0) (69.48%)

Start "Ewald Explorer" with default options

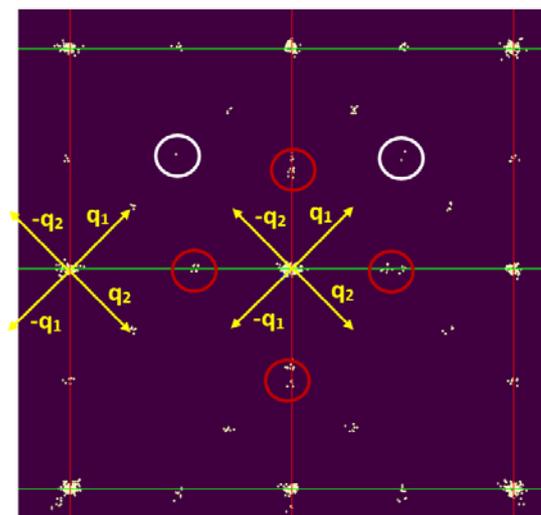
Use the buttons **a\*** **b\*** **c\*** to see projections of the found peaks along the unit cell axes.

Set projection along  $c^*$



The projection shows main reflections with radial distribution of spurious peaks. These peaks are tails of very strong reflection and their radial distribution allows quick conclusion that these are not satellites.

Enlarge the peak projection using the right mouse button

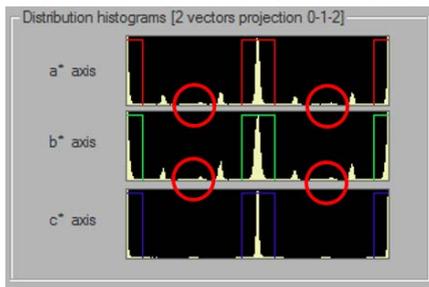


Majority of satellite peaks can be described by two  $q$ -vectors:  $q_1 = (\alpha, \alpha, 0)$ ,  $q_2 = (-\alpha, \alpha, 0)$ . The positive direction of  $a^*$  and  $b^*$  is indicated in the Ewald view by very small labels.

The peaks indicated by white circles are  $\lambda/2$  reflections. The experiment was done with classical Mo x-ray tube and graphite monochromator and with this equipment, such reflections may exist between very strong regular reflections.

The most important are weak reflections indicated by red circles. These reflection are described by combination of  $q_1$  and  $q_2$ , and this proves that our structure is (3+2)-dimensional. Without these reflections observed, there would also be possibility of a (4+1)-dimensional crystal twinned by  $90^\circ$  rotation around  $c^*$ .

The combined satellites are also visible in the projections:



The projections also indicate that the combined satellites may be overlapped due to short distance between them

In the next step, we will visualize the reciprocal plane  $0,k,l$  and  $1,k,l$  to see better the combined satellites

#### 4. Unwarping

Close the Ewald explorer

In Lattice wizard, press "Unwarping – precession images"

NEXT; NEXT

[On the screen: Step 3: Creation of a layer list"]

Press "Generate layers"

Type 1 for "max order", 1.2 for "resolution"

Delete all layers except  $1\_k\_l$

NEXT

[On the screen: Step 4: Use background subtraction"]

Check "Use background subtraction"

NEXT

[On the screen: Step 5: Data corrections"]

Press "Edit user scale"

Define a user scale 40 (to see weak features)

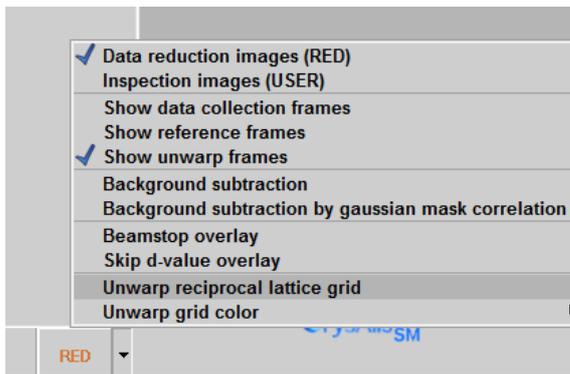
Check "Don't apply final convolution filter" (to see better separation of spots)

FINISH

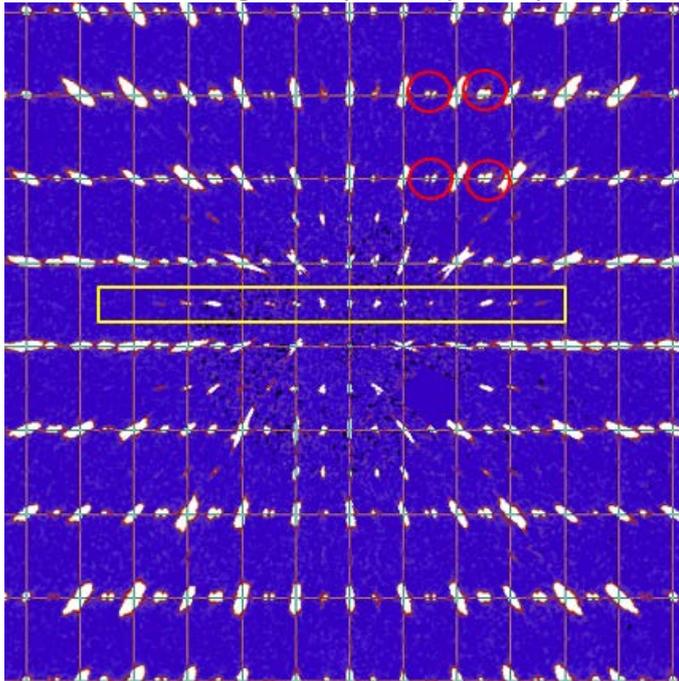
Check the radio button "Layer" to see the progress of the unwarp procedure.

Wait until the layer is finished

Open the menu in the lower right corners of CrysAlis and select "Unwarp reciprocal lattice grid"



*This is the resulting unwarped reciprocal plane (precession-like image):*



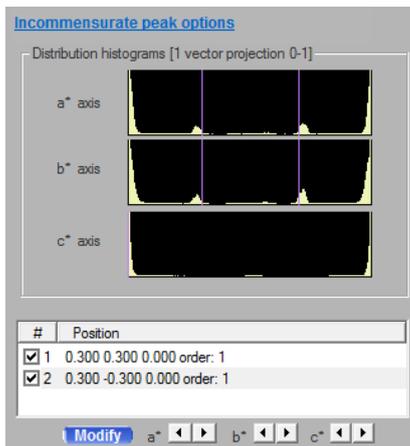
*The weak spots indicated by yellow rectangle are the  $\lambda/2$  reflections. The ones indicated by red circles are the combined satellites. Again, the possibility of overlaps between the combined satellites is evident.*

##### **5. Setting up the (3+2)d structure, refinement of q-vectors**

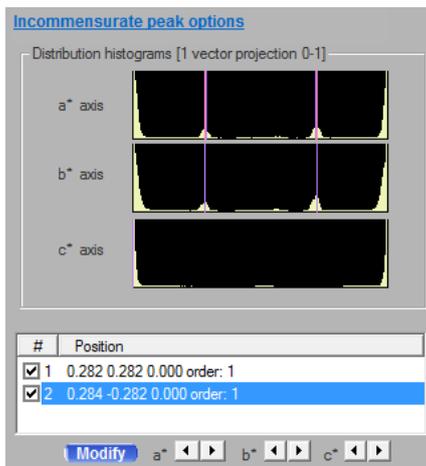
Start Lattice wizard and Ewald explorer

Press "Activate incommensurate peaks" and select "Add 2d modulation vectors (hklmn)"

Define two q-vectors: (0.3, 0.3, 0) and (-0.3, 0.3, 0) with maximum satellite index 1



Using the sliders, modify the components to fit with the projected peaks



Close Ewald explorer

In Lattice wizard, press "Incommensurates/Quasi-crystals"

Use default settings (with  $m_{max} = 1$ ); OK

*The refined unit cell + q-vectors index 92% of peaks. The procedure could index about 1800 combined satellites.*

```

LATTICE
Current cell (CSD: 0 +8L)
 7.8437(3) 7.8451(2) 5.01487(15) 90.005(2) 90.005(3) 90.005(3) 308.587(17)
Constrained current cell
 7.8448(2) 7.8448(2) 5.01429(18) 90.0 90.0 90.0 308.587(17)
Lattice reduction
selected cell
 7.8437 7.8451 5.0149 90.0053 90.0049 90.0054 tP 21
reduced cell
 5.0149 7.8437 7.8451 90.0054 90.0053 90.0049 308.6
Incommensurate/quasi-crystal information
q(1): 0.2815(3) 0.2822(4) 0(3e-004) q(2): 0.2819(3) -2.819e-001(4) 0(2e-004)

PEAK TABLE
Peak hunting table
UB fit with 28137 obs out of 30622 (total:30622,skipped:0) (91.88%)
19823 main refl.; 3285 q1 ; 3187 q2 satellites; 1842 cross q1/q2

```

## 6. Combined satellites in Jana2006 indexing tool

Using Jana2006 indexing tool is not necessary for getting results in this example.

Open options of "Save information" and select "Save specific peak table only"

Save peak table as, e.g., forjana.tabbin

Quit Lattice wizard

Start Jana2006 and open any structure (File → Structure → Open)

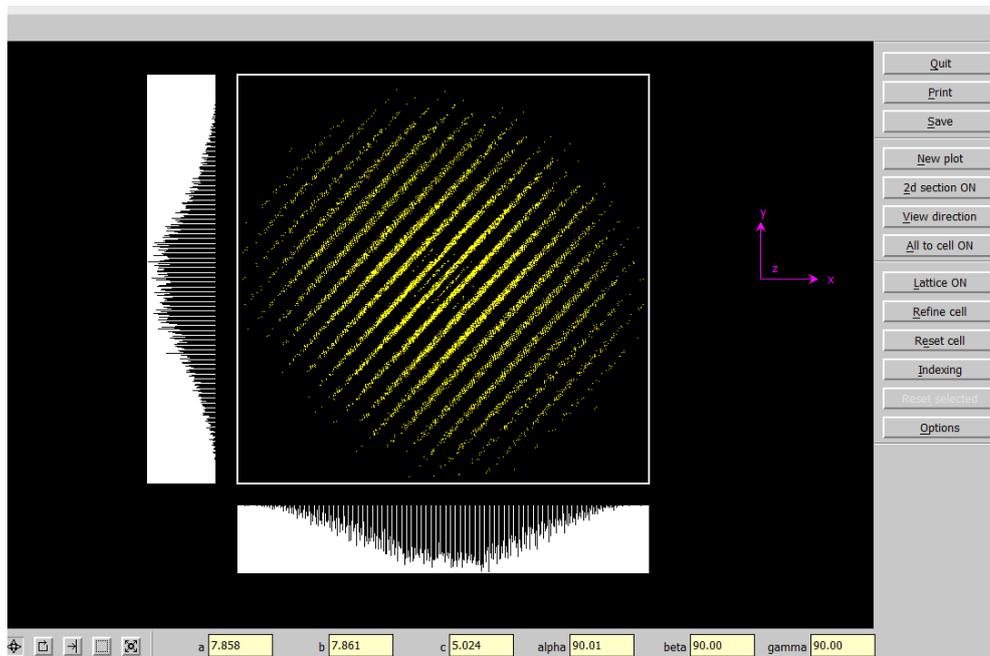
*It might be the structure in “some\_jana2006\_structure” subfolder of the melilite example*

Start Tools → Graphic → Indexing

In the file manager of Jana2006, locate forjana.tabbin; double click it; OK

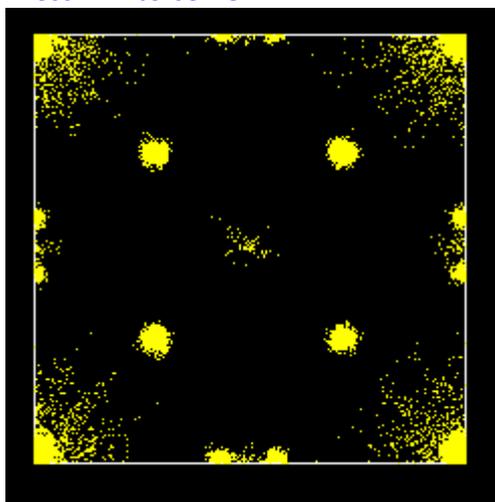
Select Mo KAlpha radiation; OK

[On the screen: Jana2006 indexing tool]



Press “View direction” and select c\*; OK

Press “All to cell ON”



*The resulting image projects all peaks positions into one unit cell. We can recognize q1 and q2 satellites, combined satellites (the double-points in the middle of the unit cell axes) and the  $\lambda/2$  reflections in the middle of the plot.*

Use  to determine satellites coordinates

Use Refine cell to obtain refined q-vectors

Quit Jana2006

## 7. Data reduction

In the right panel of CrysAlis, press “Start/Stop” and select “Data reduction with options”

[On the screen: Step1: Orientation matrix for data reduction]

Select “Other (reduction list)”

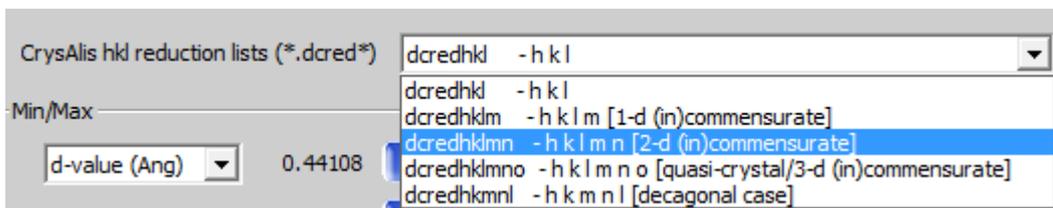
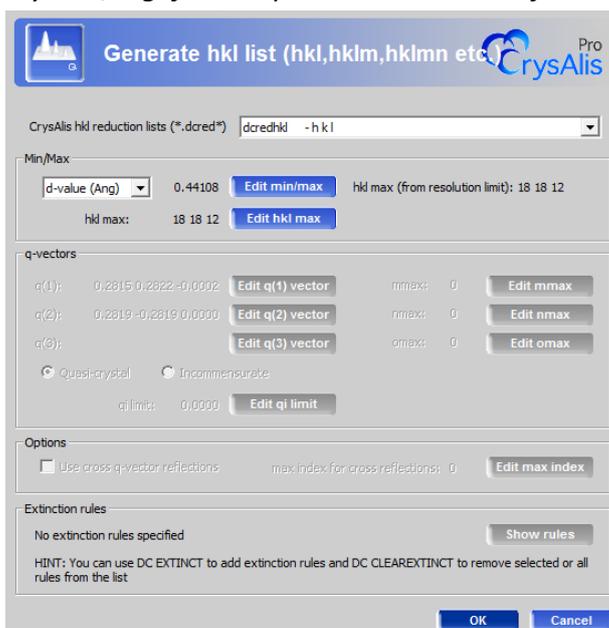
OK to confirm a message about non-existing reduction list

Press “Generate”

[On the screen: Profit reduction list generation]

This tool generates list of reflections, which will be used for the data reduction.

CrysAlis could also read an existing list of reflections (the “Load” button). This list could also be produced by Jana2006 and it is very useful for cases when the list cannot be generated by CrysAlis, e.g. for composite structures or for structures with X centering vectors. In this case,



Check “use cross q-vector reflections”

**Generate hkl list (hkl,hklm,hklmn etc)** Pro CrysAlis

CrysAlis hkl reduction lists (\*.dcred\*) `dcredhklmn -h k l m n [2-d (n)commensurate]`

**Min/Max**  
 d-value (Ang) 0.44108 [Edit min/max](#) hkl max (from resolution limit): 18 18 12  
 hkl max: 18 18 12 [Edit hkl max](#)

**q-vectors**  
 q(1): 0.2815 0.2822 -0.0002 [Edit q\(1\) vector](#) mmax: 1 [Edit mmax](#)  
 q(2): 0.2819 -0.2819 0.0000 [Edit q\(2\) vector](#) nmax: 1 [Edit nmax](#)  
 q(3): [Edit q\(3\) vector](#) omax: 0 [Edit omax](#)  
 Quasi-crystal  Incommensurate  
 qi limit: 0.0000 [Edit qi limit](#)

**Options**  
 Use cross q-vector reflections max index for cross reflections: 1 [Edit max index](#)

**Extinction rules**  
 No extinction rules specified [Show rules](#)  
 HINT: You can use DC EXTINGT to add extinction rules and DC CLEAREXTINGT to remove selected or all rules from the list

[OK](#) [Cancel](#)

*In the case of a structure with well separated spots, the generated list could be used for all data.*

*In the case of Melilite, the combined (cross) satellites need a special treatment. The previous attempts showed that these satellites are partially overlapped and that the best way to process them is making the data reduction with a large integration mask. With such mask, the pairs of close combined satellites are integrated as a one spot and this can be taken into the account in the Jana2006 refinement. However, this large mask is not suitable for main reflections and for the q1/q2 satellites. For this reason, the combined satellites must be processed separately.*

### Step 1 - data reduction for q1 and q2 satellites

Clear “use cross q-vector reflections”

**Generate hkl list (hkl,hklm,hklmn etc)** Pro CrysAlis

CrysAlis hkl reduction lists (\*.dcred\*) `dcredhklmn -h k l m n [2-d (n)commensurate]`

**Min/Max**  
 d-value (Ang) 0.44108 [Edit min/max](#) hkl max (from resolution limit): 18 18 12  
 hkl max: 18 18 12 [Edit hkl max](#)

**q-vectors**  
 q(1): 0.2815 0.2822 -0.0002 [Edit q\(1\) vector](#) mmax: 1 [Edit mmax](#)  
 q(2): 0.2819 -0.2819 0.0000 [Edit q\(2\) vector](#) nmax: 1 [Edit nmax](#)  
 q(3): [Edit q\(3\) vector](#) omax: 0 [Edit omax](#)  
 Quasi-crystal  Incommensurate  
 qi limit: 0.0000 [Edit qi limit](#)

**Options**  
 Use cross q-vector reflections max index for cross reflections: 1 [Edit max index](#)

**Extinction rules**  
 No extinction rules specified [Show rules](#)  
 HINT: You can use DC EXTINGT to add extinction rules and DC CLEAREXTINGT to remove selected or all rules from the list

[OK](#) [Cancel](#)

OK; NEXT; NEXT

In the Step 3, clear “Follow significant sample wobbling”; NEXT; NEXT

In the Step 5, use outlier rejection for 4/m; NEXT

In the Step 6, press "Change output name" and define "q1\_xor\_q2" as an output file name OK; FINISH

The program makes data reduction for main reflections, q1 satellites and q2 satellites, using the default integration mask



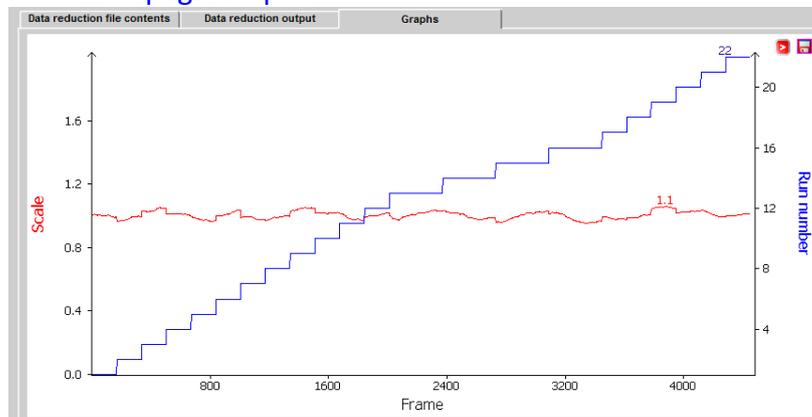
In the left toolbar of Crysalis, press

Select the page "Data reduction output" and look at Rint of main reflections and satellites

Main reflections										
Statistics vs resolution - point group symmetry: P4/m										
resolu- tion(Å)	# measured	# kept	# unique	average redundancy	mean F2	mean F2/sig(F2)	Rint	Rsigma	RsigmaA	
inf-1.01	5291	5280	181	29.2	31566.87	105.58	0.018	0.022	0.007	
1.01-0.80	5776	5773	181	31.9	11264.42	47.38	0.021	0.025	0.016	
0.80-0.69	4924	4924	181	27.2	6738.68	31.62	0.024	0.027	0.025	
0.69-0.63	4160	4158	181	23.0	3836.20	21.45	0.028	0.033	0.036	
0.63-0.58	3254	3254	181	18.0	2863.33	17.59	0.028	0.033	0.045	
0.58-0.54	2852	2851	181	15.8	1956.26	13.90	0.036	0.044	0.057	
0.54-0.51	2355	2355	181	13.0	1638.44	12.03	0.038	0.049	0.063	
0.51-0.49	858	856	182	4.7	1307.86	12.08	0.036	0.043	0.065	
0.49-0.47	802	802	181	4.4	764.54	8.81	0.047	0.054	0.088	
0.47-0.45	662	662	185	3.6	685.43	8.59	0.049	0.057	0.092	
-----										
inf-0.45	30934	30915	1815	17.0	9761.42	39.60	0.021	0.027	0.016	
inf-0.80	10916	10902	357	30.5	21106.57	75.59	0.019	0.023	0.010	
Satellite reflections										
Statistics vs resolution - point group symmetry: P4/m										
resolu- tion(Å)	# measured	# kept	# unique	average redundancy	mean F2	mean F2/sig(F2)	Rint	Rsigma	RsigmaA	
inf-1.21	18677	18259	2099	8.7	391.24	10.24	0.283	0.141	0.074	
1.21-0.93	20306	20183	2100	9.6	289.83	6.57	0.322	0.170	0.121	
0.92-0.79	18154	18087	2088	8.7	251.25	4.97	0.328	0.192	0.156	
0.79-0.71	15747	15720	2090	7.5	215.78	4.12	0.343	0.216	0.195	
0.71-0.65	14015	13996	2090	6.7	153.35	2.97	0.401	0.261	0.269	
0.65-0.60	12016	11988	2099	5.7	140.98	2.65	0.355	0.255	0.302	
0.60-0.57	9505	9479	2083	4.6	117.99	2.33	0.399	0.314	0.355	
0.57-0.54	7392	7354	2085	3.5	96.71	1.99	0.409	0.351	0.410	
0.54-0.50	4420	4364	2083	2.1	77.42	1.77	0.476	0.440	0.471	
0.50-0.45	3600	3545	2010	1.8	58.78	1.50	0.477	0.499	0.564	
-----										
inf-0.45	123832	122975	20827	5.9	220.71	4.86	0.331	0.210	0.173	
inf-0.80	55943	55338	6148	9.0	311.47	7.30	0.307	0.163	0.110	

The Rint of satellites is poor but we should consider that the program does not show separately the observed satellites. Rint of observed satellites will be shown in the Reflection report of Jana2006.

Select the page Graphs



The graph of frame scaling is almost flat, indicating sufficient absorption correction

## Step 2 - data reduction for combined (cross) satellites

In the next step, we will process the combined satellites. We want to ignore the real position of the cross satellites, use instead the position between the pairs of close satellites and large integration mask to cover the complete pairs. For this, we have to disable refinement of instrument parameters and profile analysis.

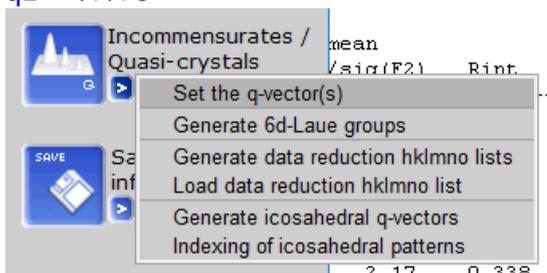
Quit the tool "Inspect data reduction results"

Start Lattice wizard

Use the ">" button at "Incommensurate/quasicrystal" and set q-vectors

q1 =  $\frac{1}{4} \frac{1}{4} 0$

q2 =  $-\frac{1}{4} \frac{1}{4} 0$



Close Lattice wizard

In the right panel of CrysAlis, press "Start/Stop" and select "Data reduction with options"

[On the screen: Step1: Orientation matrix for data reduction]

Select "Other (reduction list)"

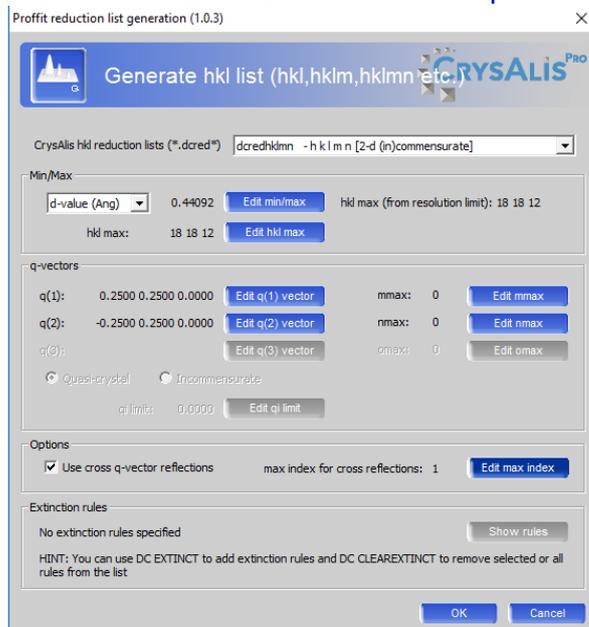
Press "Generate"

In the line for q1, press "Edit mmax" and define mmax=0

In the line for q1, press "Edit mmax" and define mmax=0

Check "Use cross q-vector reflections"

Press "Edit max index" for the cross q-vector reflections and define mmax=1



OK; YES to confirm that we really want such a list

Ignore two warnings

Out of CrysAlis, go to the experimental directory and open in a text editor the file

run.dcredhklmn

0	5	-8	0	0
1	5	-8	0	0
2	5	-8	0	0
3	5	-8	0	0
4	5	-8	0	0
5	5	-8	0	0
6	5	-8	0	0
7	5	-8	0	0
8	5	-8	0	0
9	5	-8	0	0
10	5	-8	0	0
11	5	-8	0	0
-11	6	-8	0	0
-10	6	-8	0	0
-9	6	-8	0	0
-8	6	-8	0	0
-7	6	-8	0	0
-6	6	-8	0	0
-5	6	-8	0	0

The file only contains main reflections. This means the current version of CrysAlis cannot generate simply the list we need. However, we can use the full list + a custom extinction rule

CANCEL; CANCEL

In the main window of CrysAlis - the left toolbar, press the button CMD

Type command "dc extinct hklmn 0 0 0 1 1 2 1"; ENTER

This defines that reflections with m+n odd will be skipped

In the right panel of CrysAlis, press "Start/Stop" and select "Data reduction with options"

[On the screen: Step1: Orientation matrix for data reduction]

Select "Other (reduction list)"

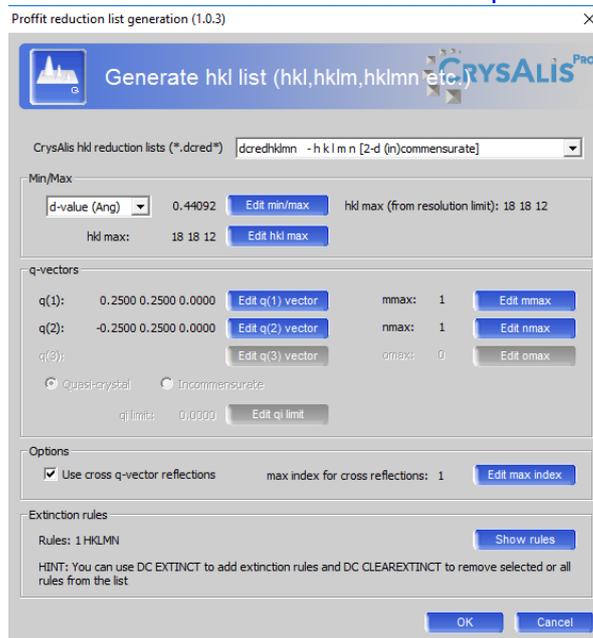
Press "Generate"

In the line for q1, press "Edit mmax" and define mmax=1

In the line for q1, press "Edit mmax" and define mmax=1

Check "Use cross q-vector reflections"

Press "Edit max index" for the cross q-vector reflections and define mmax=1



At the bottom of the "Generate hkl list" window we can see that our custom extinction rule is active. It can be checked by "Show rules" button

OK;

CrysAlis displays warning about missing "nada/um q-vector refinement" but this is OK because we do not want to refine q-vectors

Out of CrysAlis, go to the experimental directory and open in a text editor the file run.dcredhklmn

-1	-4	-11	-1	-1
0	-4	-11	-1	-1
1	-4	-11	-1	-1
2	-4	-11	-1	-1
-2	-3	-11	-1	-1
-1	-3	-11	-1	-1
0	-3	-11	-1	-1
1	-3	-11	-1	-1
2	-3	-11	-1	-1
3	-3	-11	-1	-1
-3	-2	-11	-1	-1
-2	-2	-11	-1	-1
-1	-2	-11	-1	-1
0	-2	-11	-1	-1
1	-2	-11	-1	-1
2	-2	-11	-1	-1
3	-2	-11	-1	-1

Now the file contains the combined satellites and main reflections. Main reflections can be used for verification of the same scale for both data sets during their combining in Jana2006, and then discarded

(Back in Crysalis)

NEXT; NEXT

[On the screen: Step3: Basic algorithm parameters]

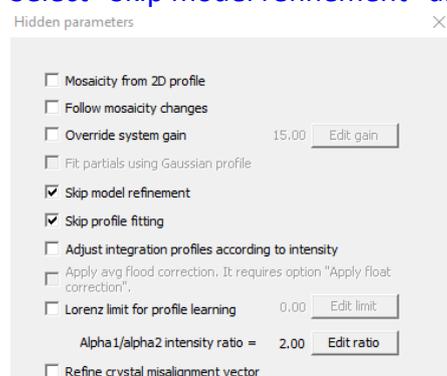
Press "Edit special pars"

Check "Override integration mask size"

Define size 1.75 (this number was found by trials and errors)

Press Alt-E to display hidden options

Select "Skip model refinement" and "Skip profile fitting"



OK; OK; NEXT; NEXT;

For outlier rejection, select Laue symmetry "1", Friedel pairs equivalent

NEXT;

OK; "Change output name" -> q1\_and\_q2

FINISH

## 8. Results of data reduction

After finishing the data reduction, start "Inspect data reduction" by pressing



The results for combined satellites are poor but this might be caused by their weakness. We cannot make any conclusion without refinement of a structure model.

## Main reflections

Statistics vs resolution - point group symmetry: P4/m

resolu- tion(Å)	# measured	# kept	# unique	average redundancy	mean F2	mean F2/sig(F2)	Rint	Rsigma	RsigmaΔ
inf-1.01	5163	5146	180	28.6	35764.85	78.28	0.014	0.017	0.010
1.01-0.79	5668	5666	180	31.5	12811.56	35.01	0.019	0.023	0.022
0.79-0.69	4866	4866	180	27.0	7870.36	23.36	0.022	0.025	0.034
0.69-0.63	4004	4004	180	22.2	4507.89	15.59	0.030	0.036	0.050
0.63-0.58	3223	3223	180	17.9	3227.97	12.26	0.034	0.040	0.065
0.58-0.54	2843	2840	180	15.8	2269.34	9.65	0.045	0.056	0.083
0.54-0.51	2366	2366	181	13.1	1920.51	8.29	0.053	0.071	0.094
0.51-0.49	867	867	180	4.8	1543.35	8.10	0.050	0.060	0.098
0.49-0.47	829	829	181	4.6	872.08	5.50	0.082	0.095	0.144
0.47-0.45	716	716	185	3.9	806.62	5.45	0.079	0.092	0.149
inf-0.45	30545	30523	1807	16.9	11041.32	28.81	0.019	0.025	0.022
inf-0.80	10645	10626	354	30.0	23965.73	56.01	0.016	0.018	0.013

## Satellite reflections

Statistics vs resolution - point group symmetry: P4/m

resolu- tion(Å)	# measured	# kept	# unique	average redundancy	mean F2	mean F2/sig(F2)	Rint	Rsigma	RsigmaΔ
inf-1.12	8502	8237	1167	7.1	460.76	7.64	0.221	0.201	0.120
1.12-0.86	9781	9706	1166	8.3	376.96	4.92	0.232	0.213	0.187
0.86-0.75	8992	8954	1171	7.6	344.02	3.69	0.277	0.259	0.242
0.75-0.67	8426	8381	1165	7.2	294.04	2.82	0.309	0.298	0.308
0.67-0.62	6738	6725	1179	5.7	214.31	2.04	0.343	0.357	0.438
0.62-0.57	6015	5998	1166	5.1	196.01	1.76	0.362	0.390	0.486
0.57-0.54	5662	5640	1174	4.8	137.51	1.26	0.482	0.568	0.650
0.54-0.51	3528	3505	1170	3.0	142.87	1.29	0.457	0.518	0.623
0.51-0.48	2018	2004	1167	1.7	101.75	1.03	0.450	0.496	0.753
0.48-0.45	1850	1836	1111	1.7	91.11	0.90	0.521	0.601	0.755
inf-0.45	61512	60986	11636	5.2	283.07	3.39	0.291	0.305	0.294
inf-0.80	22759	22397	2905	7.7	403.28	5.72	0.233	0.214	0.166

The input files for Jana2006 are in the directory /struct/tmp:

q1\_xor\_q2.hkl; q1\_xor\_q2.cif\_od  
q1\_and\_q2.hkl; q1\_and\_q2.cif\_od

The example 5.5.2. where structure of melilite is solved uses different input files: 4d data for q1, 4d data for q2 and 5d data for combined satellites. The reason is that we need to have the user-independent results. Data created in this example are tested at the end of the Example 5.5.2.



# Example 5.5.2: Melilite

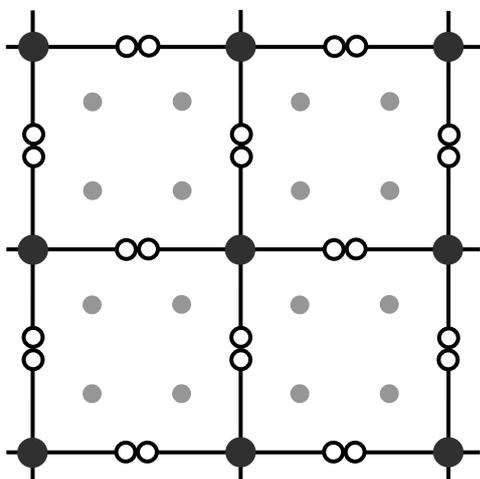
Solution of a (3+2)-dimensional incommensurately modulated structure with overlaps of satellites.

**Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>**

Revised: 4 September 2019

Single crystal data measured with Oxford Diffraction four-cycle diffractometer

The structure has two  $q$ -vectors:  $q_1=(\alpha,\alpha,0)$  and  $q_2=(-\alpha,\alpha,0)$ . Satellite reflections  $h,k,l,m,0$  and  $h,k,l,0,n$  are always well separated in the CCD frames. Combined satellites  $hklmn$ ,  $m\neq 0$ ,  $n\neq 0$ , are sometimes separated and sometimes overlapped, depending on their geometry in particular CDD frame (i.e. angle  $\psi$ ). The combined satellites needed different data processing strategy using large integration mask because we want to treat them like “always fully overlapped”.



Schematic view of the diffraction pattern in melilite. Main reflections are indicated by large dark circles, small circles symbolize first-order satellites (grey for  $m \times n = 0$  and white for  $m \times n = \pm 1$  satellites, respectively).

Input files:

q1.hkl, q1.cif\_od (main reflections + satellites described by  $q_1$ )

q2.hkl, q2.cif\_od (main reflections + satellites described by  $q_2$ )

q1q2.hkl, q1q2.cif\_od (main reflections + combined overlapped satellites)

Frame scaling, absorption correction: done with software of the diffractometer

## 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane – textbox: type “melilite”

OK

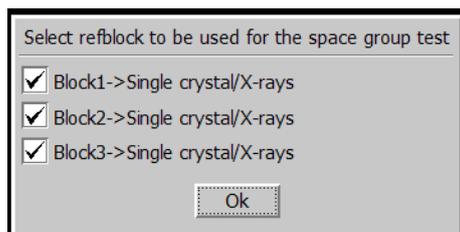
## 2. Import Wizard

Select “Known diffractometer formats”; NEXT

Select "Oxford Diffraction – CCD";  
 For "File name" select q1.hkl; NEXT  
 In "Define basic input file" select "Input from cif\_od file"; OK  
 Change the modulation vector to 0.278 0.278 0; NEXT  
*The used q-vector refinement software (CrysAlis) does not allow restriction that would keep all components of the two q-vectors the same*  
 [On the screen: Define the reference cell / split by twinning]  
 Change target dimension to 5  
 For 2<sup>nd</sup> modulation vector type -0.278 0.278 0; NEXT  
*The program reads 92323 reflections*  
 For absorption correction select "None or done before importing"; NEXT  
 FINISH  
 [On the screen: Data repository]  
 Import new  
 Select "Known diffractometer formats"; NEXT  
 Select "Oxford Diffraction – CCD";  
 For File name choose q2.hkl; NEXT  
 In "Define basic input file" select "Input from cif\_od file"; OK  
 Change the 1<sup>st</sup> modulation vector to -0.278 0.278 0; NEXT  
 Check "Import only satellites";  
*New import of the same main reflections would bias their weighting scheme*  
 Define transformation matrix (1 0 0 0 | 0 1 0 0 | 0 0 1 0 | 0 0 0 1 | 0 0 0 1 0); OK  
*This will convert hklm from the input file to hkl0n*  
 NEXT  
*The program reads 92522 reflections, including discarded main reflections*  
 For absorption correction select "None or done before importing"; NEXT  
 FINISH  
 [On the screen: Data repository]  
 Import new;  
 Select "Known diffractometer formats"; NEXT  
 Select "Oxford Diffraction – CCD";  
 For File name choose q1q2.hkl; NEXT  
 In "Define basic input file" select "Input from cif\_od file"; OK  
 Change the 1<sup>st</sup> modulation vector to 0.278 0.278 0  
 Change the 2<sup>nd</sup> modulation vector to -0.278 0.278 0; NEXT  
 Check "Import only satellites"; NEXT  
 [On the screen: warning about changed unit cell parameters]  
 "Continue with the old reference cell parameters"; OK  
*The program reads 147857 reflections, including discarded main reflections*  
 For absorption correction select "None or done before importing"; NEXT  
 FINISH  
 OK; YES to accept the data sets

### 3. Symmetry Wizard

Use all data blocks for the space group test



[On the screen: Tolerances for crystal system recognition]

For “Maximal ave(I/sig(I)) for extinctions type “20”; NEXT

Select tetragonal Laue symmetry 4/mmm

Select P centering

Select space group P-421m

At this point there is no difference between P-421m and P4212, the decision is expected from the symmetry test of Superflip

Accept the superspace group in the original cell

For five-dimensional structures the wizard does not offer selection of superspace group. It will be done later on manually.

### 4. Creating refinement reflection file

Follow steps of the reflection wizard, the data sets are **on the same scale**

The program discards 206 reflections, 96 observed,  $R_{int}(all)=3.31\%$

In case that the same scale of the data sets would not be sure, a temporary structure should be created with data sets imported together with main reflections. Then we could select “different scales” and Jana would use main reflections for finding scaling factors. Then the data set would be re-imported with the found scale factors and with main reflections only in the first data set.

### 5. Structure solution wizard

Quit

### 6. Solution of average structure

Superflip for five-dimensional structure returns five-dimensional electron density map.

However, Jana2006 would not evaluate initial modulation functions from this map and we would get only the average structure. For this reason solution will be done separately for average structure

Start “Tools → Transformation → Go to average 3d structure”

For name use “aver”

Follow steps of the Reflection wizard

**Continue with the new structure**

Start “Run → Structure solution”

For Formula type “Ca Mg Si O”

Select “Superflip” and “Peaks from Jana2006”

Select “Use a specific random seed” and type “333” for random seed

With this option result of charge flipping will be the same in most computers and origin position and special atomic position will be equivalent with this cookbook. For normal work Random seed should not be fixed.

“Run solution”

Superflip converges with R around 13% and confirms the selected space group

“Accept last solution”

Start EditM50; Go to the page “Composition”; for “Formula units” type “2”; press “Formula from M40”age

It returns  $\text{Ca}_2 \text{MgO Si}_3 \text{O}_7$ . The expected formula is  $\text{Ca}_2 \text{Mg Si}_2 \text{O}_7$ , therefore one of silicon atoms is probably magnesium.

Run Refinement

Refinement converges with Robs around 14%

Open “Dist” commands; clear “d(max) derived from atomic radii and typical distances”; run “Dist”

Open listing of “Dist” and check Si-O distances.

Si2-O3 distances are unusually large (around 1.921 Å), that means Si2 should be changed to magnesium

Using “Edit Atoms”, change atomic type of Si2 to Mg and its name to Mg1

Run refinement

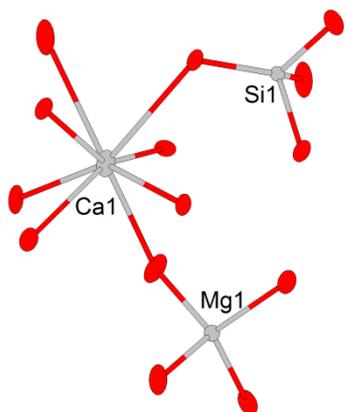
Refinement converges with Robs around 14%

“Edit atoms”: change ADP of all atoms to harmonic

Run refinement

Refinement converges with Robs 3.7%

“Plot structure”



The structure looks normally but ADPs are unusually large

## 7. Back to the modulated structure

“File → Structure → Open”: open “melilite”

“EditM50, Composition page”: type formula  $\text{Ca}_2 \text{Mg Si}_2 \text{O}_7$ , Z=2

Close Editm50, save changes

“File → Structure → Copy in”: open “aver” and import **only** M40

Run refinement to confirm R value for the average structure:

```
R factors : [15790=11843+3947/34], Damping factor: 1.0000
GOF(obs)= 33.63 GOF(all)= 29.16
R(obs)= 56.89 wR(obs)= 77.51 R(all)= 59.48 wR(all)= 77.55
R factors for main reflections : [1832=1784+48]
R(obs)= 3.73 wR(obs)= 5.62 R(all)= 3.83 wR(all)= 5.63
R factors for satellites +(1,0) : [7128=4979+2149]
R(obs)= 100.00 wR(obs)= 100.00 R(all)= 100.00 wR(all)= 100.00
R factors for satellites +(1,1) : [6830=5080+1750]
R(obs)= 100.00 wR(obs)= 100.00 R(all)= 100.00 wR(all)= 100.00
Last wR(all): 77.55
Maximum change/s.u. : -0.0017 for x[Si1]
```

## 8. Superspace symmetry

We will need to complete the translation part of superspace symmetry operators.

“EditM50 → Symmetry”: focus the textbox with the space group symbol and press TAB.

The program shows two symmetry operators where the translation part in  $x_4$  and  $x_5$  needs to be completed:

**Complete translational part for the operator:**

**x2 -x1 -x3 x5 -x4**

Rotation	Translation
0 1 0 0 0	0
-1 0 0 0 0	0
0 0 -1 0 0	0
0 0 0 0 1	<input style="width: 50px;" type="text" value="0"/>
0 0 0 -1 0	<input style="width: 50px;" type="text" value="0"/>

and

**Complete translational part for the operator:**

**x1 +1/2 -x2 +1/2 -x3 -x5 -x4**

Rotation	Translation
1 0 0 0 0	1/2
0 -1 0 0 0	1/2
0 0 -1 0 0	0
0 0 0 0 -1	<input style="width: 50px;" type="text" value="0"/>
0 0 0 -1 0	<input style="width: 50px;" type="text" value="0"/>

Each translation part has two elements which can be either 0 or 1/2. Thus we have sixteen combinations:  $0\ 0 + 0\ 0$ ,  $0\ 0 + 1/2\ 0$ ,  $0\ 0 + 0\ 1/2$ ,  $0\ 0 + 1/2\ 1/2$  ... However, some of them are forbidden because they lead to a non-consistent translation vector, which cannot be used for generation of the superspace group. Finally, we have only eight combinations. In the following table we show number of extinct reflections (observed/unobserved) which Jana2006 reports for each of these possibilities:

Translations in $x_4, x_5$	0 0	1/2 1/2
0 0	96/206	181/5369
1/2 1/2	181/5369	96/206
1/2 0	96/206	181/5369
0 1/2	181/5369	96/206

Only four possibilities lead to additional extinctions. They are all equivalent as we can judge from the exactly same number of extinct reflections as well as from the fact that EditM50 does not offer creation of new refinement reflection file when we switch between them. Another four possibilities without additional extinctions are equivalent, too. The equivalency can also be confirmed by the Stokes & Campbell SSG-test which is directly accessible from the symmetry page at EditM50.

Thus we have two possibilities for the superspace group: with and without additional extinctions. The choice is simple because the additional extinctions mostly concern unobserved reflections and therefore the symmetry leading to additional extinctions is confirmed by the experiment.

In order to be consistent with the published structure we will choose 0 0 for the first symmetry operator and 1/2 1/2 for the second one.

Select 0 0 and 1/2 1/2 for the first and the second symmetry operator, respectively  
Close EditM50, save the result  
Create new refinement reflection file

### 9. Refinement of modulated structure – position modulation

Start “File → Structure → Save As” and make backup copy: “melilite\_backup”

Start “Parameters → Options”

Press “Define wave vectors”

For the third wave define 1 1

*This means modulation wave vector given by a sum of the q vectors*

For the fourth wave define 1 -1

*This means modulation wave vector given by a difference of the q vectors*

OK; OK; YES to save changes

“Edit atoms”: set two position modulation waves for all atoms

*This means one harmonic wave with wave vector q1 and one harmonic wave with wave vector q2*

In Refinement commands switch to window “Modulation”; for “Overlap option” select “Closest reflections”; “max. satellite index” 1; “max. difference in degs” 0.5

*With this settings pair of combined satellites will be treated as fully overlapped reflections.*

Run refinement

*Refinement converges after approx. 20 cycles with the following Robs values for all reflections, main reflections,  $\pm(1,0)$  and  $\pm(1,1)$  satellites: 23%, 10%, 28%, 36%*

“Edit atoms”: add another two position modulation waves for all atoms

*This means one harmonic wave with wave vector  $q1+q2$  and one harmonic wave with wave vector  $-q1+q2$*

Run refinement

*Refinement converges with the following Robs values for all reflections, main reflections,  $\pm(1,0)$  and  $\pm(1,1)$  satellites: 9%, 6%, 13%, 11%*

### 10. Contour sections and ADP modulation

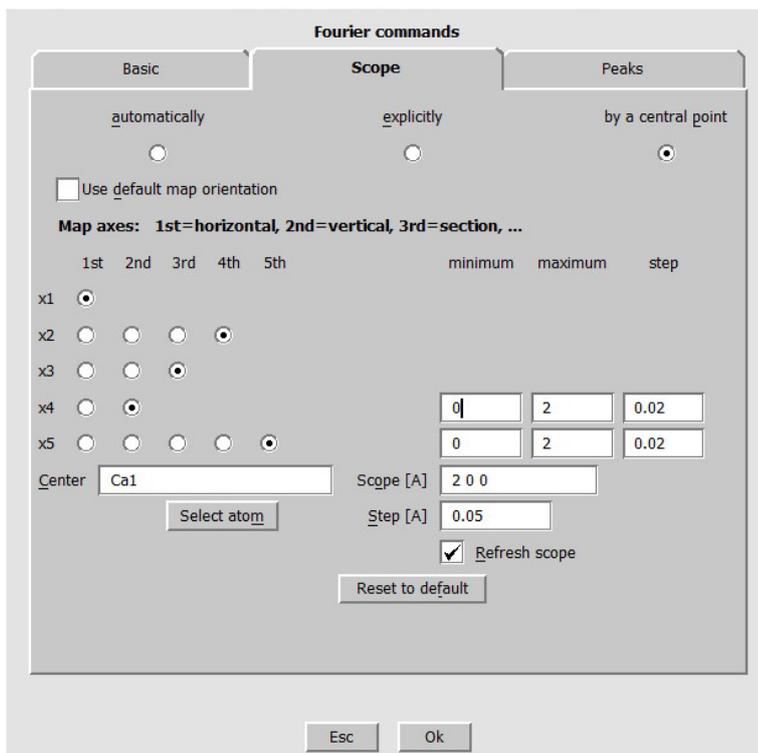
“Start Contour → New plot → Calculate new ones”

*(If no old map exists from previous calculations this option is not active but Contour will use it)*

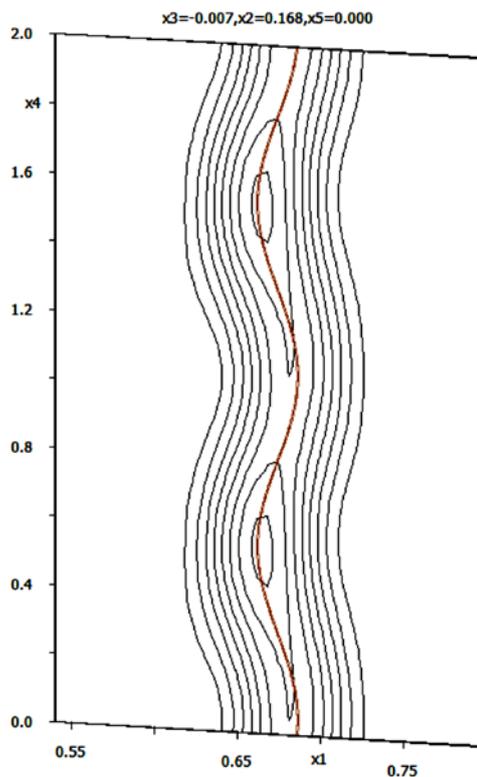
Select observed Fourier

For “Scope” define Ca1 as a central atom

For map axes select x1, x4, x3, x2, x5 with limits as shown below

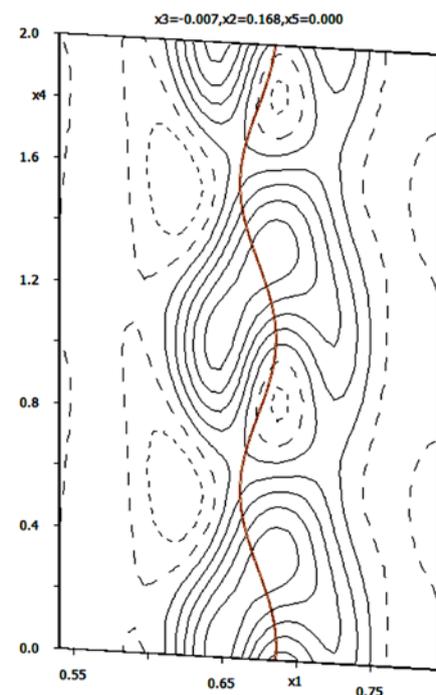


*This will calculate section x1-x4 through Ca1 as a function of x5*  
 OK to calculate Fourier map  
 In Contour press "Atoms edit" and add Ca1



Press "Movie" to see the changes of this figure with x5. ESC to stop.

Press “New plot” and calculate difference Fourier map for the same section



*The difference maxima around Ca1 indicate ADP modulation*

Calculate and plot corresponding difference Fourier sections for the other atoms

*All atoms have strong difference maxima and minima*

“Edit atoms”: set two ADP modulation waves for all atoms

Run refinement

*Refinement converges with the following Robs values for all reflections, main reflections, 1<sup>st</sup> and 2<sup>nd</sup> order satellites: 6.1%, 3.7%, 5.3%, 11.1% for 166 parameters*

Start Contour and repeat plotting of the difference section through Ca1

*The difference maxima are not so large but still not acceptable*

“Edit atoms”: set additional two ADP modulation waves for all atoms

Run refinement

*Refinement converges with the following Robs values for all reflections, main reflections, 1<sup>st</sup> and 2<sup>nd</sup> order satellites: 4.8%, 3.1%, 4.5%, 8.1% for 238 parameters*

Run Graph and investigate distances, bond valence sums etc. All obtained graphs will depend on “u” coordinate, which can be changed by “Movie” button.

### **11. Using the data prepared in Example 5.5.1**

Make backup copy of your structure

“File → Reflection file → Import/modify the reflection file”

[On the screen: Data repository]

Delete all data sets

“Import New”

Follow steps of the import wizard to import the file “q1\_xor\_q2.hkl”, i.e. main reflections + q1/q2 satellites. The files are located in the struct/tmp directory of the CrysAlis job, input and target dimension is 5

**Complete/correct experimental parameters**

Cell parameters: 7.8426 7.8457 5.01464 90.006 90.004 90.001

Number of input indices: 5 Info about metrics parameters

1st modulation vector: 0.2792 0.2796 0

2nd modulation vector: -0.2783 0.2787 0

3rd modulation vector:

X-ray tube

Wave length: 0.71073

Temperature: 293

**Polarization correction:**

Circular polarization

Perpendicular setting Info

Parallel setting Info

Guinier camera

Linearly polarized beam

**Monochromator parameters:**

Perfectness: 0.5

Glancing angle: 6.082144 Set glancing angle

As reference cell parameters, use the ones from previous refinement because they already have corrected q-vector components

**Relationship to the reference cell/split by twinning**

Cell parameters: 7.8375 7.8404 5.0116 90.004 90.001 90.001

Target dimension: 5  Twinning Twinning matrices

1st modulation vector: 0.2780 0.2780 0.0000 Number of domains:

2nd modulation vector: -0.2780 0.2780 0.0000 Data related to domain#:

Max. satellite index:

Accuracy:

Define transform

Cell parameters and modulation vectors as follows from the reference ones:  
7.8375 7.8404 5.0116 90.004 90.001 90.001  
0.2780 0.2780 0.0000  
-0.2780 0.2780 0.0000

Cell parameters and modulation vectors as found in data collection:  
7.8426 7.8457 5.0146 90.006 90.004 90.001  
0.2792 0.2796 0.0000  
-0.2783 0.2787 0.0000

Difference seems to be too large

Continue with the old reference cell parameters

Use the new cell parameters as the reference ones

Quit the import process

Ok

Do not close the Data repository.

“Import New”

Follow steps of the import wizard to import **only satellites** from the file “q1\_and\_q2.hkl”.

**Relationship to the reference cell/split by twinning**

Cell parameters: 7.8375 7.8404 5.0116 90.004 90.001 90.001

Target dimension: 5  Twinning Twinning matrices

1st modulation vector: 0.2780 0.2780 0.0000 Number of domains:

2nd modulation vector: -0.2780 0.2780 0.0000 Data related to domain#:

Max. satellite index:

Accuracy:

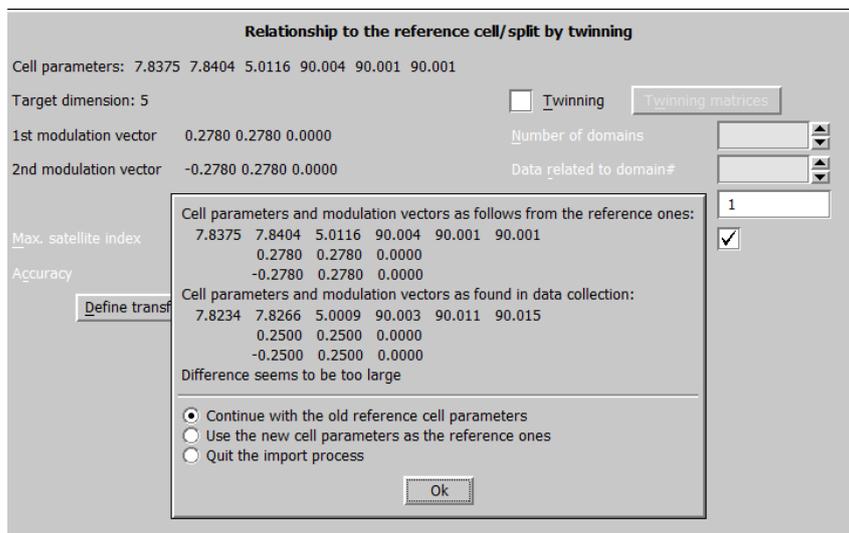
Define transformation matrix

Multiply input F(hkl)/I(hkl) by:

Import only satellites

Back Next Cancel

Use the old reference parameters - this causes that 0.25 artificial components of q-vectors will not be used



Accept changes in data repository

Follows steps to create refinement reflection file (both data sets are on the same scale)

Run refinement

*Refinement converges with the following Robs values for all reflections, main reflections, 1<sup>st</sup> and 2<sup>nd</sup> order satellites: 4.4%, 2.3%, 4.1%, 7.9% for 238 parameters*

# Example 5.6: Iodomol

A molecular modulated structure from single crystal data – molecular modulations and tests of positional vs occupational modulation

Revised: 13 March 2018

Single crystal data measured with a four-circle diffractometer and CCD detector.

Input files: Iodomol.p4p, Iodomol.ram

absorption correction: done

## 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click Iodomol

## 2. *Import Wizard*

Select “known diffractometer formats”; NEXT

Select “Bruker-CCD”;

Click the button “Browse” and double click “Iodomol.ram”; NEXT

[On the screen: complete/correct experimental parameters]

Leave all settings default; NEXT;

[On the screen: Define the reference cell/split by twinning]

Set target dimension to 4; NEXT; OK TO confirm the import of 52313 reflections

In the text window, leave all settings default; NEXT; Finish

## 3. *Data Repository*

The line in data repository window corresponds to one data set.

OK; YES to accept the data set

[On the screen: “Information about starting symmetry wizard”]

NEXT

## 4. *Symmetry Wizard*

[On the screen: “Tolerances for crystal system recognition”.]

Symmetry wizard can be started separately by “File → Reflection file → Make space group test”.

Leave all settings of the wizard default; NEXT

[On the screen: “Select supercell”.]

Confirm “continue with the basic unit cell”; NEXT

[On the screen: Select Laue symmetry – the Rint values are quite elevated]

Confirm monoclinic Laue symmetry; NEXT

[On the screen: Select cell centering]

Confirm primitive unit cell; NEXT

[On the screen: Select space group]

Confirm P21/m; NEXT

[On the screen: Select superspace group]

Select P21/m(a0g)0s – out of 1038 potentially absent reflection none is observed, this space

group is thus the most likely.

[On the screen: Final step of the superspace test]

Accept the superspace group transformed into the original cell: P21/m(a0g)0s; FINISH

### 5. Creating refinement reflection file

We have finished creation of the file M95 (reflections converted from diffractometer format to Jana format) and M50 (cell parameters, symmetry). At this step, we will create the file M90 containing data set merged by symmetry, with forbidden reflections omitted.

NEXT to confirm threshold 3sigma;

OK; OK to confirm information about imported reflections

[On the screen: settings for merging of reflections]

Leave all settings default; NEXT

The  $R_{int}$  for observed reflections will be 19.57%

OK

Accept the data block and calculate coverage; FINISH; OK

[On the screen: Information that structure solution will start]

### 6. Structure Solution Wizard

[On the screen: window of Structure solution]

In "Formula" textbox type list of chemical elements: C O H I P

Check the check box "Use a specific random seed"

This option is here only to ensure the reproducibility of the calculation. In normal practice, it is not necessary.

Keep all other settings default

Click "Run solution"

Superflip converges within a few seconds. It confirms the symmetry P21/m(a0g)0s.

-----  
Space group derived from the symmetry operations:  
-----

```
Tentative HM symbol: P121/m1(a0g)0s
Fingerprint:         4300220R960028dXM5 (0,3/4,0,0)
Symmetry operations:
      1:           x1           x2           x3           x4
  m|s(0,1,0):     x1          1/2-x2          x3          1/2+x4
  2_1|0(0,1,0):  -x1          1/2+x2          -x3          1/2-x4
      -1:         -x1           -x2          -x3           -x4
```

This is symmetry found by Superflip in the electron density map

```
#####
# Search for the origin of the space group #
#####
```

Position of the origin in the CF map:

0.7549 0.6015 0.5496 0.9909

Agreement factors of individual generators:

```
Number smb agreement
 4  m|s      0.68
 2  21|0     2.20
```

This is fit of symmetry elements supplied by user (small numbers <10) = good fit

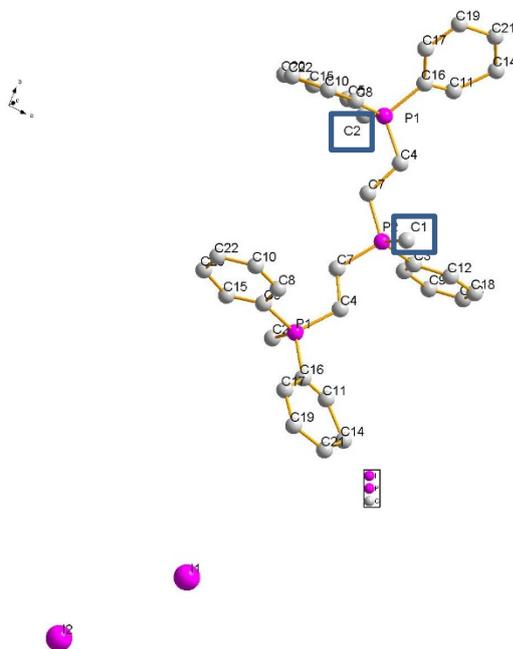
Close the viewer of the listing, wait until the structure solution is interpreted

Click “Draw structure”

Choose the radio button “Draw average structure”

If you have followed this tutorial exactly, you should see a picture identical to the following

(to obtain the picture in Diamond, click the icon “Get molecules directly” - )



If the structure looks slightly different (e.g. shifted by  $\frac{1}{2}$  along a or b), you may still continue with the tutorial, but the details (atom names, atom positions) may be different.

Alternatively, you may rerun Superflip until you obtain the solution in the correct setting.

The structure looks correctly interpreted and complete. Only atoms C1 and C2 should be oxygen atoms.

Close the structure viewer and exit the solution wizard by clicking “Accept last solution”

## 7. Checking the structure

First of all, we will correct the wrong atomic types.

Double click the icon “Edit atoms”

Double click atom C1

Type “O\*” in the text box “Name”; Press TAB

The name changes to the first free number for oxygen, O1 in this case

Change the atomic type to O;

Repeat the procedure for atom C2

OK; Yes to confirm the changes and return to the main window.

We will now check the modulation functions for all atoms

Double click the icon “Contour”

Click the button “New plot”

Select the radio button “Show de Wolff’s sections”

Set the scope of the sections: primary scope to 3, secondary to 0.5

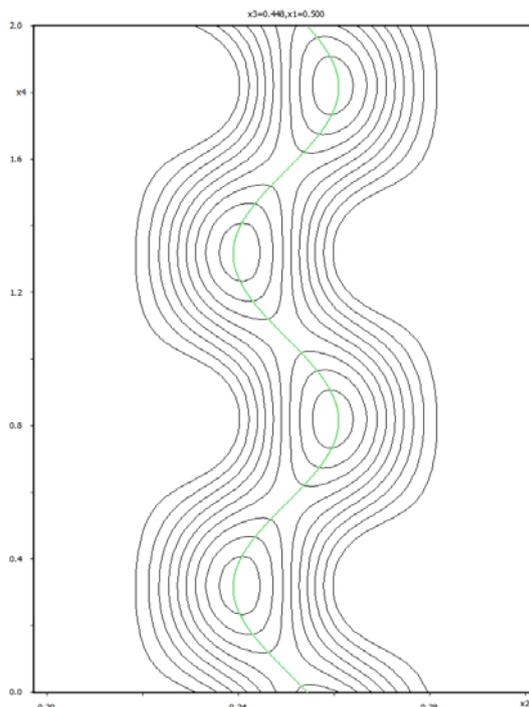
Click the button “Define atoms for de Wolff’s sections

In the text box “Atoms” type \* (a single star) and click the button “Add”; OK

OK

*The program calculates the Fourier maps for modulation functions of all atoms (x, y and z direction for each atom). It may take some time.*

Go through the de Wolff’s sections for all atoms (using the buttons “W-“ and “W+“ or by selecting from the list and check, if the modulation functions suggested by Jana2006 follow the domains in the Fourier maps. This is an example of the x2-x4 section for I1:



*You should conclude that all atoms have been interpreted correctly and the modulation functions are a good starting point for the refinement. The only exception is the x1 modulation function of the atom C11. This could be corrected manually (invert the signs, shift the average position), but the refinement is robust enough to correct this single problem automatically.*

Quit Contour and return to the main window.

## 8. Initial structure refinement

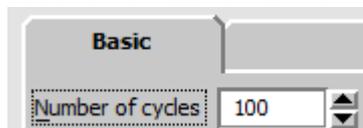
Go to “File->Structure->Save as”

In the lower right text box type “Iodomol-solution”; OK

No to continue with the new structure

Right-click the icon Refine

Set the number of refinement cycles to 100:



OK; Yes + Start

*The refinement converges to the following R-values:*

```
R factors : [10571=4902+5669/216], Damping factor: 1.0000
GOF(obs)= 5.26 GOF(all)= 3.78
R(obs)= 12.60 wR(obs)= 12.34 R(all)= 23.85 wR(all)= 13.17
R factors for main reflections : [3513=1875+1638]
R(obs)= 12.54 wR(obs)= 12.81 R(all)= 21.64 wR(all)= 13.58
R factors for satellites +-(1) : [7058=3027+4031]
R(obs)= 12.66 wR(obs)= 11.63 R(all)= 26.00 wR(all)= 12.55
Last wR(all): 16.88 13.64 13.22 13.17 13.17
Maximum change/s.u. : 0.0408 for x[C11]
```

## 9. Refinement of ADP

*So far the atomic displacement parameters (ADPs) are refined as isotropic. We will now set them for anisotropic refinement:*

Open "Edit atoms"

Select all atoms

Double click any of the selected atoms

Select the radio button "harmonic (anisotropic)"

OK; OK; Yes to quit "Edit atoms"

Double click Refine to refine anisotropic displacement parameters.

*The refinement converges to the following R-values:*

```
R factors : [10571=4902+5669/328], Damping factor: 1.0000
GOF(obs)= 3.62 GOF(all)= 2.65
R(obs)= 8.84 wR(obs)= 8.40 R(all)= 18.93 wR(all)= 9.19
R factors for main reflections : [3513=1875+1638]
R(obs)= 7.60 wR(obs)= 7.82 R(all)= 15.49 wR(all)= 8.62
R factors for satellites +-(1) : [7058=3027+4031]
R(obs)= 10.23 wR(obs)= 9.18 R(all)= 22.25 wR(all)= 9.94
Last wR(all): 9.19
Maximum change/s.u. : -0.0152 for z[C20]
```

*Sometimes the displacement parameters themselves are modulated. This may be important especially for the heavy atoms. We can try to add one harmonic modulation wave for the iodine atoms:*

Open "Edit atoms"

Select the atoms I1 and I2

Double click any of the selected atoms

increase the number of ADP harmonic waves from 0 to 1"

OK; OK; Yes to quit "Edit atoms"

Double click Refine.

*The refinement converges to the following R-values:*

```

R factors : [10571=4902+5669/344], Damping factor: 1.0000
GOF(obs)= 3.28 GOF(all)= 2.42
R(obs)= 7.83 wR(obs)= 7.60 R(all)= 17.59 wR(all)= 8.39
R factors for main reflections : [3513=1875+1638]
R(obs)= 7.34 wR(obs)= 7.58 R(all)= 15.18 wR(all)= 8.41
R factors for satellites +-(1) : [7058=3027+4031]
R(obs)= 8.38 wR(obs)= 7.63 R(all)= 19.92 wR(all)= 8.36
Last wR(all): 8.61 8.39 8.39
Maximum change/s.u. : -0.0185 for U13[C20]

```

The R-value on the satellite reflections decreased by almost 2%, the modulation of ADPs seems significant.

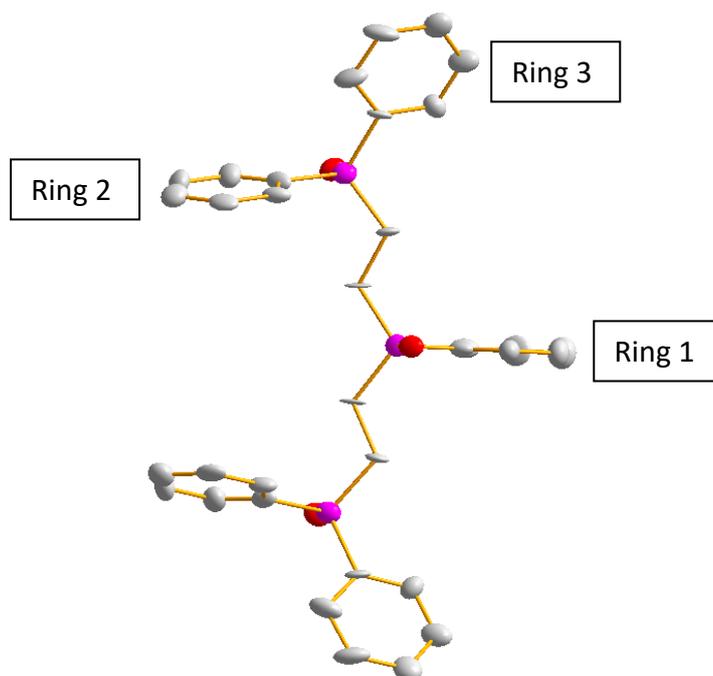
## 10. Defining phenyl rings as molecules

Go to “File->Structure->Save as”

In the lower right text box type “Iodomol-ref”; OK

NO to continue with the new structure

Draw the average structure and check the geometry. Plot the structure with thermal ellipsoids. The molecule looks like this:



The result is not a disaster, but the displacement parameters are uneven. The data quality may not be sufficient to refine all atoms independently. We can define the three phenyl rings as three positions of the same molecule.

Note the atom names for the free phenyl rings. Marking the phenyl rings as in the image above, you should get the following lists:

Ring 1: C3, C6, C9, C13, C18, C12

Ring 2: C5, C15, C20, C22, C10, C8

Ring 3: C16, C17, C19, C21, C14, C11

Close the structure viewer.

Go to Parameter -> Molecules -> New molecule;

Type "phenyl" in the text box "Name of the molecule"; Next

Select atoms C3, C6, C9, C13, C18, C12 from the list; OK;

Choose gravity center as the molecular reference point; Next;

*Note that the occupancy of this position is set to 0.5, because Ring 3 is located on the mirror plane.*

Click "Apply + Next position".

Add the next position by identifying the model atoms with the atoms of the next phenyl ring. Fill the table according to the following picture:

**Define and complete molecular position # 2:**

Apply inversion

	Model atom	Actual position/atom
1st point	<input type="text" value="C3"/>	<input type="text" value="C5"/>
2nd point	<input type="text" value="C9"/>	<input type="text" value="C20"/>
3rd point	<input type="text" value="C18"/>	<input type="text" value="C10"/>

**Options for removing of atoms from atomic block coinciding with those generated from molecular position # 2:**

Maximal coincidence distance

Click "Show coinciding atoms". You will obtain six coinciding atoms between the model molecule and the new position:

	Individual atomic positions				distance to	
C3	0.424231	0.885928	0.156607	0.000	C5	
C6	0.290276	0.889040	0.036048	0.026	C15	
C9	0.156783	0.880658	0.107011	0.022	C20	
C12	0.420711	0.874865	0.338918	0.086	C8	
C13	0.156072	0.869826	0.286922	0.065	C22	
C18	0.284822	0.866971	0.400538	0.134	C10	

Click "Apply + Next position"

Define the third position of the molecule:

**Define and complete molecular position # 3:**

Apply inversion

	Model atom	Actual position/atom
1st point	C3	C16
2nd point	C9	C19
3rd point	C18	C14

Check again that all six atoms of the model molecule coincide with the actual atoms in the atomic part of the model.

Click "Apply + End"

*Now we defined all three phenyl rings as instances of a single molecule. The positions of atoms in the molecule will still be refined, but one molecule will be placed in three positions in the crystal. We also have to redefine the modulation parameters – remove the modulation from the atoms and add modulation of the molecular parameters – position and rotation.*

Open "Edit atoms"

Select the six atoms shown in blue – these are the atoms belonging to the molecular part

Set the number of positional modulation waves to 0

Reset the displacement parameters to isotropic

OK; OK; Yes;

Go to Parameters -> Molecules -> Edit;

For each position increase the number of positional modulation waves to 1:

**Modulations:**

Occupancy

Position

TLS parameters

Use:  Crenel

Use:  Saw-tooth  zig-zag

Type of modulation functions:

harmonics (0, 1)

OK; Yes;

Double click Refine to refine the new model.

The refinement converges to the following values:

```
R factors : [10571=4902+5669/194], Damping factor: 1.0000
GOF(obs)= 3.33 GOF(all)= 2.47
R(obs)= 7.97 wR(obs)= 7.84 R(all)= 17.76 wR(all)= 8.62
R factors for main reflections : [3513=1875+1638]
R(obs)= 7.58 wR(obs)= 7.92 R(all)= 15.41 wR(all)= 8.72
R factors for satellites +-(1) : [7058=3027+4031]
R(obs)= 8.42 wR(obs)= 7.74 R(all)= 20.03 wR(all)= 8.48
Last wR(all): 17.06 10.40 8.65 8.62 8.62 8.62
Maximum change/s.u. : -0.0244 for U11[C9]
```

Note that the R-values are only marginally higher than in the previous refinement, but the number of parameters decreased by a factor of two, from 344 to 194.

For future convenience, we will now rename the atoms in the molecule sequentially as C1...C6:

Open "Edit atoms"

Select all atoms

Click Action -> Rename selected atoms manually

Rename atom C4 to C8 (to avoid name conflict with the newly named C4) and rename the other atoms according to this image:

#1	I1=>	I1
#2	I2=>	I2
#3	P1=>	P1
#4	P2=>	P2
#5	O1=>	O1
#6	O2=>	O2
#7	C4=>	C8
#8	C7=>	C7
#9	C3=>	C1
#10	C6=>	C2
#11	C9=>	C3
#12	C12=>	C6
#13	C13=>	C4
#14	C18=>	C5

OK; OK; Yes

Go to "File->Structure->Save as"

In the lower right text box type "Iodomol-mol"; OK

No to continue with the new structure

## 11. Adding of hydrogen atoms

Double click "Edit atoms"

Select all carbon atoms

Click "Action -> Adding of hydrogen atoms"

Leave all settings default; OK

*Ten hydrogen atoms have been added automatically: four in the atomic parts and six in the molecular part.*

OK; Yes to confirm changes

View the average structure to check, if the hydrogen atoms have been added correctly.

*Hydrogen atoms have been added on all carbons of the phenyl molecule – Jana does not recognize bonds between the molecular and atomic part. The atom H1C1 should be deleted.*

Close the structure viewer

Double click "Edit atoms"

Right-click atom H1C1; Delete selected atoms; Yes

OK; Yes to confirm changes

Double click Refine to refine the structure

## 12. Viewing and interpreting the structure

*We have so far not looked at the modulated structure in detail. We will now try to interpret the modulation.*

*Traditionally the modulation functions are interpreted with the help of plots of distances, angles, bond-valence sums etc. as a function of the modulation phase. This may be difficult for molecular crystals, where the modulation is usually quite complex. It is more useful to view the structure either in a supercell or as an animation of the modulation.*

### **Plotting the supercell**

Open the structure iodomol-mol with the harmonic modulation of the molecules.

Double click the icon "Plot structure"

Select "Draw approximant structure"

Set the range of x from 0 to 5 and for z from 0 to 6

*5x1x6 supercell closely corresponds to the reciprocal values of the modulation vector components of (0.19,0, 0.15). We should see a good representation of various phases of the modulation.*

Click "Draw+continue"

In Diamond fill the unit cell and draw bonds (  icons and  ).

If Diamond is too slow, you can speed it up by switching off the rendering – icon 

The best view of the structure is along  $a$ . You can see how the rows of the hydrogen iodide molecule (only iodine present) form a wave, followed by the oxygen, to which the hydrogen iodide molecule forms a hydrogen bond. Therefore the distance iodine-oxygen remains quite constant. Also the large changes of the torsion angle of Ring 3 are visible throughout the supercell. However, it is still difficult to make sense of the interactions between the molecule and the overall picture of the modulation.

### Looking at the movie of the modulation

The program MoleCoolQt can read and display modulated structure refined by Jana. Unfortunately, so far it cannot read modulated molecules. To see the movie, we first need to transform the molecular model to purely atomic model.

First save the structure as iodomol-atomic and continue with the new structure

Open “Edit atoms”

Select all carbons and hydrogens from the phenyl molecule (in blue)

Click “Action -> Atoms from molecule to atomic part

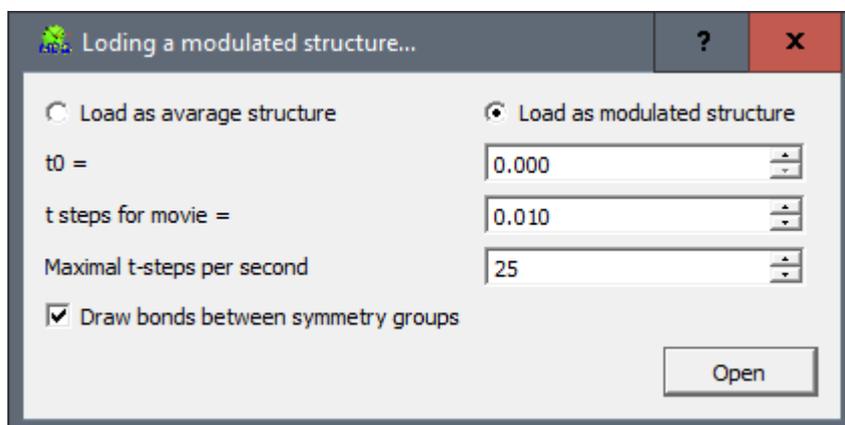
OK; Yes

Start the program MoleCoolQt

Go to “File -> Open...”, locate the file iodomol-atomic.m50 and open it

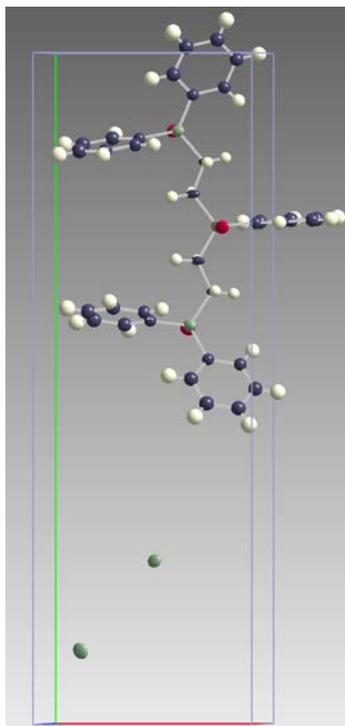
You may also drag an icon of M50 displayed in your file manager on the icon of MoleCoolQt

Keep the selection “Load as modulated structure”; Open



Switch off the atom labels – icon  in the top toolbar

You should obtain this image:



Press the key **t** on the keyboard

*Modulation movie starts. It shows the molecule as a function of modulation phase. Keep in mind that this is NOT a movie of the actual molecular motion, although it is tempting to interpret it like this! These are snapshots of the unit cell configurations at various modulated phases, which are distributed across the whole crystal.*

*You may use the options in the menu "Pack" to fill larger part of the structure to see the intermolecular interactions and their changes with the modulation phase.*

# Example 5.7: CaCNi

A simple molecular modulated structure from single crystal data with crenel functions

Revised: 1 October 2017

Single crystal data measured with KUMA four-circle diffractometer and point detector.

Reference: Petříček, Dušek and Černák (2005), Acta Cryst. B61, 280-286

Input files: cacni.hkl

absorption correction: done

## 1. *Creating new jobname*

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click CaCNi

## 2. *Import Wizard*

Select "reflection file corrected for LP and absorption"; NEXT

Select "General file on I";

In the text box "Input format" Type "\*" (single star, without quotes); NEXT

[On the screen: complete/correct experimental parameters]

Fill unit cell parameters: 8.4867 15.9511 7.6038 90 90.48 90

Type the modulation vector on the "1<sup>st</sup> modulation vector" box: 0.4365 0 0.1307; NEXT;

In the text window, leave all settings default; NEXT; OK; Finish

## 3. *Data Repository*

The line in data repository window corresponds to one data set.

OK; YES to accept the data set

[On the screen: "Information about starting symmetry wizard"]

NEXT

## 4. *Symmetry Wizard*

[On the screen: "Tolerances for crystal system recognition".]

Symmetry wizard can be started separately by "File → Reflection file → Make space group test".

Leave all settings of the wizard default; NEXT

[On the screen: "Select supercell".]

Confirm "continue with the basic unit cell"; NEXT

[On the screen: Select Laue symmetry]

Confirm monoclinic Laue symmetry; NEXT

[On the screen: Select cell centering]

The data were measured with C-centering assumed. Confirm C centered unit cell; NEXT

[On the screen: Select space group]

Confirm C2/c; NEXT

[On the screen: Select superspace group]

Confirm C2/c(a0g)0s suggested by Jana based on systematic absences

*[On the screen: Final step of the superspace test]*

Accept the superspace group transformed into the original cell: C2/c(a0g)0s; FINISH

#### **5. Creating refinement reflection file**

*We have finished creation of the file M95 (reflections converted from diffractometer format to Jana format) and M50 (cell parameters, symmetry). At this step, we will create the file M90 containing data set merged by symmetry, with forbidden reflections omitted.*

NEXT to confirm threshold 3sigma;

OK; OK to confirm information about imported reflections

*[On the screen: settings for merging of reflections]*

Leave all settings default; NEXT

*The  $R_{int}$  for observed reflections will be 2.82%*

OK

Accept the data block and calculate coverage; FINISH

*[On the screen: Information that structure solution will start]*

OK

#### **6. Structure Solution Wizard**

*[On the screen: window of Structure solution]*

In "Formula" textbox type list of chemical elements: Ni Cd C N H

Check the check box "Use a specific random seed"

*This option is here only to ensure the reproducibility of the calculation. In normal practice it is not necessary.*

Keep all other settings default

*The default solution program in Jana is Superflip. If you have other software available (SIR, SHELXT), you may link it to Jana in Tools/Programs*

Click "Run solution"

*Superflip converges within a few seconds. It confirms the symmetry C2/c(a0g)0s.*

-----  
Space group derived from the symmetry operations:  
-----

```
Tentative HM symbol: C12/c1(a0g)0s
Fingerprint:         431222C0R960028dXM3 (0,0,0,3/4)
Centering vectors:
  0.000  0.000  0.000  0.000
  0.500  0.500  0.000  0.000
Symmetry operations:
      1:          x1          x2          x3          x4
c|s(0,1,0):     x1         -x2        1/2+x3        1/2+x4
2|0(0,1,0):     -x1          x2        1/2-x3        1/2-x4
      -1:        -x1         -x2         -x3         -x4
```

This is symmetry found by Superflip in the electron density map

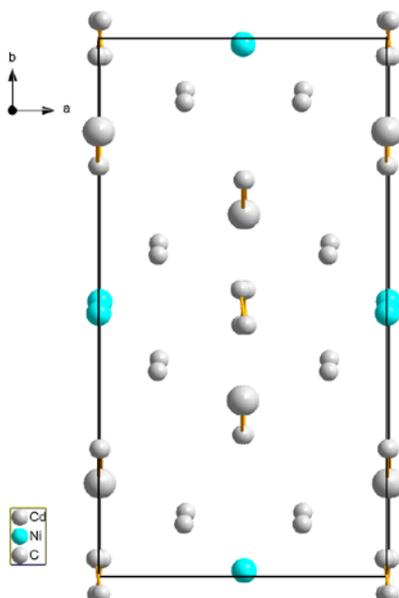
```
#####
# Search for the origin of the space group #
#####
```

```
Position of the origin in the CF map:
  0.9314  0.8649  0.7583  0.6811
Agreement factors of individual generators:
Number smb agreement
  4  c|s      0.58
  2  2|0      3.59
```

This is fit of symmetry elements supplied by user (small numbers = good fit)

Click "Draw structure" (select Draw average structure; Draw+continue)

If you have followed this tutorial exactly, you should see a picture identical to the following, after filling the unit cell with atoms and viewing it down the c-axis:



If the structure looks slightly different (e.g. shifted by  $\frac{1}{2}$  along a or b), you may still continue with the tutorial, but the details (atom names, atom positions) may be different. Alternatively you may rerun Superflip until you obtain the solution in the correct setting.

Close the structure viewer and exit the solution wizard by clicking “Accept last solution”

## 7. Checking the structure

All atoms in the structure are located in the planes a-b at  $z=0.25$ , or in the plane b-c,  $x=0.5$ . We shall view the structure in these planes to understand it better.



Double click the icon Contour in the main window of Jana:

Click “New plot”; OK;

You see now the Fourier map of the structure. A few settings need to be modified to see the relevant features:

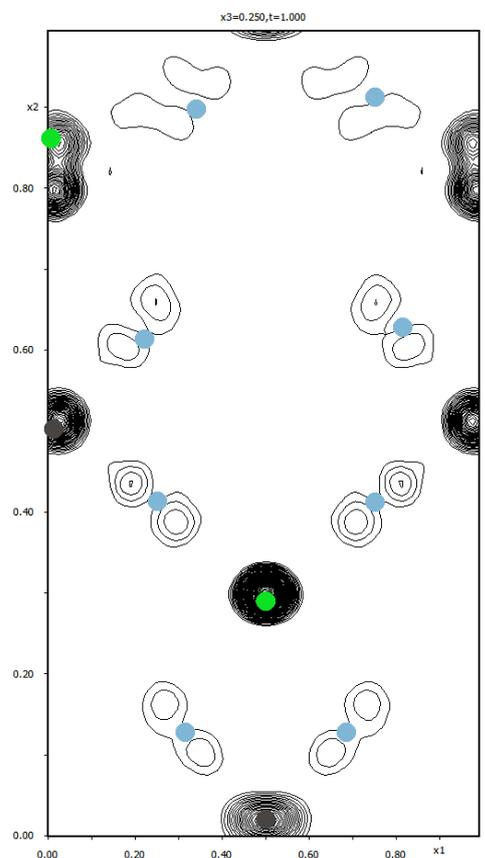
Click t-map ON; OK

Click the button “Go to” and set  $x_3$  to 0.25

Click the button “Contours” and set positive contours to 3; OK

Click on each atom in the view and check the check boxes to draw the position of the atoms (max. distance up to 1 Å)

You should obtain an image similar to this (inverted colors)



Obviously, Jana placed a single carbon atom in place of every cyano group. There is also a split Cd atom of which only one position is marked. However, this picture is just one of many unit cells in the modulated structure. To see the complete picture, we will run a movie of all configurations:

Click the button “Movie”, set the start and end of  $x_3$  to 0.25, set delay time to 0.5 s and run the movie by clicking OK. The movie can be interrupted by pressing Esc. Watch the movie carefully and try to understand, what happens in the structure.

These are the conclusions we can make from the movie:

- Atoms C2 and C3 should be deleted and replaced by properly placed C and N atoms of the cyano group
- Atom Cd is modelled by a continuous modulation function, but in fact it is jumping between two positions and it is better modelled with a split position.

We shall now make these modifications by first deleting atoms Cd1, C2 and C3 and then placing them in the correct positions:

Quit Contour by clicking the button Quit

Double click the icon "Edit atoms" 

Select Cd1, C2 and C3 (hold Ctrl while clicking the atoms), right click and select Delete selected atoms; Confirm deleting by "Yes to all". OK to close the form, Yes to confirm changes.

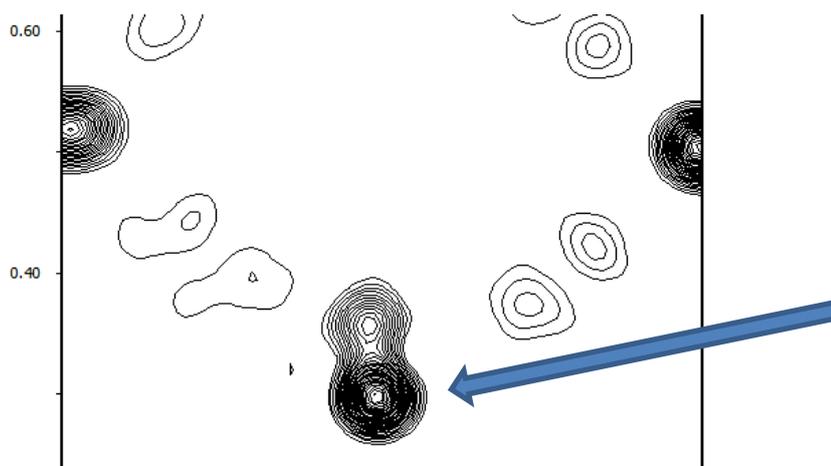
Return to Contour and make the same plot as before.

Click t-map ON; OK

Click the button "Go to" and set x3 to 0.25 (as before) and t to 0.2.

Set positive contours to 3

Click the lower of the two split positions of Cd according to the following picture:



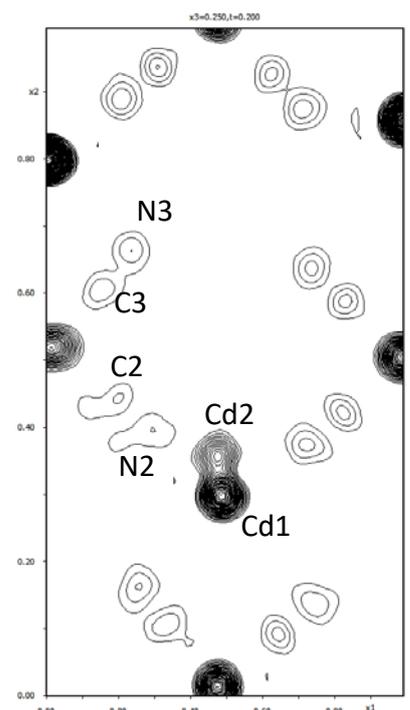
In the form that opens, click "Include the selected point as a new atoms in M40"

Fill the next form according to this picture (i.e. atoms Cd1, atomic type Cd):

Complete information for the new atom	
Name of the atom	<input type="text" value="Cd1"/> <input type="button" value="Info"/>
Uiso	<input type="text" value="0.037995"/>
Site symmetry order:	2
Occupancy reduction	<input type="text" value="1"/>
Atomic type	<input type="text" value="Cd"/> ▲
<input type="button" value="Esc"/> <input type="button" value="Ok"/>	

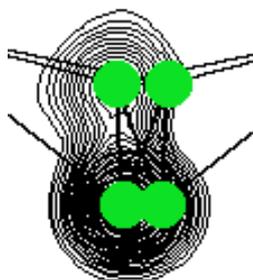
OK;

Repeat the procedure with the second split Cd position and with atoms C2, C3, N2 and N3. You should add six atoms according to the following scheme:



Please make sure to follow the scheme, so that the atomic names further in the tutorial correspond to your structure model.

*If you now click on the Cd atoms and let Jana show the position, you will probably see something like this:*



*The Cd atom sits on the special position (two-fold axis) and the clicked position was slightly away. We will correct this offset later.*

Click the button Quit and confirm adding new atoms in the structure model.

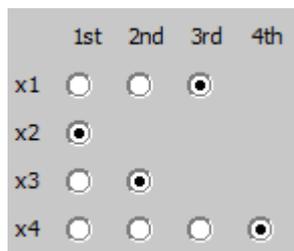
Now we will similarly check the other section of the structure, the plane b-c at  $x=0.5$ :

Double click the icon Contour;

Click the button "New plot"

On the left check the radio button Calculate new ones; OK

In the subsequent form open the tab “Scope”, uncheck the box “Use default map orientation” and define the b-c plane as the primary plane of the Fourier map according to the following scheme:



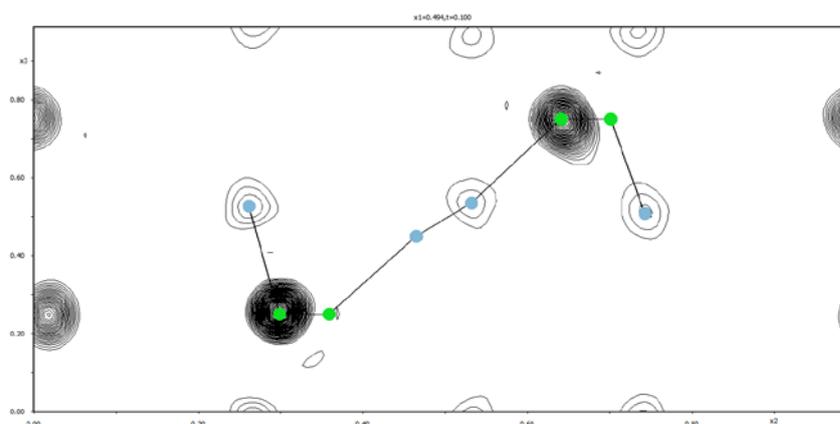
Select the radio button “Whole cell; OK

Click the button t-map ON; OK

Set Contour level to 3 (button Contours)

Click the button “Go to” and set x1 to 0.5, t = 0

Click atoms in the view and draw their position. You should obtain this result:



Run movie (button movie, set x1 range to 0.5-0.5, delay time to 0.5) and investigate the behavior of the modulation in this plane. Do we need to modify the structure model?

*Your conclusion should be that the model is essentially OK. Atom C4 is modulated between two positions and is always present close to the neighboring Cd atoms. The Cd atom oscillates between four-fold and two-fold coordination (in this plane!). Atom C4 should be nitrogen (ammonium). Atom C1 should also be a nitrogen atom. We can now make the final corrections to the initial model:*

Click “Quit” to quit Contour

Double click the icon “Edit atoms”

Double click atom Cd1

on the tab “Edit” change the x-coordinate to 0.5

Click the button Show/reset site occupancy and update the site occupancy to 0.5; Yes; OK

Repeat the procedure with the atom Cd2

Double click the atom C4

Type “N\*” in the text box “Name”; Press TAB

*The name changes to the first free number for nitrogen, N1 in this case*

Change the type to N;

Repeat the procedure for the C1 atom. It will become N4

OK; OK; Yes to confirm the changes and return to the main window.

*Now we have checked and updated the basic structure – atomic types and positions. Now we can check the modulation functions of individual atoms. Jana tries to assign harmonic modulation functions to each atom after the solution.*

## 8. Setting up modulation functions

*We will now check the modulation function for all atoms and modify them where necessary.*

Double click the icon “Contour”

Click the button “New plot”

Select the radio button “Show de Wolff’s sections”

Set the scope of the sections: primary scope to 3, secondary to 0.5

Click the button “Define atoms for de Wolff’s sections”

In the text box “Atoms” type \* and click the button “Add”; OK

OK

*The program calculates the Fourier maps for modulation functions of all atoms (x, y and z direction for each atom). It may take some time.*

Go through the de Wolff’s sections for all atoms (using the buttons “W-” and “W+” or by selecting from the list and make notes about the type of modulation for each atom and for special function note their centers (denoted  $x_0$ , it is the  $x_0$  coordinate of the center of the domain) and widths (length of the domain along  $x_0$ , denoted  $\Delta$ ).

*You should obtain the following conclusions:*

- Ni1: Saw tooth function:  $x_0 = 0.75$  (exactly, by symmetry),  $\Delta = 1$
- N4: harmonic, existing function is a good first approximation
- N1: crenel function,  $x_0 = 0.75$  (this time not fixed by symmetry, the atom is not on special position),  $\Delta = 0.5$
- Cd1: crenel function,  $x_0 = 0.25$  (exactly, by symmetry),  $\Delta = 0.5$
- Cd2: crenel function,  $x_0 = 0.75$  (exactly, by symmetry),  $\Delta = 0.5$ ; Cd atoms have complementary Crenel intervals
- N2 atom: needs to be split into two positions, N2 and N2b. N2 has a crenel function with  $x_0 = 0.59$ ,  $\Delta = 0.5$ ; for N2b  $x_0 = 0.09$   $\Delta = 0.5$ . Splitting is the most prominent in the x-direction.  $x(N2) = 0.21$ ,  $x(N2b) = 0.29$
- C2 atom: needs to be split into two positions, C2 and C2b. C2 has a crenel function with  $x_0 = 0.57$ ,  $\Delta = 0.5$ ; for C2b  $x_0 = 0.07$   $\Delta = 0.5$ . Splitting is the most prominent in the x-direction.  $x(C2) = 0.12$ ,  $x(C2b) = 0.19$
- C3: continuous function, can be harmonic
- N3: continuous function, can be harmonic

*We will now set up these functions for individual atoms*

Quit Contour

Double click “Edit atoms”

Double click atom Ni1

Click the check box “Use crenel”

In the form that opens set delta to 1,  $x_0$  to 0.75; OK

Select the radio button “Legendre polynomials in crenel interval”

*Note: we defined the function as crenel, although it looks like a saw tooth. Legendre polynomials contain a linearly sloping term, and a crenel function can turn to a saw tooth during the refinement.*

Repeat the procedure for N1, Cd1, Cd2, set the parameters according to the list above  
Right click atom N2, select “Split atomic position”

Set the atom name to N2b; Uncheck the option “Generate restrict commands for REFIN”;  
Apply

Double click atom N2 and set its Crenel function according to the list above. On the “Edit” tab set its x-coordinate to 0.21. Repeat for N2b, set parameters according to the list above. Repeat the whole splitting procedure, setting of Crenels and change of x coordinates for the atom C2.

*As a last step we will release the width of the crenel domain of Cd1 for later refinement. Only this parameter needs to be explicitly released, other domain widths and centers will be restricted before the refinement – see below.*

Double click the atom Cd1

On Card “Edit” click “Occupancy” next to the text “Edit modulation parameters”

Check the check box next to “delta”

OK; OK; OK; Yes to quit “Edit Atoms”

*Now we will check that the functions were correctly set:*

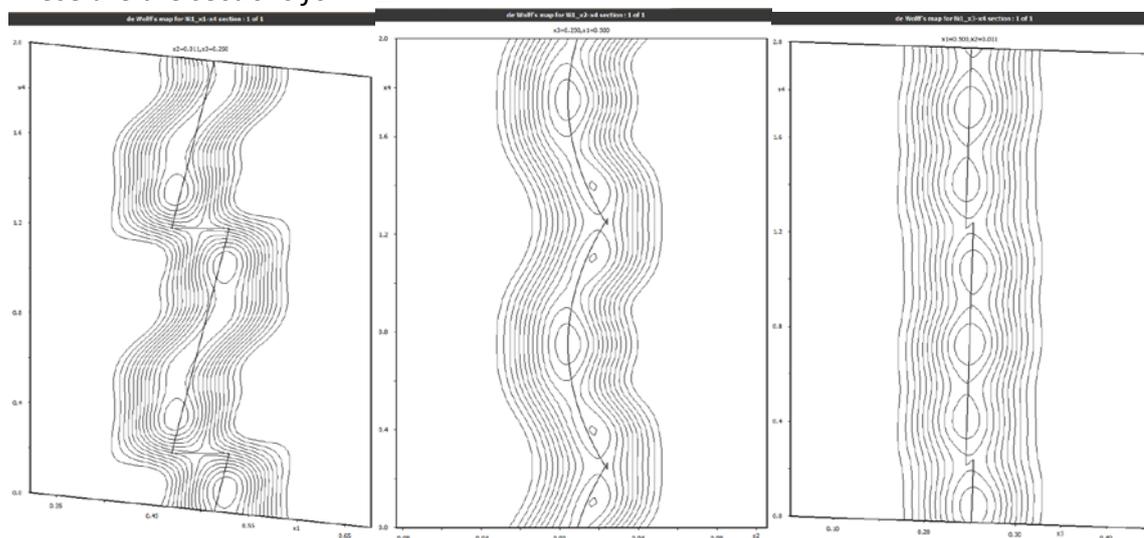
Double click Contour

Calculate new de Wolff’s sections; use the option “Update existing sections” in the form

Go through the de Wolff’s sections again and check that the functions are properly set.

Correct the mistakes you might have done.

*These are the sections for Ni1:*



*The difficult part of the work is over. We have set up the structure model, we have understood the structure in quite a detail and now we can start the refinement from a good, elaborated structure model.*

Quit Contour and return to the main window.

## 9. Initial structure refinement

**Important: what you have done up to now is very precious. Make sure you copy the job to a new job name to preserve the original and to have the chance to return to this point.**

Go to “File->Structure->Save as

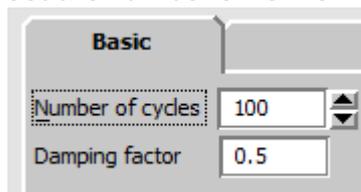
In the lower tight text box type “CaCNI-ref”; OK

Yes to continue with the new structure

Plot the average structure. Use “Draw and Continue”, keep the structure view open and return to Jana2006

Right-click the icon Refine

Set the number of refinement cycles to 100 and damping factor to 0.5:



*The last step we need to make before the refinement is setting up restrictions on the modulation parameters. The logic of the structure requires that the groups Cd1+N2b+C2b have the same “domain of existence”, i.e. are present together in the structure. The group Cd2+N2+C2 should also be present together and the two groups are mutually exclusive. Furthermore, no vacancy is expected, i.e. either Cd1 or Cd2 is always present. Thus, the centers of the crenel domains within each triplet should be equal and between the triplet shifted by 0.5. The length of the domains is equal within each triplet, and the domain lengths of one triplet are complementary to 1 with the domain lengths of the second triplet. We need to define these relationships by means of equations between the atomic parameters:*

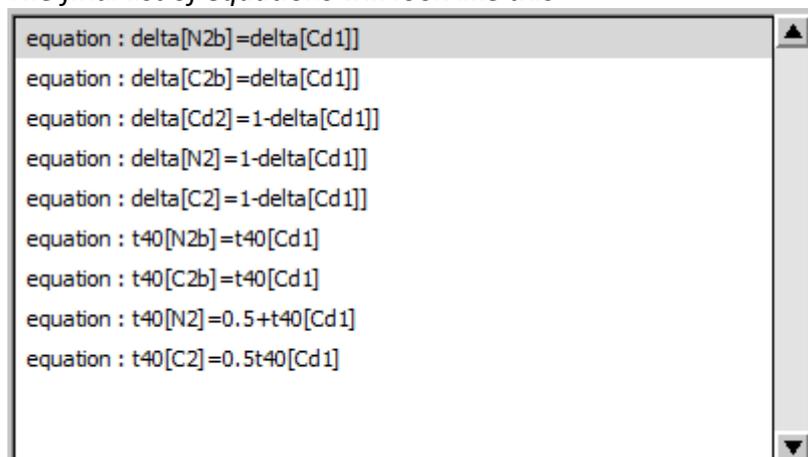
Go to card “Various”; Click the button “Equations”

In the text box “Equation” type  $\delta[N2b]=\delta[Cd1]$

Click the button Add to add the equation

Add further equations restricting the domain lengths (parameter delta) and domain centers (parameter t40).

*The final list of equations will look like this*



*Note: There is no equation on t40 of Cd2, because this parameter is fixed by symmetry.*

OK; OK; Yes + Start

The refinement converges to the following R-values:

```
R factors : [7894=3502+4392/55], Damping factor: 0.5000
GOF(obs)= 12.59 GOF(all)= 8.40
R(obs)= 24.88 wR(obs)= 31.14 R(all)= 42.29 wR(all)= 31.30
R factors for main reflections : [1136=833+303]
R(obs)= 10.42 wR(obs)= 13.97 R(all)= 14.81 wR(all)= 14.05
R factors for satellites +(-1) : [2257=1599+658]
R(obs)= 27.09 wR(obs)= 34.37 R(all)= 36.05 wR(all)= 34.47
R factors for satellites +(-2) : [2246=668+1578]
R(obs)= 57.43 wR(obs)= 62.00 R(all)= 103.56 wR(all)= 62.21
R factors for satellites +(-3) : [2255=402+1853]
R(obs)= 42.61 wR(obs)= 41.45 R(all)= 104.59 wR(all)= 42.06
Last wR(all): 31.30
Maximum change/s.u. : 0.0446 for x[N1]
```

It is a promising start. The high R-values for the 2<sup>nd</sup> and 3<sup>rd</sup>-order satellites are not surprising, we have not added higher-order positional modulation yet.

## 10. Add harmonic waves

Satellites up to third order are observed. We may add up to three harmonic waves, but first we will add only one waves for each light atom and two waves for the heavy atoms.

Open "Edit atoms"

Double click Ni1

Increase the number of positional waves to 2

Repeat for other atoms, use 2 waves also for Cd1 and Cd2 and 1 wave for all other atoms.

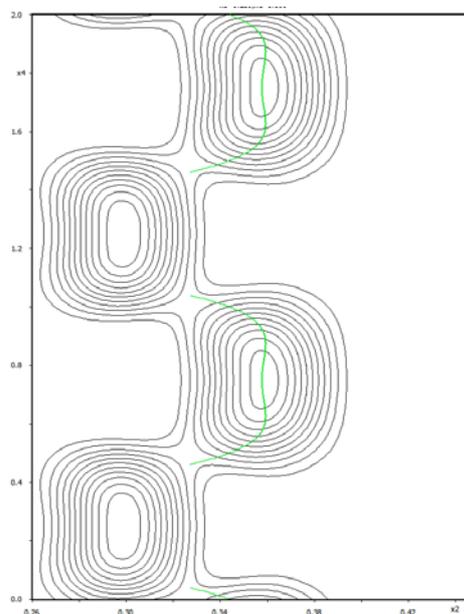
Close Edit atoms and run refinement again.

The refinement converges to the following R-values:

```
R factors : [7894=3502+4392/106], Damping factor: 0.5000
GOF(obs)= 3.69 GOF(all)= 2.52
R(obs)= 7.63 wR(obs)= 9.06 R(all)= 24.56 wR(all)= 9.37
R factors for main reflections : [1136=833+303]
R(obs)= 5.24 wR(obs)= 6.94 R(all)= 8.55 wR(all)= 6.99
R factors for satellites +(-1) : [2257=1599+658]
R(obs)= 5.67 wR(obs)= 6.56 R(all)= 11.60 wR(all)= 6.66
R factors for satellites +(-2) : [2246=668+1578]
R(obs)= 15.73 wR(obs)= 17.84 R(all)= 66.15 wR(all)= 18.79
R factors for satellites +(-3) : [2255=402+1853]
R(obs)= 25.48 wR(obs)= 25.63 R(all)= 105.59 wR(all)= 26.76
Last wR(all): 9.57 9.45 9.40 9.38 9.37 9.37 9.37 9.37
Maximum change/s.u. : -0.3940 for yort2[Cd2]
```

Recalculate de Wolff's sections and check, if the newly refined modulation functions are still follow the traces in the Fourier maps.

The sections look OK, the modulation functions are appropriately describing the electron density. The only exception may be the Cd1 and Cd2 atoms, where the functions are too curved towards the end of the occupancy domain:



*The number of waves may thus be decreased to 1. However, testing leads to a significant increase of the R-values and we therefore keep two modulation waves on Cd1 and Cd2 at least for now.*

*Checking the shapes of the modulation waves is an important check to be made after every significant change of the structure model to avoid divergence of the model to unrealistic parameters.*

### **11. Refinement of ADP**

*So far the displacement parameters are refined as isotropic. We will now set them for anisotropic refinement:*

Open "Edit atoms"

Select all atoms

Double click any of the selected atoms

Select the radio button "harmonic (isotropic)"

OK;

Set also the number of modulation waves for Cd1 and Cd2 to 1

OK; Yes to quit "Edit atoms"

Double click Refine to refine anisotropic displacement parameters.

*The refinement converges to the following R-values:*

```

R factors : [7894=3502+4392/149], Damping factor: 0.5000
GOF(obs)= 4.80 GOF(all)= 3.24
R(obs)= 9.80 wR(obs)= 11.70 R(all)= 25.94 wR(all)= 12.00
R factors for main reflections : [1136=833+303]
R(obs)= 5.29 wR(obs)= 7.08 R(all)= 8.42 wR(all)= 7.12
R factors for satellites +-(1) : [2257=1599+658]
R(obs)= 7.17 wR(obs)= 8.43 R(all)= 13.56 wR(all)= 8.53
R factors for satellites +-(2) : [2246=668+1578]
R(obs)= 24.51 wR(obs)= 26.59 R(all)= 77.29 wR(all)= 27.54
R factors for satellites +-(3) : [2255=402+1853]
R(obs)= 35.57 wR(obs)= 34.19 R(all)= 95.87 wR(all)= 35.01
Last wR(all): 12.00
Maximum change/s.u. : 0.0553 for  $\gamma$ [Cd2]

```

## 12. Setting up further harmonic waves

Main reflections and first-order satellites now have nice R-factors, but the fit to the higher satellite orders is not yet good. We need to add higher harmonic positional waves to properly describe these parameters. There is not universal recipe on the number of harmonic waves to be set except that their number should almost never be larger than the number of satellite orders. At the same time, the refined waves should not be too wavy and unreasonable.

A little bit of testing (try!) shows that an acceptable setting which lowers the R-value and does not lead to unphysical modulation function is this:

Ni1: 3 waves

Cd1, Cd2, C3, N3, N4: 2 waves

N1, N2, N2b, C2, C2b: 1 wave

Set the number of waves accordingly and run refinement again.

The refinement converges to the following R-values:

```

R factors : [7894=3502+4392/176], Damping factor: 0.5000
GOF(obs)= 2.78 GOF(all)= 1.92
R(obs)= 5.60 wR(obs)= 6.76 R(all)= 21.46 wR(all)= 7.08
R factors for main reflections : [1136=833+303]
R(obs)= 4.01 wR(obs)= 5.56 R(all)= 7.05 wR(all)= 5.61
R factors for satellites +-(1) : [2257=1599+658]
R(obs)= 4.14 wR(obs)= 4.72 R(all)= 9.90 wR(all)= 4.84
R factors for satellites +-(2) : [2246=668+1578]
R(obs)= 11.58 wR(obs)= 12.51 R(all)= 59.64 wR(all)= 13.60
R factors for satellites +-(3) : [2255=402+1853]
R(obs)= 17.89 wR(obs)= 19.37 R(all)= 92.77 wR(all)= 20.60
Last wR(all): 7.08
Maximum change/s.u. : -0.0240 for  $\gamma$ [Cd2]

```

The fit is already quite good, but still not perfect. Further testing and checking of the difference Fourier maps shows that the modulation of ADPs of Cd atoms is required to improve the fit to the high-order satellites:

Open "Edit atoms"  
 Select atoms Cd1 and Cd2  
 Double click the atoms

Type Cd

**ADP parameter(s):**

isotropic

harmonic (anisotropic)

anharmonic

Use TLS

**Modulation waves:**

Occupancy 1

Position 2

ADP 2nd 1

dulation to 1:

Close "Edit atoms and run Refine

*The final refinement table looks like this:*

```

R factors : [7887=3496+4391/188], Damping factor: 0.5000
GOF(obs)= 2.07 GOF(all)= 1.45
R(obs)= 4.41 wR(obs)= 5.02 R(all)= 18.67 wR(all)= 5.35
R factors for main reflections : [1136=833+303]
R(obs)= 3.25 wR(obs)= 4.61 R(all)= 6.38 wR(all)= 4.67
R factors for satellites +-(1) : [2256=1598+658]
R(obs)= 3.30 wR(obs)= 3.65 R(all)= 8.78 wR(all)= 3.77
R factors for satellites +-(2) : [2243=666+1577]
R(obs)= 9.55 wR(obs)= 9.35 R(all)= 55.09 wR(all)= 10.43
R factors for satellites +-(3) : [2252=399+1853]
R(obs)= 12.38 wR(obs)= 12.36 R(all)= 74.21 wR(all)= 13.85
Last wR(all): 5.37 5.36 5.35 5.35 5.35 5.35 5.35 5.35
Maximum change/s.u. : -0.0390 for zort1[Cd2]
  
```

### 13. Plotting the structure

*To understand the structure, it can be plotted in a supercell, or various geometric characteristics can be drawn.*

# Example 6.1: KSm

Revised: 15 October 2018

Data	Topic	Level
X-ray Powder data	Modulated structure from powder data	Advance

## Tasks

---

Solving a modulated structure from powder data.

- Profile refinement and structure solution
- Crenel modulation to describe mixed sites in 4d.
- Stephen' formalism for modulated structures

## Initial data

---

### Data

Powder data measured with synchrotron radiation,  $\lambda = 0.7114 \text{ \AA}$

### Input files:

KSm.dat (powder profile data)

KSm.txt (additional information)

KSm.pdf (article about this compound)

KSm-solution.m40

KSm-solution.m50

### Additional information:

**Chemical formula:** K Sm Mo<sub>2</sub> O<sub>8</sub>

**Unit cell found:** 5.5304 5.3019 11.7893 90 90 91.138

**q-vector :** 0.56883 -0.12885 0

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# Instructions

---

## I. Data import

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click KSm

### 2. Import Wizard

Select “**Various CW formats**”; NEXT

*CW stands for constant wavelength*

Type “File name” **KSm.dat**

Select “**Free format of 2th, I, [sig(I)]**” and “**Another/unknown method**”; NEXT

Fill cell parameters **5.5304 5.3019 11.7893 90 90 91.138**

*The string can be copied from KSm.txt by CtrlC + CtrlV*

Change “Target dimension” to 4 and fill q vector **0.56883 -0.12885 0**

For wavelength type **0.7114** and select “**Linearly polarized beam**”; NEXT; FINISH

Accept the data in Data repository (*Step 1*); OK

Select “Yes, I would like to continue with the wizard”;

OK.

#### Step 1

Complete/correct experimental parameters

Cell parameters: 5.5304 5.3019 11.7893 90 90 91.138

Target dimension: 4 Info about metrics parameters

1st modulation vector: 0.56883 -0.12885 0

2nd modulation vector:

3rd modulation vector:

X-rays X-ray tube

Neutrons

Electrons

Kalpha1/Kalpha2 doublet

Wave length: 0.7114

Temperature: 293

Polarization correction:

Circular polarization

Perpendicular setting Info

Parallel setting Info

Guinier camera

Linearly polarized beam

Back Next Cancel

## II. Le Bail refinement

### 1. Checking data

[On the screen: Refinement of the powder profile by the Le Bail algorithm]

“Show powder profile”

Profile viewer shows experimental powder profile  
The powder profile is stored in KSm.m95 and in KSm.m90 in analogy to single crystal data

“QUIT” Leave profile viewer  
“Edit refinement commands”; **0 refinement cycles**; OK  
“Run Refine”  
“Show powder profile”

#### Notes

Now the profile viewer shows experimental and calculated powder profile. The calculated profile is based on default profile parameters. Bragg positions of satellites are **green**. By default, satellites up to the order 1 are shown.  
The calculated profile is stored in KSm.prf

Quit; Leave profile viewer

## 2. Refinement of profile parameters

“Edit profile parameters”  
[On the screen: Powder options]

#### Notes

In the initial state, all profile parameters are fixed except background parameters. In page “Profile”, GW has a non-zero initial value. All profile parameters are stored in KSm.M41.

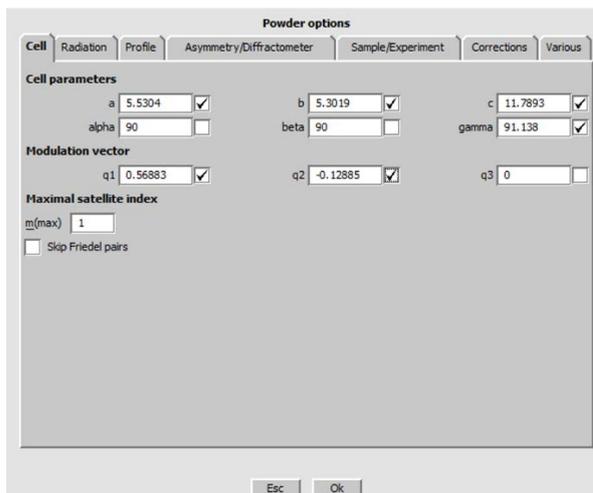
In “Profile” page activate refinement of **GW**  
In “Corrections” page activate refinement of **shift**  
Refinement of background terms is enabled by default  
OK (Leave Powder options);  
YES (save changes)  
“Edit refinement commands”  
Set **100 refinement cycles**; OK  
“Run Refine”

#### Notes

Profile R factors: [8171/7+1]  
The refinement against 8171 profiles point is based on 7 profile + 1 structure parameters.  
Refinement converges with GOF  $\approx$  2.4, Rp  $\approx$  3.7, wRp  $\approx$  8.1  
The convergence may be slow. You can interrupt the refinement when Rp reaches 3.7% by button “End” pressed at the moment when LeBail decomposition is not running

“Edit profile parameters”:  
In page “profile” activate refinement of cell parameters (**a, b, c, gamma**) and components (**q1, q2**) of the modulation vector; (Step 1)  
In page “Corrections” set number of **Legendre terms** for background to **16**; OK; YES (step 6)  
“Run Refine”

### Step 1



#### Notes

*Refinement [8171/24+1] converges with GOF  $\approx$  1.9, Rp  $\approx$  3.1, wRp  $\approx$  6.6*

Press "Edit profile parameters"

In Page "Profile" activate refinement of **GU, GV**

"Run Refine"

#### Notes

*Refinement [8171/26+1] converges with GOF  $\approx$  1.5, Rp  $\approx$  2.5, wRp  $\approx$  4.9.*

*Waiting for the full convergence is not necessary. Although the profile viewer shows that profile description could be further improved, for structure solution this starting point is sufficient.*

FINISH;

YES (to the question about closing the wizard)

NEXT open a wizard for the space group test

### 3. Space group determination

*[On the screen: Tolerances for crystal system recognition]*

Use default; NEXT

*[On the screen: Select Laue symmetry]*

Select the highest one – **monoclinic**; NEXT

*[On the screen: Select cell centering]*

Select **I centering**; NEXT

*[On the screen: Information about progress of space group tests. It takes some time...]*

*[On the screen: Select space group];*

Select **C2/c**; NEXT

*[On the screen: Final step of the space group test];*

"Accept the superspace group **transformed into the original cell**"; Finish (Step 5)

*[On the screen: "Do you want to refine profile parameters one more?"];*

Answer "Yes" to refine powder parameters once more.)

OK;

#### Notes

The used symmetry speeds up the profile refinement because we are having less Bragg reflections due to systematic absences in  $I2/b$  space group. Less reflections also causes slightly worse  $R_p$  factor.  
Refinement [8171/26+1] converges with  $GOF \approx 1.7$ ,  $R_p \approx 3.1$ ,  $wRp \approx 5.7$ .

### III. Rietveld refinement

#### 1. Structure solution

Select “Use Superflip”

Type formula **K Mo2 Sm O8**; (please use the same order it is important for the continuation of this example) **Formula units 2**

#### Notes

As in the space group  $I2/b$  the minimal site multiplicity is 4, it is clear the Sm and K are either alternatively occupying the same position or two positions with half occupancy. The first possibility would change the average density at the Sm/K position to a level similar to the Mo position, because the average atomic number of Sm/K 40.5 is close to 42 for Mo atoms. This means that then **we can expect troubles to distinguish the Mo and Sm atom.**

Select “Repeat Superflip: Number of runs”, type **10** runs and **3000** cycles

Select “Starting model” = “Patterson superposition map”

**Peak from Jana2006 but first run Fourier** (Step 1)

#### Step 1

“Run solution”

“Accept last solution” closes the structure solution wizard

[On the screen: Basic Jana window];

#### Notes

To unify the origin selection with the selection used in the Cookbook, we will not continue with the obtained structure model but we will copy the structure model from a file. The advanced users can continue with their own model but they should be aware that position of crenel functions and shape of other modulation functions may differ of the printed figures, because they depend on the origin position.

Start "File → Structure → Copy in"

Import M40 and M50 from the structure **KSm-solution**.

Start "Edit atoms" or "Edit/View → Editing of M40" and make sure the atomic positions are as follows:

**Sm1** 0.500000 0.250000 0.147357

**Mo1** 0.000000 0.750000 0.120140

## 2. Completing average structure

### Notes

Atoms in the initial structure model have already modulation functions, which were found in the electron density map from Superflip. However, for this example it is better to use the classical approach: calculating first the average structure and then refining modulation waves from small starting displacements.

Press "Edit profile",

In page "Cell":

check "**Use only satellites corresponding to existing modulation waves**"

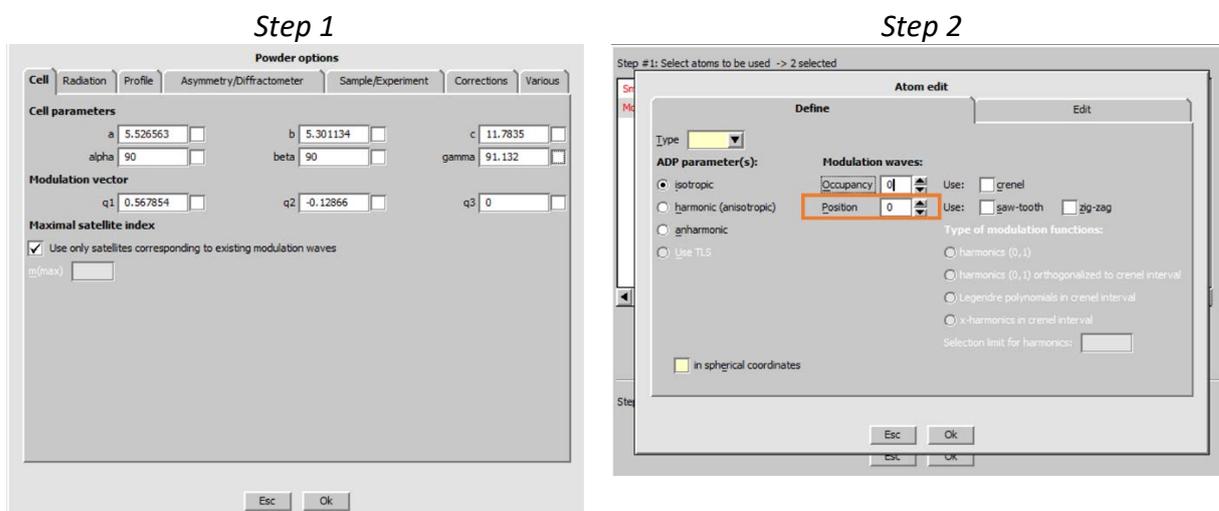
**uncheck** refinement of **q** vector components and **a, b, c and gamma**. (Step 1)

In page "Profile" **uncheck GU, GV and GW**

In page "Corrections" **uncheck shift**

In "Edit atoms" dialogue select heavy atoms (**Sm1** and **Mo1**), go to "Action → Edit/define" and set **zero modulation waves for occupancy and position**. (Step 2)

OK; OK



[On the screen: Basic Jana window];

Right click on Refine

In Refinement options go to page "Basic" and set Number of cycles to **100** and Damping factor to **0.25**

**Uncheck "Make only profile matching"**

OK; YES +Start

### Notes

*R factors [174=153+21/5]*

*(174 Bragg reflections, out of them 153 observed and 21 unobserved; 5 refined structure parameters)*

R factors for all reflections :  $R(\text{obs}) \approx 11.4$ ,  $wR(\text{obs}) \approx 15.5$ ,  $R(\text{all}) \approx 13.0$ ,  $wR(\text{all}) \approx 15.5$   
R factors for main reflexions :  $R(\text{obs}) \approx 11.4$ ,  $wR(\text{obs}) \approx 15.5$ ,  $R(\text{all}) \approx 13.0$ ,  $wR(\text{all}) \approx 15.5$   
R factors for satellites (not listed)  
Profile R factors : [8171/16+5]  
 (8171 profile points, 16 refined profile parameters, 5 refined structure parameters)  
 $GOF \approx 8.5$ ,  $R_p \approx 21.6$ ,  $wR_p \approx 29.1$   
 Warning: ADP of Mo1 is negative

Press "Edit atoms" Select **Sm1** → Action → Edit/Define atoms  
 In page "Edit" activate **refinement of occupancy** (parameter "ai") for Sm1  
 OK; OK; YES  
 Run "Refine"

#### Notes

*R<sub>p</sub> slightly improves, Occupancy of Sm1 changes from 0.5 to 0.4 and ADP of Mo1 becomes positive. The decrease in occupancy of Sm1 indicates that it could be mixed with potassium.*

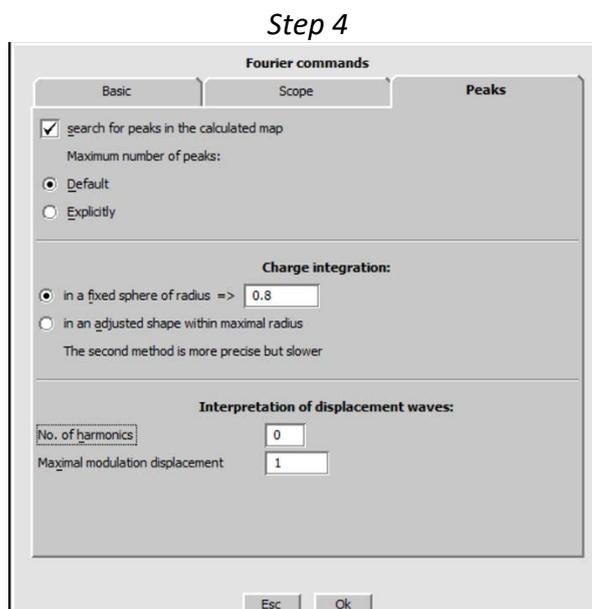
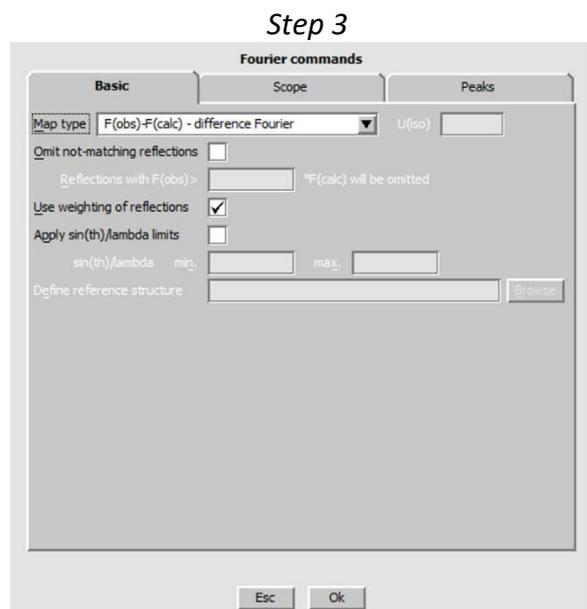
[On the screen: Basic Jana window];

Right Click on "Fourier"

In page "Basic" select in Map type "**F(obs)-F(calc)-difference Fourier**", (Step 3)

In page "Scope" and check "**use default map orientation**".

In the "Peaks" page – "Interpretation of displacement waves" change "**No. of harmonics**" to 0. (Step 4)

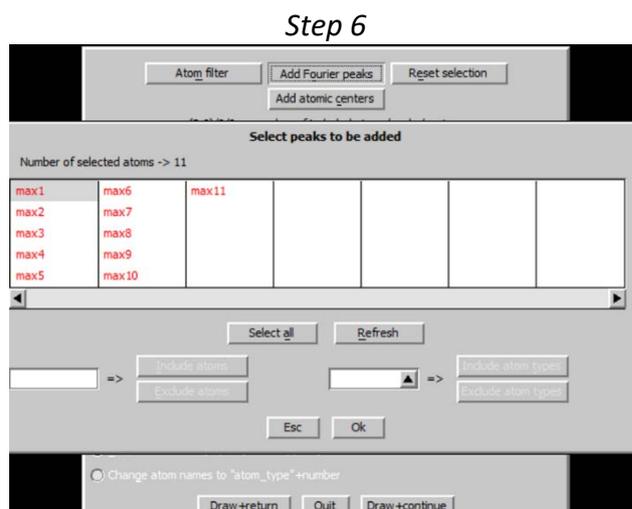
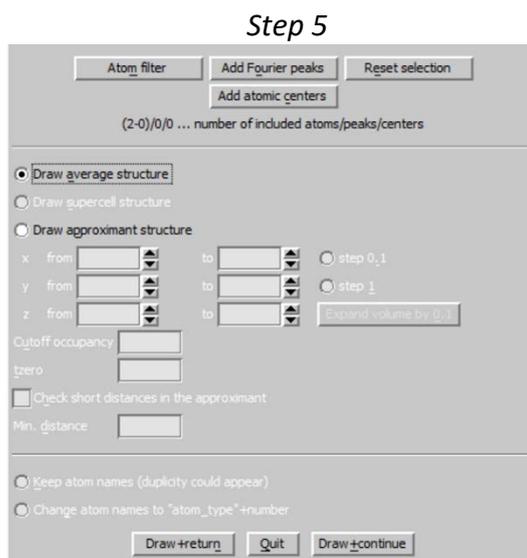


OK; Yes + Start (Run difference Fourier)  
 NO (skip procedure for including new atoms)

#### Notes

*The fact that both heavy atoms are located at special positions with interatomic vector about (0.5,0.5,0) leads to a false symmetry in the map. However, the true maxima should form a tetrahedron around Mo1. In the next steps, we will plot Mo1 and neighboring Fourier maxima in Diamond.*

Run "Plot structure"; Select "Draw average structure"; (Step 5)  
 Press "Add Fourier peaks"; select all maxima; OK; (Step 6)



Draw+continue" to start Diamond

[On the screen: window of Diamond]

#### Notes

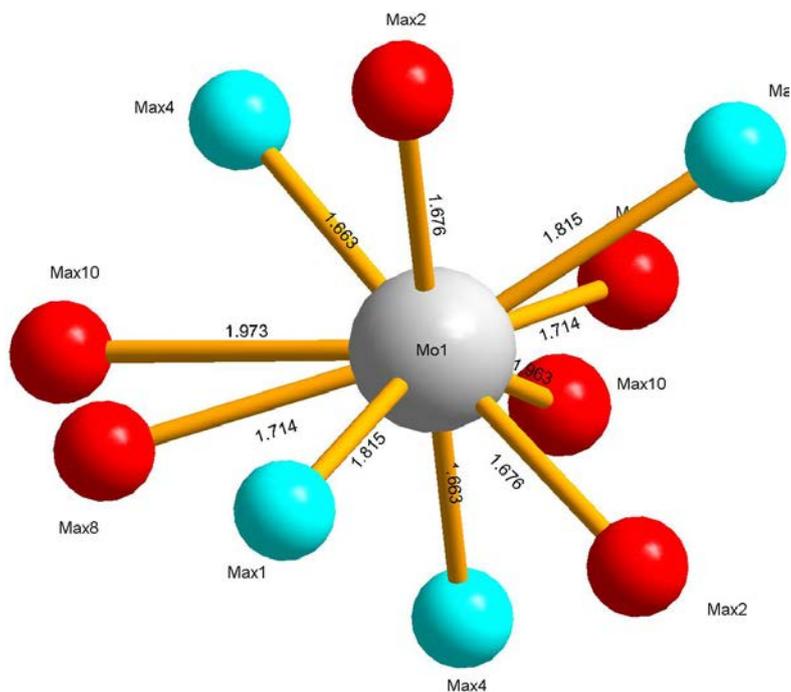
Jana2006 assigns to the Fourier maxima the lightest chemical element in the formula. For our formula, this is the oxygen. Sometimes it may be practical to append another light atom to the end of the formula, for instance hydrogen, but not in our case.

Delete the automatically created structure

With button  from the bottom toolbar select Mo1 as the only atom to be plotted  
 With "Build → Connectivity" focus Mo-O distance and set the limits above 1.5 Å and below 2 Å; OK

Click Mo1 and create its coordination with button 

Rotate the plot until you recognize a tetrahedron formed by four maxima

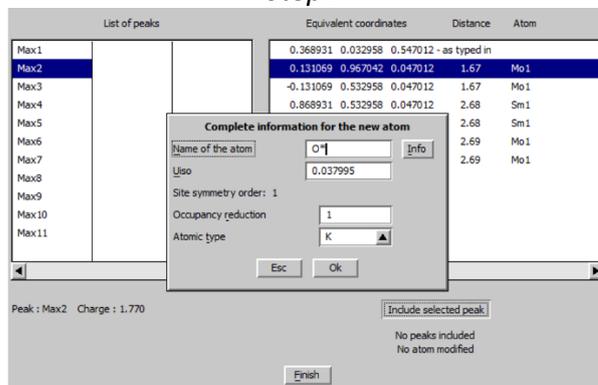


### Notes

The reason, why we are concentrating on Mo coordination, is that Mo-O bonds are the strongest ones in the structure and they make usually tetrahedron around the central atom. From the chemical formula  $\text{KMo}_2\text{SmO}_8$  and the number of 2 structural units in the cell, it follows that we are looking two pairs of atoms related by two-fold axis going through Mo1 atom. The only acceptable positions for oxygen atoms are indicated in the figure by cyan color. This means that only two peaks (Max1 and Max4) are to be included to our structure model.

- From the basic Jana window run "Parameters→Atom→New";
- Select "Peaks from the last Fourier calculation"; OK
- Select the first peaks recognized in the Diamond and press "Include selected peak" write the name of atom O\* ; OK (Step 7)
- Repeat the procedure for the second maximum
- Finish; Yes (to include new atoms)
- Run "Refine"

### Step 7



### Notes

Refinement,  $[174=146+28/14]$  and  $[8171/16+14]$  converges with  
R factors for all reflections :  $R(\text{obs}) \approx 5.2$ ,  $wR(\text{obs}) \approx 7.2$ ,  $R(\text{all}) \approx 7.6$ ,  $wR(\text{all}) \approx 7.3$   
R factors for main reflexion :  $R(\text{obs}) \approx 5.2$ ,  $wR(\text{obs}) \approx 7.2$ ,  $R(\text{all}) \approx 7.6$ ,  $wR(\text{all}) \approx 7.3$   
R factors for satellites (not listed)  
Profile R factors :  $\text{GOF} \approx 6.9$   $R_p \approx 13.9$   $wR_p \approx 23.5$

Start "File → Structure → Save As" and make a backup copy of the average structure, for instance **KSm\_ave**

**No** ( you don't want to continue with the new structure)

### 3. Refinement of modulated structure

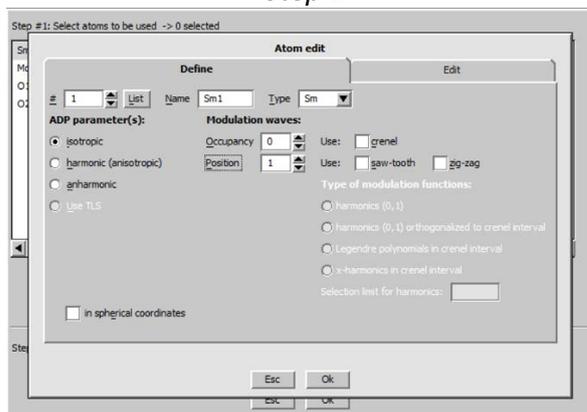
Start "Edit atoms" (Select **Sm1** → Action → Edit define) and set **1** position modulation wave for Sm1 (Step 1)

Run "Refine"

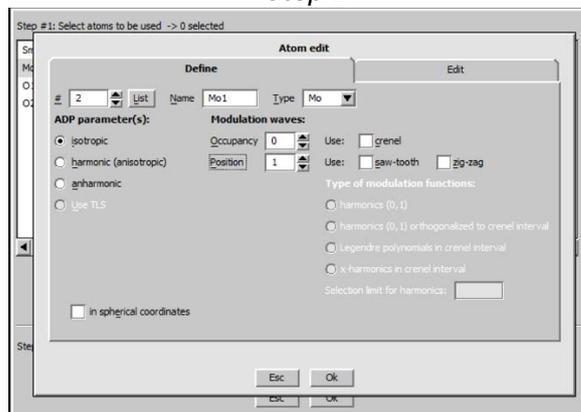
Start "Edit atoms" (Select **Mo1** → Action → Edit define) and set **1** position modulation wave for Mo1 (Step 2)

Run "Refine"

Step 1



Step 2



#### Notes

Refinement:  $[515/501+14/20]$  and  $[8171/16+20]$  converges with  
R factors for all reflections :  $R(\text{obs}) \approx 9.6$   $wR(\text{obs}) \approx 12.5$   $R(\text{all}) \approx 12.7$   $wR(\text{all}) \approx 12.8$   
R factors for main reflections :  $R(\text{obs}) \approx 5.2$   $wR(\text{obs}) \approx 9.1$   $R(\text{all}) \approx 5.8$   $wR(\text{all}) \approx 9.1$   
R factors for satellite reflections:  $R(\text{obs}) \approx 15.7$   $wR(\text{obs}) \approx 14.4$   $R(\text{all}) \approx 17.6$   $wR(\text{all}) \approx 14.6$   
Profile R factors :  $\text{GOF} \approx 6.2$   $R_p \approx 12.9$   $wR_p \approx 21.1$

[On the screen: Basic Jana window]

Press "Contour",

Press "New plot",

Select "Show de Wolff's sections";)

Select "F(obs)-Fourier"; Define primary and secondary scope 2 and 1 Å, respectively;

Check that the option "Sum maps over secondary sections" is activated; (step 3)

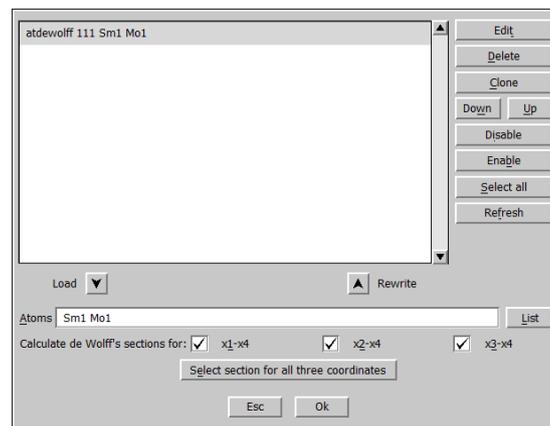
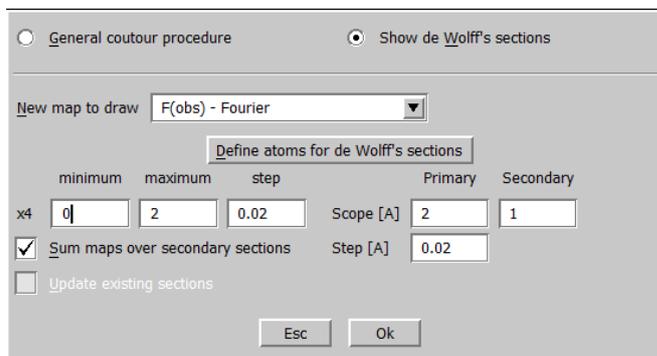
Press "Define atoms for de Wolff's sections"

Select **Sm1** and **Mo1** atoms and all three sections **x1-x4**, **x2-x4** and **x3-x4**; (step 4)

OK; OK

Step 3

Step 4



## Notes

With buttons “W-”, “W+” and “From list” we can see modulation curves for Sm1 and Mo1 atoms. The x2-x4 map for Sm1 will be analyzed in more detail to find possible Sm/K ordering.

The resulting modulation function of Sm1 looks continuously. However, when we follow the line by mouse cursor the Density window in the lower right corner displays fluctuation of density between 64 and 51 e/A<sup>3</sup>.

Because position of potassium does not appear in the average structure and the occupation of samarium is lower than 0.5 we assume that samarium mixes with potassium.

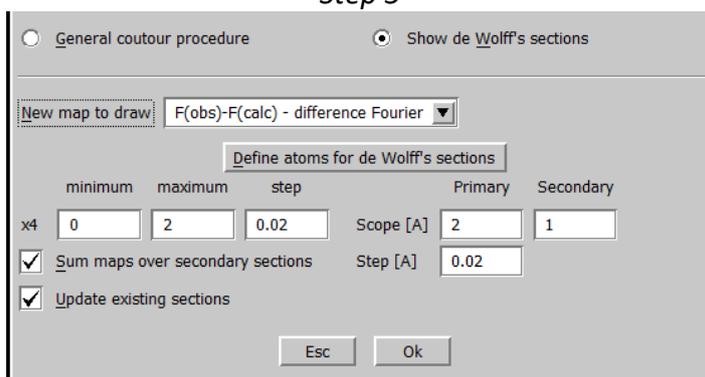
In modulated structure, classical disorder is often replaced by distribution of elements along x4. We can speculate that the area with lower electron density corresponds to the interval (in x4) where potassium exists instead of samarium. However, better background for this consideration will be difference Fourier map.

*[On the screen: Contour window]*

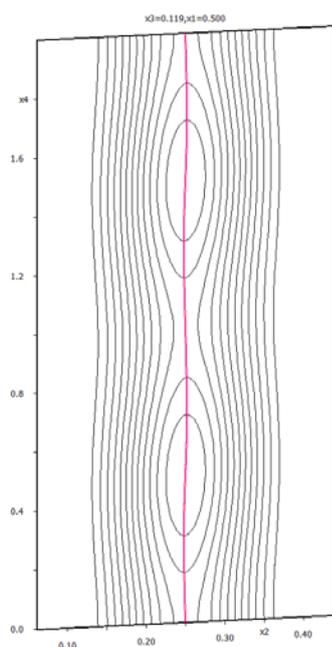
Press “New plot”, select “**Show de Wolff’s sections**”; OK;

Change “New map to draw” to “**F(obs)-F(calc) - difference Fourier**”; OK; (step 5)

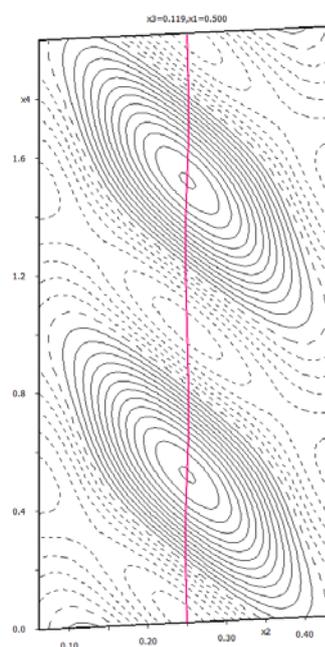
### Step 5



$F(\text{obs})$ -Fourier



$F(\text{obs})-F(\text{calc})$  - difference Fourier



#### Notes

The positive maximum in the difference map indicates region with lack of electron density. This is the area where fully occupied samarium should be present (instead of the partially occupied one). From this map, we can conclude that the definition interval of potassium has center in  $x_4=0$  and width 0.5. Samarium would occupy a complementary interval with center at  $x_4=0.5$  and width 0.5.

QUIT (Leave Contour)

Start "Edit atoms"

Right-click **Sm1** and select "**Split atomic position**" (step 6)

In the dialogue that follows:

Type **K1** for "Name of the split atom"

Select "**K**" for "Atomic type"

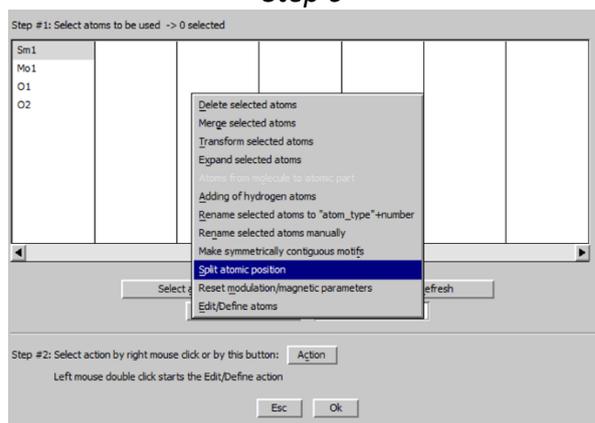
Type "0.5" for "Relative occupancy of the split atom"

Type "0 0 0" for "Shift of the split atom"

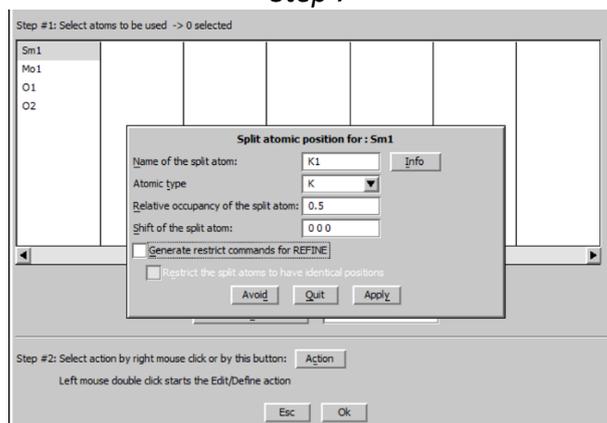
**Uncheck** "Generate restrict command for Refine" (step 7)

Apply

### Step 6



### Step 7



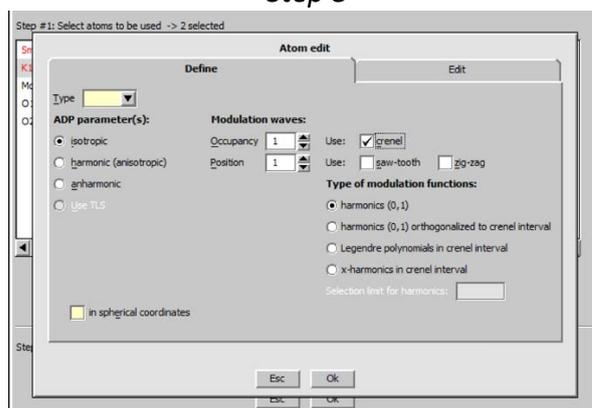
### Notes

By this way, we have duplicated Sm1, assigned the name K1 and chemical type K to the duplicated atom and reduced occupancy of both atoms by 1/2.

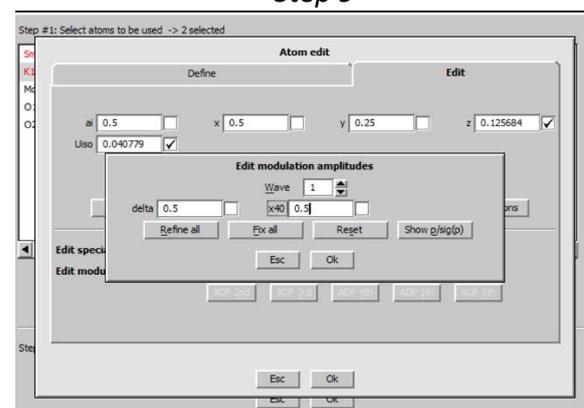
[On the screen: list of atoms in "Edit atoms"]

Select **Sm1** and **K1**, go to "Action → Edit/define atoms" and check "crenel" (step 8)

### Step 8



### Step 9



Switch to the page "Edit", ensure that "a" = 0.5 and its refinement is disabled

Press "Occupancy"

Type **0.5** for "delta" and **0.5** for **x40**, OK, OK (step 9)

### Notes

By this way, we have defined two identical crenel functions for both atoms Sm1 and K1. Note that the occupancy "a" was recalculated back from 0.25 to 0.5 because the reduction of occupancy is now managed by the reduced definition interval of the crenel function.

[On the screen: list of atoms in "Edit atoms"]

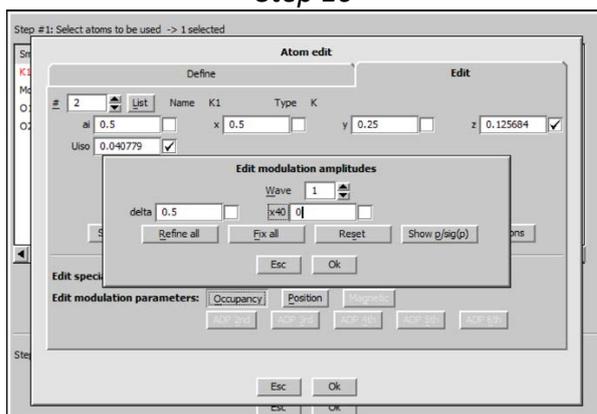
Unselect Sm1

Right-click **K1**, go to "Action → Edit/define atoms"

Switch to page "Edit"; press "Occupancy", change **x40** from 0.5 to 0; OK; OK (step 10)

Close "Edit atoms" and Yes (save changes)

## Step 10



Start "Contour"

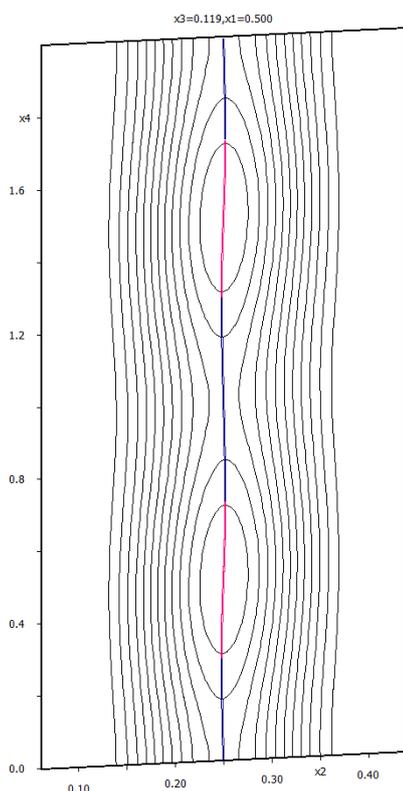
Press "New plot", select "Show de Wolff's Use old maps"; OK; (you obtain the **Fourier map difference**)

Press **Sum** on x2 and x3 to make summation OK;

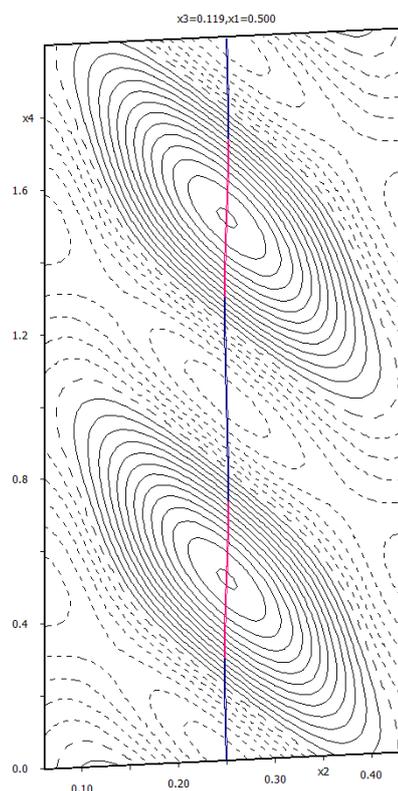
Press "Atoms edit" and add **K1** to the list

Repeat the procedure for observed **Fourier map**

*Fourier map*



*Difference Fourier map*



### Notes

*The section shows complementary modulation functions of Sm1 and K1*

[On the screen: Basic Jana window]

Right click on "Refine"

In Refinement options, go to the page "Various", press "Restrictions"

In the textbox type **Sm1 K1**

Check “Coordinates”, “Modulations” and “ADP parameters”  
For “Occupancies” select “not restricted”; press “Add” (step 11)

### Step 11



#### Notes

*This restriction makes the two atoms Sm1 and K1 identical except the definition interval in x4*

Leave Refinement options, save them **without** starting refinement (**YES**)

File → structure → Save as (Create backup copy) **KSm\_crenel**

**NO** (you don't want to continue with the new structure)

Run “**Refine**”

#### Notes

*Refinement: [515/507+8/19] and [8171/16+19] converges with*

*R factors for all reflections : R(obs) ≈4.5, wR(obs) ≈ 6.1, R(all) ≈ 4.8, wR(all) ≈6.1*

*R factors for main reflections : R(obs) ≈2.4, wR(obs) ≈4.4, R(all) ≈2.7, wR(all) ≈4.4*

*R factors for satellite reflections: R(obs) ≈7.1, wR(obs) ≈6.9, R(all) ≈7.4, wR(all) ≈7.0*

*Profile R factors : GOF ≈2.7, Rp ≈ 6.4, wRp ≈ 9.3*

“Edit atoms”; select **O1** and **O2**

“Edit/Define atoms”; add **1** position modulation wave for O1 and O2

“Refine”

#### Notes

*Refinement: [515/509+6/31] and [8171/16+31] converges with*

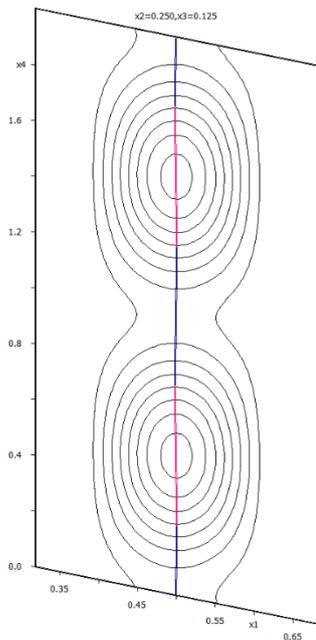
*R factors for all reflections : R(obs) ≈3.8, wR(obs) ≈ 5.1, R(all) ≈ 4.1, wR(all) ≈5.1*

*R factors for main reflections : R(obs) ≈2.2, wR(obs) ≈3.6, R(all) ≈2.5, wR(all) ≈3.7*

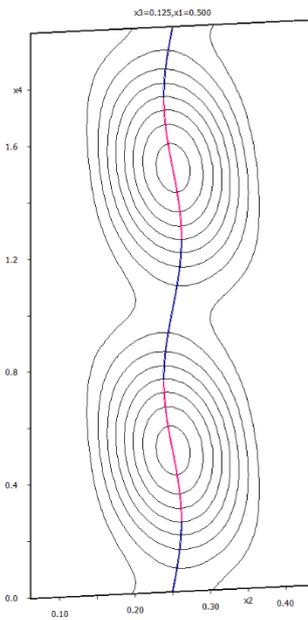
*R factors for satellite reflections: R(obs) ≈5.9, wR(obs) ≈5.7, R(all) ≈6.1, wR(all) ≈5.8*

*Profile R factors : GOF ≈2.6, Rp ≈ 6.2, wRp ≈ 8.7*

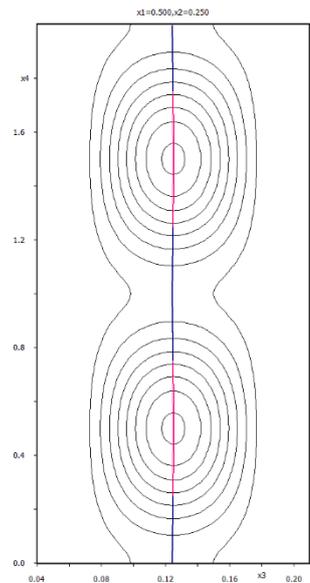
Using the previously described steps, plot **observed** and **difference Fourier** map for **Sm1**



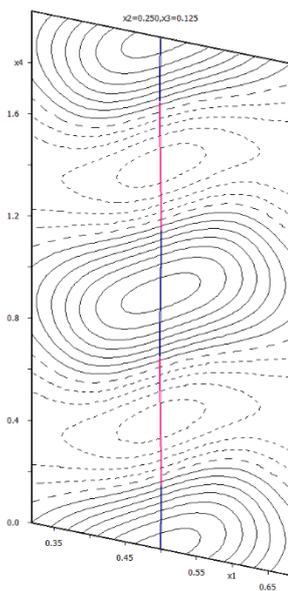
*x1-x4 observed*



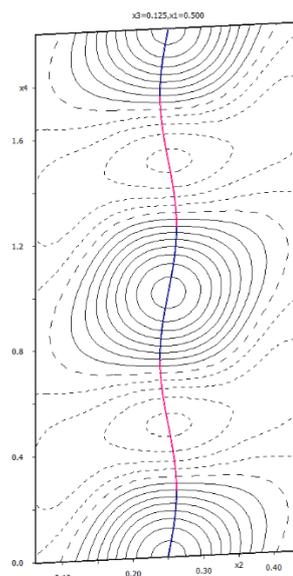
*x2-x4 observed*



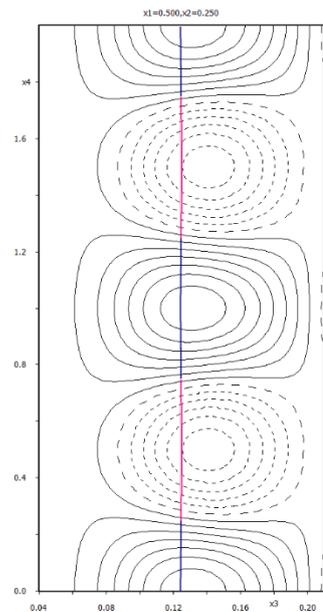
*X3-x4 observed*



*x1-x4 difference*



*x2-x4 difference*



*X3-x4 difference*

#### Notes

*Contour step in the observed and difference map are 10 and 0.2 e/A<sup>3</sup>, respectively The residua in the difference Fourier map are smaller and in different places than before. The position modulation now occurs in x2-x4 section. The previously observed modulation in the x1-x4 section was caused by pseudosymmetry.*

#### 4. Better profile description

File -> structure -> Save as (Create backup copy) **KSm\_mod**

**NO** (you don't want to continue with the new structure)

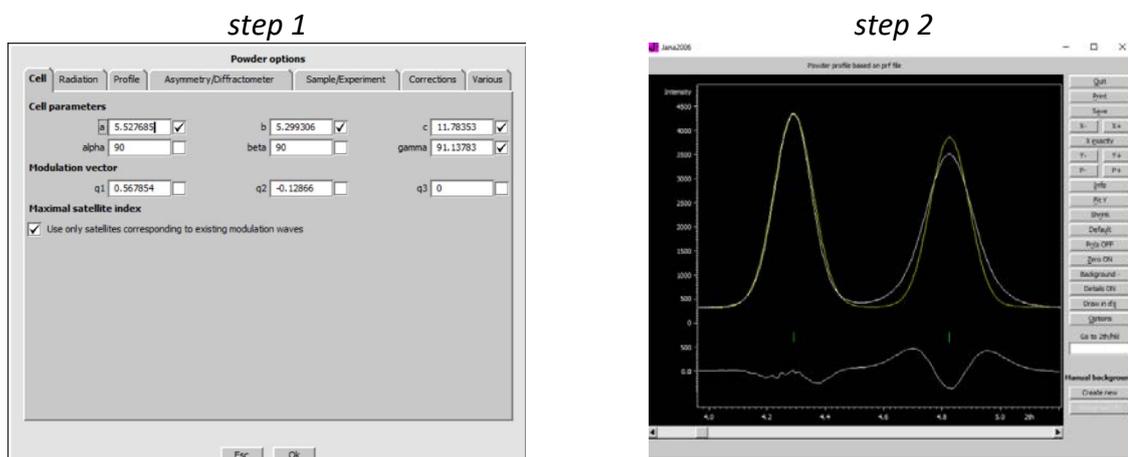
In page "Cell", and check **a, b c** and **gamma**. (step 1)

In page "Profile" check **GU, GV** and **GW**

In page "Correction" check **shift**; OK; **YES**

Run refine

Press "Profile viewer" and examine the first two peaks of the profile (step 2)



#### Notes

*The profile width could be probably better described with anisotropic strain broadening*

[On the screen: Basic Jana window]

Start "Edit profile", in the page "Profile"

Select "Tensor method"

(This method correspond to Stephen's formalism more description in example 2.9)

Press "Edit tensor parameters"

Press "Refine all" (step 3)

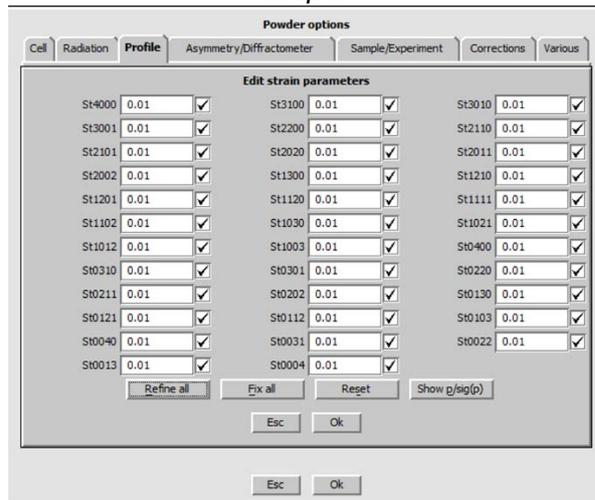
Leave "Powder options"

Right click on "Refine"

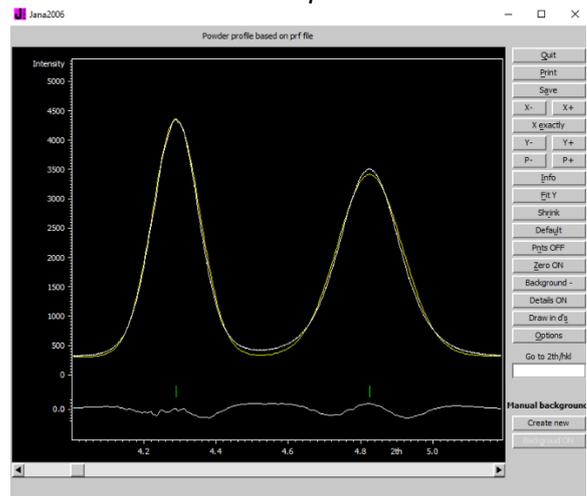
In Refinement options go to page "Basic" and select "Use Marquart technique" with the default "Fudge factor" **0.001**

OK; Yes + start

### step 3



### step 4



#### Notes

Refinement:  $[515=515+0/31]$  and  $[8171/45+31]$  converges with  
*R* factors for all reflections :  $R(\text{obs}) \approx 2.4$ ,  $wR(\text{obs}) \approx 3.4$ ,  $R(\text{all}) \approx 2.4$ ,  $wR(\text{all}) \approx 3.4$   
*R* factors for main reflections :  $R(\text{obs}) \approx 1.8$ ,  $wR(\text{obs}) \approx 3.2$ ,  $R(\text{all}) \approx 1.8$ ,  $wR(\text{all}) \approx 3.2$   
*R* factors for satellite reflections:  $R(\text{obs}) \approx 3.1$ ,  $wR(\text{obs}) \approx 3.5$ ,  $R(\text{all}) \approx 3.1$ ,  $wR(\text{all}) \approx 3.5$   
 Profile *R* factors :  $GOF \approx 1.6$ ,  $R_p \approx 3.8$ ,  $wRp \approx 5.5$

Press "Profile viewer" (step 4)

The width of reflections is now described properly

QUIT

Press "Edit profile", go to the page "Profile"

Select "Pseudo-Voight" and activate refinement of "Lx" and "Ly"

Run "Refine"

#### Notes

Refinement:  $[515=515+0/31]$  and  $[8171/47+31]$  converges with  
*R* factors for all reflections :  $R(\text{obs}) \approx 1.8$ ,  $wR(\text{obs}) \approx 2.7$ ,  $R(\text{all}) \approx 1.8$ ,  $wR(\text{all}) \approx 2.7$   
*R* factors for main reflections :  $R(\text{obs}) \approx 1.4$ ,  $wR(\text{obs}) \approx 2.9$ ,  $R(\text{all}) \approx 1.4$ ,  $wR(\text{all}) \approx 2.9$   
*R* factors for satellite reflections:  $R(\text{obs}) \approx 2.3$ ,  $wR(\text{obs}) \approx 2.6$ ,  $R(\text{all}) \approx 2.3$ ,  $wR(\text{all}) \approx 2.6$   
 Profile *R* factors :  $GOF \approx 1.3$ ,  $R_p \approx 3.0$ ,  $wRp \approx 4.6$

Some *St* tensor component may cause oscillations. A careful analysis would be needed to select the *St* components necessary for profile description. We can for instance fix the components with low parameter-to-sigma ratio (using the button "Show p/sig(p)" to see the ratio)

Start "Edit profile", in the page "Profile"

Press "Edit tensor parameters" then press "Show p/sig(p)"

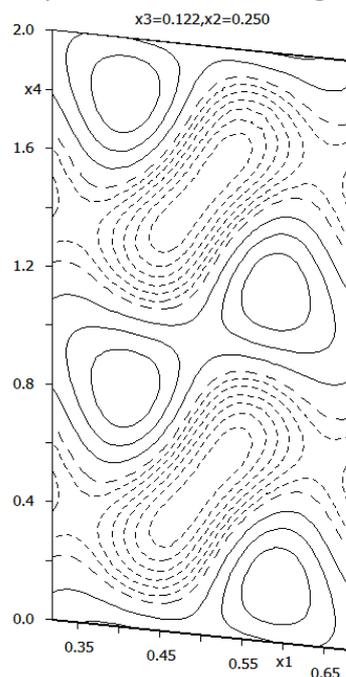
Fix to 0 all *St*\* parameters with  $p/\text{sig}(p) < 3 \cdot \text{su}$  and uncheck their OK; YES

Run "Refine"

Plot difference Fourier for Sm1, section x1-x4

#### Notes

The section now displays very small residual density ( $\approx \pm 0.4$ ). Depending on the fixed  $St$  components, the resulting section may look differently.

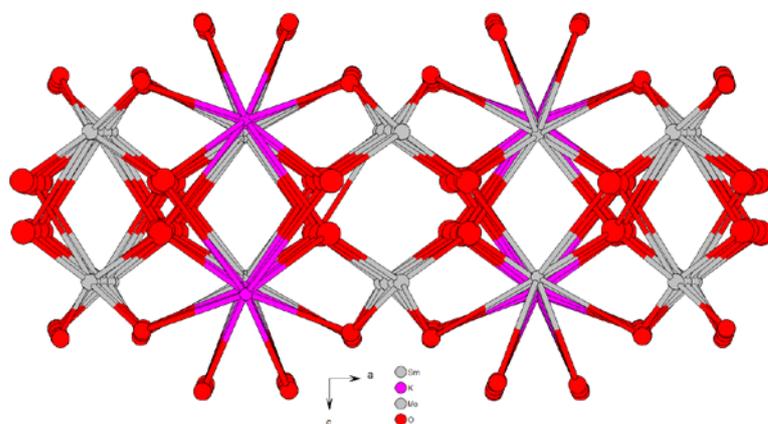


[On the screen: window of Diamond]

Start “Plot structure” and try to plot the structure in Diamond

#### Notes

For modulated structures, sufficiently large area must be selected for the plot because in Diamond we can only plot the supplied atoms. No symmetry transformation (rotation as well as translation) is allowed in Diamond because it cannot calculate modulation displacements of the transformed atoms. The recommended way is to add atoms supplied by Jana2006 using button , connect them using button  and then make only selections and rotations.



## References

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A. Arakcheeva, P. Pattison, G. Chapuis, M. Rossell, A. Filaretov, V. Morozov, G. Van Tendeloo,  $\text{KSm}(\text{MoO}_4)_2$ , an incommensurately modulated and partially disordered scheelite-like structure, *Acta Cryst.* **B64**, 2008, 160-171

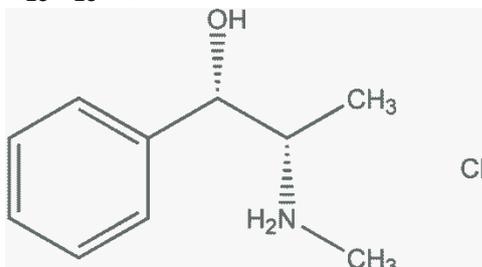


# Example 7.1: Ephedrine

Commensurately modulated structure

Revised: 3 December 2018

$C_{10}H_{16}NOCl$



Single crystal data measured with Bruker four-circle diffractometer

Input files: Ephedrine.hkl, Ephedrine.ins

Frame scaling, absorption correction: done

## 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click Ephedrine

## 2. Import Wizard

Select “reflection file corrected for LP and absorption”; NEXT

Select “SHELX on I”; File “Ephedrine.hkl” NEXT

*The measurement was done in a supercell using three indices*

*[On the screen: complete/correct experimental parameters]*

Fill supercell parameters as used in data collection. They can be copied (Ctrl-C) from the file Ephedrine.ins and pasted (Ctrl-V) to the “Cell parameters” textbox; NEXT

*[On the screen: Define the reference cell/split by twinning]*

Change target dimension for 4

Define modulation vector 0 0 1/4

Press “Define transformation matrix” and fill the matrix array by

1 0 0

0 1 0

0 0 1/4

NEXT; FINISH

## 3. Data Repository

*The line in data repository window corresponds to one data set.*

OK; YES to accept the data set

#### 4. Symmetry Wizard

[On the screen: "Tolerances for crystal system recognition".]

Leave all settings default; NEXT

[On the screen: Select Laue symmetry]

Select Orthorhombic Laue symmetry; NEXT

[On the screen: Select cell centering]

Select P centered unit cell; NEXT

[On the screen: Select space group]

Select P212121; NEXT

[On the screen: Select superspace group]

P212121(00g)000

[On the screen: Final step of the superspace test]

Accept the superspace group transformed into the original cell: P212121(00g)000; FINISH

[On the screen: Define superspace group]

OK

#### 5. Creating refinement reflection file

In this step we have M95 (i.e. the data from diffractometer converted to Jana format) and symmetry. For refinement we need M90 containing data set merged by symmetry and with discarded extinct reflections.

NEXT to confirm threshold  $3\sigma$

[On the screen: settings for merging of reflections]

Leave all settings default; NEXT

Accept the data block; FINISH

#### 6. Structure Solution Wizard

[On the screen: window of Structure solution]

In "Formula" textbox type list of chemical elements for  $C_{10}H_{16}NOCl$ : C H N O Cl

Select "Superflip", "Peaks from Jana2006 but first run Fourier"; Run Solution

[On the screen: window of Superflip replaced later on by listing of Superflip]

Superflip converges (after noise suppression) with R value between 20 and 30%.

Note that we don't fix random seed and the exact result of Superflip will differ between runs

Close the listing of Superflip

Press "Accept last solution"

#### 7. Verification of the structure solution

Start EditM50; go to page "Composition"; press "Formula from M40"

[On the screen: Information about formula]

It should display formula  $C_{10}H_{16}NOCl$  which means that all atoms except hydrogen atoms were localized. In the case that some atoms are missing they can be found from subsequent refinement and difference Fourier maps. In the case that the Superflip gives some additional false atoms they usually are detected in the refinement as atoms having non-realistic (too high) isotropic ADP and they will be automatically eliminated by putting their occupancy to zero. The atoms being eliminated can be later deleted in "Edit atoms" with help of button "Select rejected".

Start "Plot structure" to check assignment of chemical types (by comparing with the structure formula given at the beginning of this chapter). Use the option "Draw average

structure”.

If some atom in the plot looks like a false maximum it should be deleted by “Atoms edit”

### 8. Refinement of the modulated structure

Start Refine with default parameters.

You should get R values about 9.3%, 7.5%, 7.6% and 31.2%.

If some atoms are missing they should be found in difference Fourier, added to the structure model and the refinement should be repeated

Start “Edit atoms”, select all atoms, change ADP to harmonic (anisotropic) ones and repeat the refinement.

You should get R values about 8.4%, 6.4%, 6.5% and 31.4%.

### 9. Adding hydrogen atoms

Start “Edit atoms”, select all carbon and nitrogen atoms and add hydrogen atoms automatically.

For nitrogen atoms automatic procedure is not reliable, hydrogen atoms will be added manually

[On the screen: Adding of hydrogen atoms for N1]

Select “Tetrahedral”, change number of neighbors to 2

You can verify the neighbors by focusing the textbox with the first neighbor and clicking “Select neighbors”

Define names of hydrogens, for instance H1N1 and H2N1

“Apply”

Run EditM50 and go to page Composition, press Formula from M40. The found formula should be C10 H15 N O Cl which means that one hydrogen atom bounded to O is missing. This atom will be localized later from the Fourier map.

Run refinement

Refinement converges with R value about 6.2%, 3.4%, 4.9% and 31.6%.

### 10. Localization of the remaining hydrogen atom

Right-click the icon of Fourier

In page “Basic” select “Map type” as “F(obs)-F(calc) – difference Fourier”

In page “Basic” select “Apply sin(th)/lambda limits” and set tli limits from 0 to 0.5

This will suppress noise originated from high order reflections, to which H atoms contribute negligibly

In page “Scope” select “Automatically” and use the default parameters for “Independent parallelepiped”

Run Fourier.

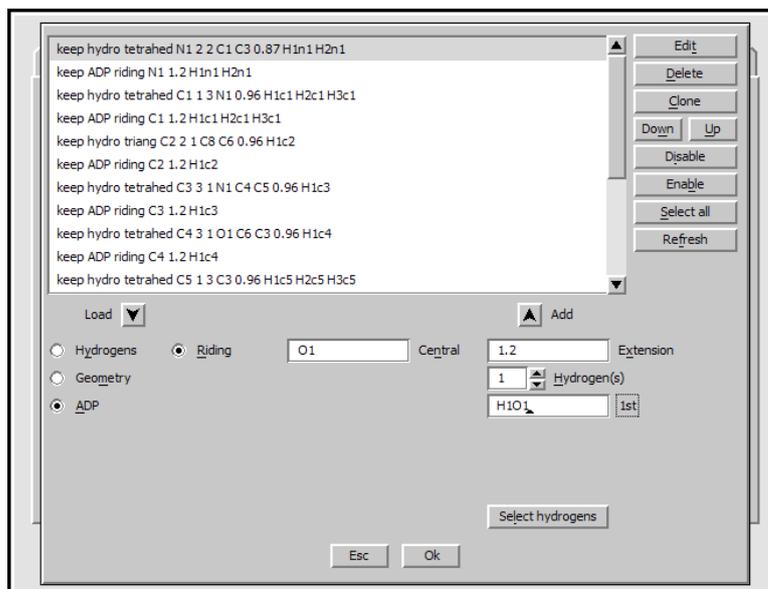
[On the screen: Do you want to start the procedure for including of new atoms?]

Answer yes.

One of the dominating maxima should have a reasonable hydrogen distance to the oxygen atom O1. Add it as a new hydrogen atom (named e.g. H1O1).

Right-click the icon of Refine; select page “Various”; press the button “Keep commands”

Restrict ADP parameter of the newly introduced hydrogen atom.



Add the new keep command and start the refinement procedure.

*Refinement converges with R value about 6.0%, 3.2%, 4.9% and 31.60%.*

Verify by plotting that the hydrogen in OH has a reasonable position

Save the structure with a new name e.g. "Ephedrine-incomm" but continue with the old one. This structure will be used for a final comparison with two commensurate cases.

## 11. Introduction of the commensurate option and twinning

Start EditM50, go to page Cell.

Select "Commensurate case" and "Use simple supercell"

In text box "Supercell" type "1 1 4"

Press button: "Select supercell group" and select  $T_{zero} = 0 + n/4$  which represent monoclinic symmetry with two-fold screw axis along a.

*As the supercell symmetry is lower than orthorhombic we may have two twinning domains related either by two fold axis along b or along c direction.*

Select twinning and define the twinning matrix as a 180 degrees rotation along c axis.

*The selection of the commensurate model leads to different Laue symmetry and different extinctions and therefore we should generally redo the creation of the reflection file for the refinement. But for better comparison of tested models we shall skip this point.*

YES to the question "Do you want to rewrite M50 file ?"

"DO you want to re-create refinement reflection file now?" NO in order to skip re-creation of the reflection file

Go to "Parameters/Twin fractions" and allow refinement of twol2

Run Refine.

*Refinement converges with R value about 3.6%, 2.7%, 3.9% and 8.0%.*

Save the structure with a new name e.g. "Ephedrine-comm-1" but continue with the old one.

*This structure will be used for a final comparison with two commensurate cases.*

## 12. Commensurate case for $t_0=1/16$

Repeat the point 11 for  $T_{zero} = 1/16+n/4$ .

NO in order to skip re-creation of the reflection file

Run Refine.

Refinement converges with R value about 3.6%, 2.7%, 3.9% and 8.0%.

The result is similar like in the previous commensurate model

Save the structure with a new name e.g. "Ephedrine-comm-2"

### 13. Incommensurate model with overlap option

Go to "File → Structure → open" and select files containing the incommensurate refinement.

In the incommensurate refinement, we are not taking into account the fact that main reflections are overlapped with satellites of fourth order and the satellites of the first order are overlapped with those of the third order. Even more serious are overlaps of the second order satellites as they have in average similar intensities.

For the commensurate structure, the program calculates structure factors as a summation over really existing  $t$  sections, taking into account  $t_0$  value and with symmetry elements being closed in the supercell. Thus we get the same result for reflections:

$(h,k,l,m)$ ,  $(h,k,l+1,m-4)$ ,  $(h,k,l-1,m+4)$  e.t.c.

On the other hand, in incommensurate structure model overlaps must be determined based on the proximity of reflection angles

Start Refinement options

Select page "Modulation" and activate overlap option "Closest reflections"; OK

Run Refinement

Refinement converges with R value about 3.6%, 2.7%, 3.9% and 8.0%.

Conclusion: Modulations are not very strong and therefore all three models give very similar results

Further possible steps:

- for selected model second modulation wave can be added, but it has just a minor effect: R value about 2.9%, 2.5%, 2.9% and 6.5%.

- we can deactivate twinning and verify by refinement if it was really needed (it was!)

- hydrogen of OH group probably should not have individual modulation waves. They can be made the same like modulations of the parent atom in "Refinement options → page Various → Restrictions"

- In the incommensurate refinement the overlaps detected by the program can be printed in the refinement listing if we activate the option in "Refinement options → page Select/Listing → Print twin/overlap details"



# Example 7.2: CrPOcom

Revised: 14 March 2018

$\text{Cr}_2\text{P}_2\text{O}_7$

Single crystal data measured with Oxford Diffraction four-cycle diffractometer

Input files: CrPOcom.hkl, CrPOcom\_red.sum

Frame scaling, absorption correction: done with software of the diffractometer

## 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click CrPOcom

## 2. *Import Wizard*

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction – CCD”; NEXT

Define basic input file: select Input from “sum” file; OK

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

For absorption correction select “None or done before importing”; NEXT

FINISH

## 3. *Data Repository*

*The line in data repository window corresponds to one data set.*

OK; YES to accept the data set

## 4. *Symmetry Wizard*

Use default tolerances for crystal system recognition

Select monoclinic Laue symmetry

Select C centering

Select space group C2/m

Select superspace group C2/m(a0g)0s

Accept the superspace group in the original cell

## 5. *Creating refinement reflection file*

Follow default steps of the wizard

## 6. *Structure solution wizard*

Type the formula Cr<sub>2</sub> P<sub>2</sub> O<sub>7</sub>, two formula units

Select “Superflip” and “Peaks from Jana2006”; “Run solution”

*Superflip converges with R around 25%, confirms the selected superspace group*

Close the listing of Superflip

“Accept last solution”

## 7. Workaround to get the same atomic positions like in this cookbook

Superflip returns arbitrary symmetry equivalent origin position. This would complicate reading of the cookbook because atomic positions and Fourier sections could be different (shifted, transformed) than it is described in the text. At this point, we shall use a saved Superflip solution compatible with the cookbook:

With your file manager:

copy superflip.m40 to jobname.m40 (“jobname” is name of your current job)

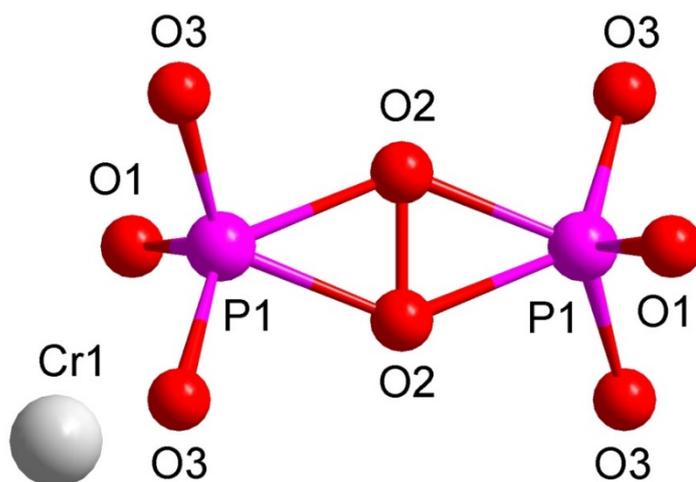
copy superflip.m80 to jobname.m80

copy superflip.m81 to jobname.m81

Jana2006 can be open during copying as it always unlocks the files when going to the basic window

M40 contains structure model from Superflip, M80 contains structure factors found by Superflip, M81 is the electron density map calculated from M80

Plot the average structure with Diamond



From the plot, it is clear that the two positions of the bridging oxygen O2 are probably separated in the modulated structure with a crenel function

Click with right mouse button on the icon “Dist” and select the listing form “with symmetry code”; OK; “Yes+start”; “Yes” to open the listing;

The short O2 – O2 distance (about 1.19 Å) is between O2 and the O2 related by the symmetry operation  $-x+2, -y, -z+1$  – Jana code O2#s3t2,0,1

## 8. Inspecting modulation functions returned by Superflip

Start Contour and “New plot”

Select “Show de Wolff’s sections” and set following parameters:

General contour procedure       Show de Wolff's sections

---

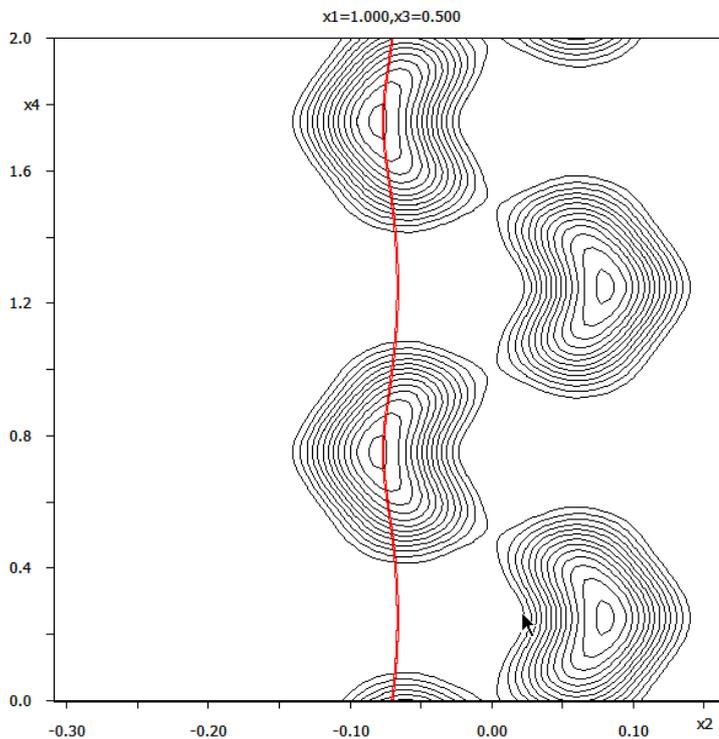
New map to draw: F(obs) - Fourier

Define atoms for de Wolff's sections

	minimum	maximum	step	Primary	Secondary
x4	0	2	0.05	Scope [A] 3	1
<input checked="" type="checkbox"/>	Sum maps over secondary sections			Step [A] 0.05	
<input checked="" type="checkbox"/>	Calculate only not yet existing de Wolff's sections				

Esc    Ok

Press "Define atoms for de Wolff's sections"  
 Add all atoms, for each of them select sections x,y,x.  
 OK; OK  
 In Contour, plot the section using "W+", "W-" and "From list"



*Oxygen O2 has  $x_2=-0.07$ , its symmetry equivalent position has  $x_2=+0.07$ . Therefore we can define a crenel function of the width 0.5 and the center 0.75 which will be transformed by the symmetry to the crenel function with the same width, the center 0.25 and  $x_2=+0.07$ . This will describe "skipping" of the bridging oxygen between two positions separated by the shift in  $x_4$ .*

*Similarly like in example 5.3.2 (incommensurate phase of  $\text{Cr}_2\text{P}_2\text{O}_7$ ), we will combine crenel functions with position modulations expressed by Legendre polynomials.*

Leave Contour, start "Edit atoms"

Edit O2: in "Define" page check "crenel" (it will add one occupation wave)

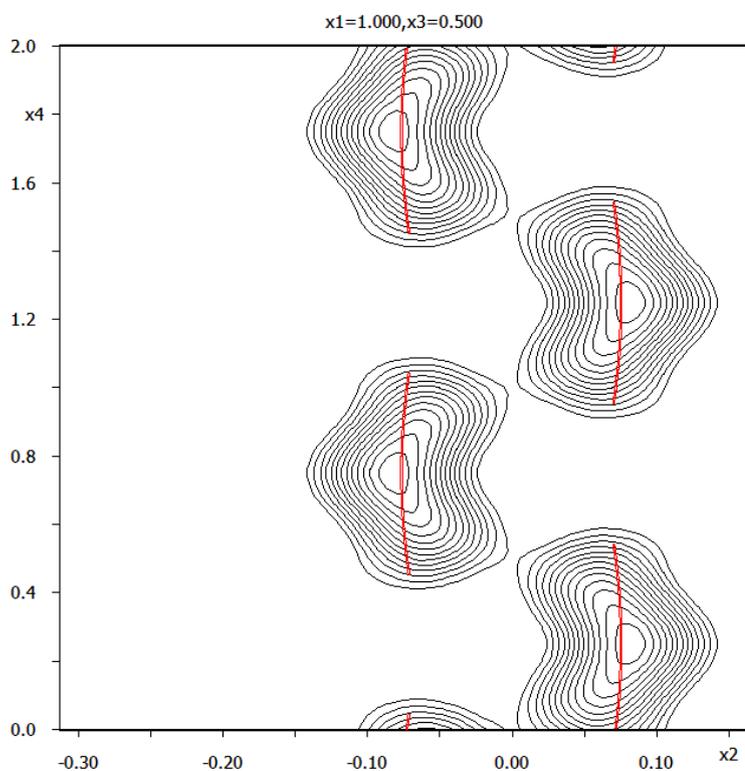
Set delta=0.5 and x40=0.75; OK

Select "legendre polynomials in crenel interval"

Leave Edit atoms (save the results)

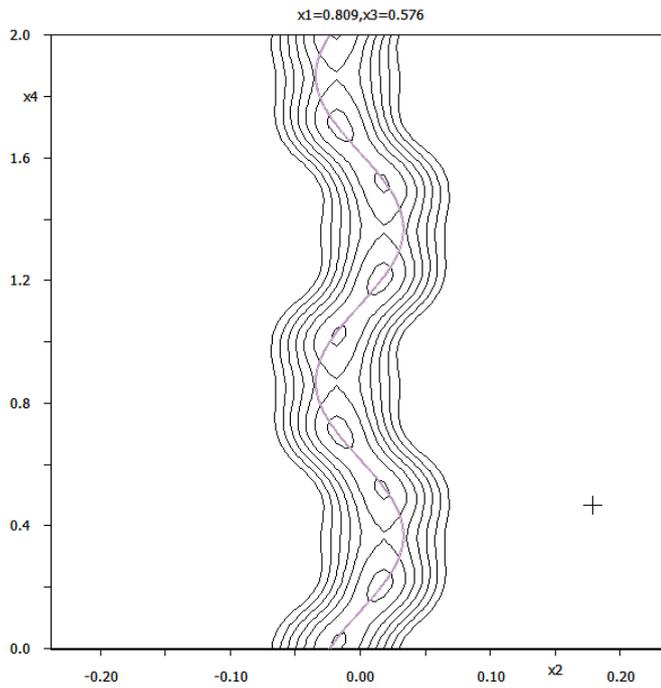
Plot the same section with Contour, using the button "From list"

In "Atoms edit" (of Contour) add atoms O2#s4



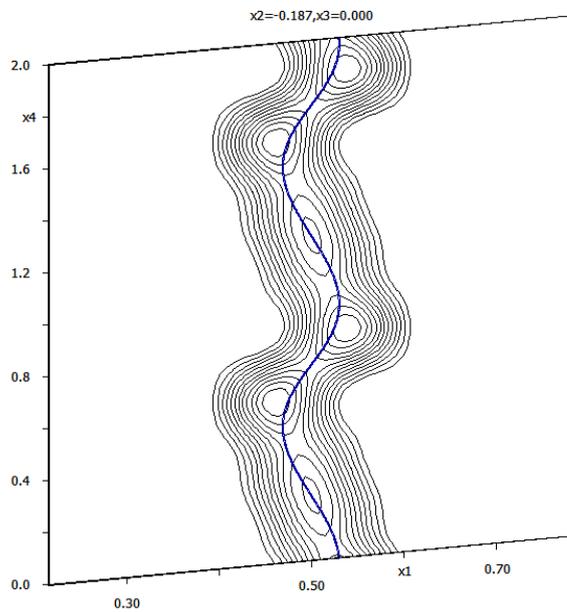
*The Contour plot now shows the two crenel functions related by symmetry operation  $-x1+2,-x2,-x3+1,-x4$*

Using the button "From list" in Contour, plot similar x2-x4 sections for P1



*P1 needs more modulation waves (will be added later)*

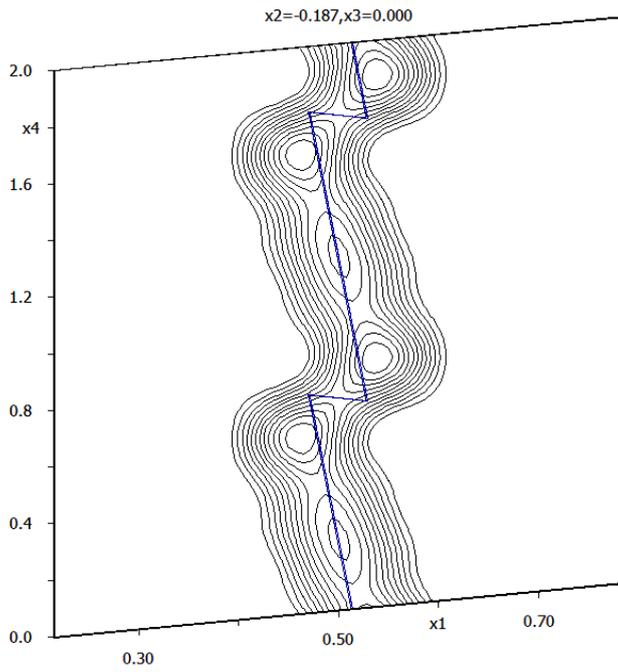
Using the button "From list" in Contour, plot x1-x4 sections for Cr1



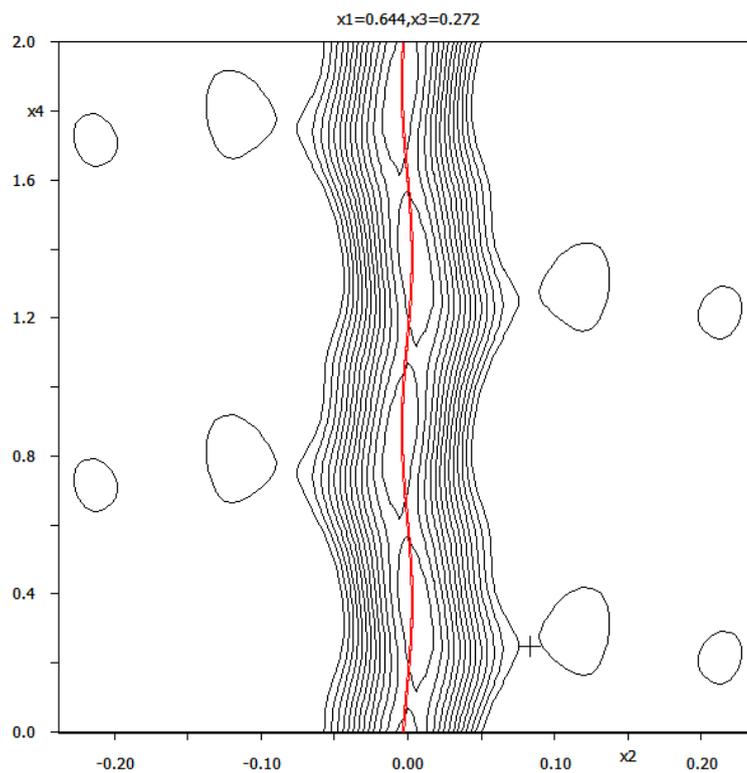
*Cr1 should be described with by crenel function with center 0.25 and width 1 combined with positional modulation to create discontinuity at x4=0.75.*

Similarly like for O2 define crenel function for Cr1:  $x40 = 0.25$ ,  $\text{delta} = 1$   
Select "Legendre polynomials in crenel interval"

Plot the same section with Contour:

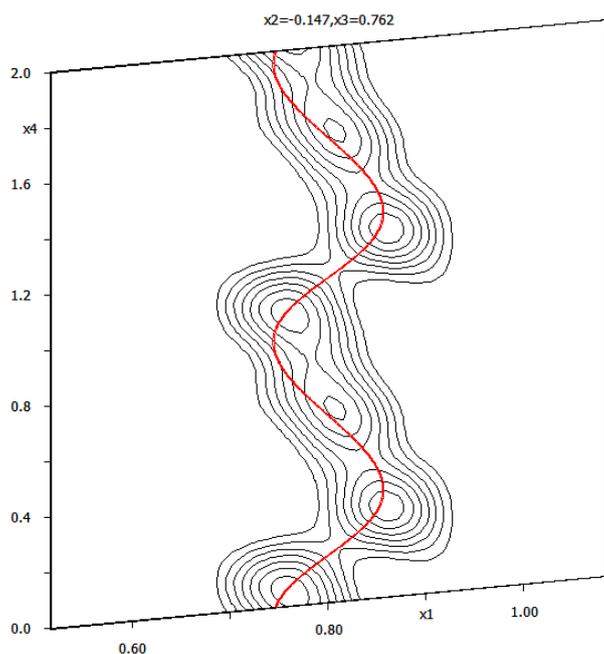


Using the button "New plot" in Contour plot  $x_2$ - $x_4$  sections for O1



*O1 has no discontinuity and only small positional modulation*

Using the button “New plot” in Contour plot x1-x4 sections for O3

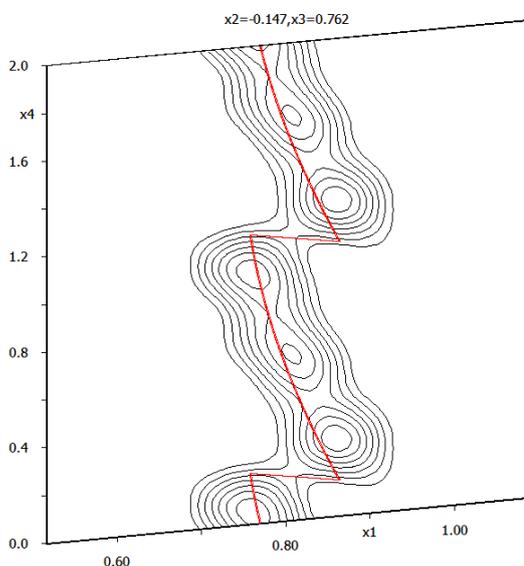


*O3 should be described with sawtooth function.*

Similarly like for O2, define crenel function for O3:  $x40 = 0.69$ ,  $\delta = 1$

Select “Legendre polynomials in crenel interval”

Plot the same section in Contour:



## 9. Refinement

*With commensurate structures, crenel function can be used but its center and width cannot be refined, as their changes give zero derivations, which would lead to singularity problems during refinement.*

Start “Editm50”: check “Commensurate case”, “Simple supercell”, supercell 3 1 2, Tzero = 0

Follow wizard for creating the refinement reflection file

Start Refinement commands: 100 cycles, damping 0.5

Refine

Refinement converges with 18%, 8%, 13%, 46% and 56% for all, main, 1<sup>st</sup> order, 2<sup>nd</sup> order and 3<sup>rd</sup> order (31 refined parameters).

Add the second position modulation wave for all atoms except O2

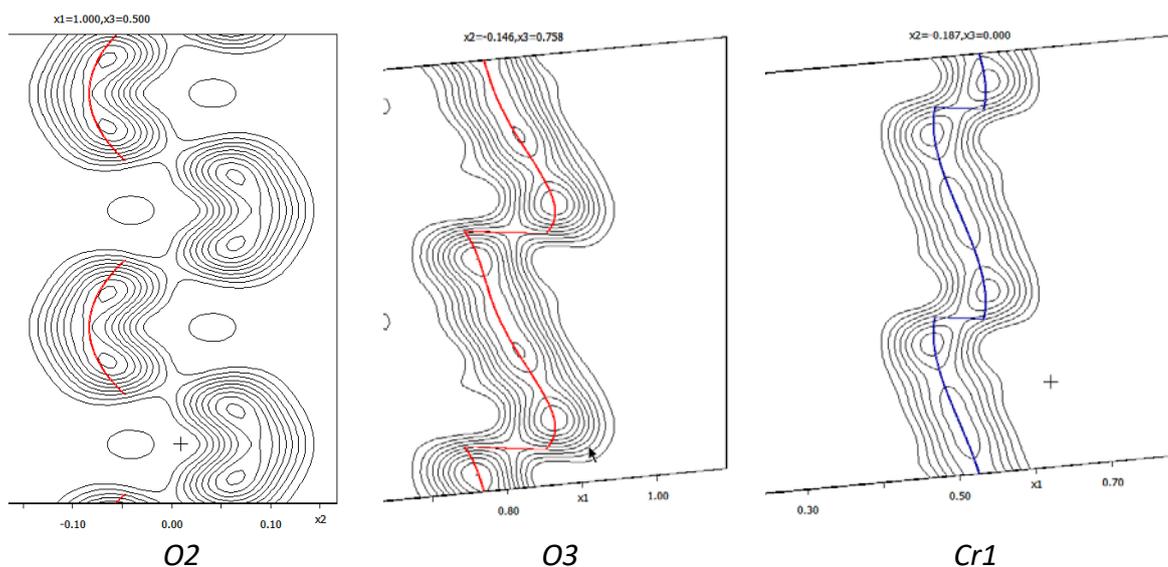
Refine

Refinement converges with 8%, 4%, 6%, 15% and 48% for all, main, 1<sup>st</sup> order, 2<sup>nd</sup> order and 3<sup>rd</sup> order (48 refined parameters).

Define harmonic ADP for all atoms

Refine

Contour: plot relevant sections for O2, O3 and Cr1



Add second position modulation wave for O2

Refine

At the message about singularity, choose “Skip warnings”

Open refinement listing and use “Go to → Singularity report”

*For commensurate refinement, the second modulation wave for O2 cannot be used. It would introduce more refinement parameters than the structure would have in a supercell description.*

Delete the 2<sup>nd</sup> position modulation wave for O2

Add the 3<sup>rd</sup> position modulation wave for all atoms except O2

Refine (with skipped warnings)

*Adding the 3<sup>rd</sup> position modulation wave improved significantly the fit!*

Look at the singularity report in the refinement listing

*The list of blocked parameters contains either “cos3” terms (for harmonic modulation) or “ort6” terms (for Legendre modulation). This means that the second halves of the third modulation waves are forbidden (for the same reason given for O2).*

“Refinement commands → Various → Fixed commands”

Use “Set individual” and set “\*cos3[\*]” to zero

Use “Set individual” and set “\*ort6[\*]” to zero

“?” and “\*” are wildcards.

Refine

Refinement converges without warning messages to 2.7%, 2.5%, 2.6%, 2.8% and 4.1% for all, main, 1<sup>st</sup> order, 2<sup>nd</sup> order and 3<sup>rd</sup> order (72 refined parameters).

Add one harmonic ADP modulation wave for all atoms

Refine

Refinement converges without warning messages to 2.1%, 2.2%, 1.9%, 2.1% and 2.6% for all, main, 1<sup>st</sup> order, 2<sup>nd</sup> order and 3<sup>rd</sup> order (104 parameters).

“Parameters → Extinction”: set isotropic Lorentzian extinction

Refine

Refinement converges without warning messages to 2.1%, 2.1%, 1.9%, 2.1% and 2.5% for all, main, 1<sup>st</sup> order, 2<sup>nd</sup> order and 3<sup>rd</sup> order.

Number of refined parameters: 105

## 10. Binding t40 of O2 and O3

Start Grapht.

With New/Edit: “Parameter to draw” = displacement - dy; “p” from -0.3 to 0.1; t from 0 to 1; Central atom P1; step in t 0.001; Color Red;

Parameter to draw: Displacement

1/3 item to be drawn

Minimum: 0, Maximum: 1, Step: 0.001

p: -0.5, 0.5

Color: Red

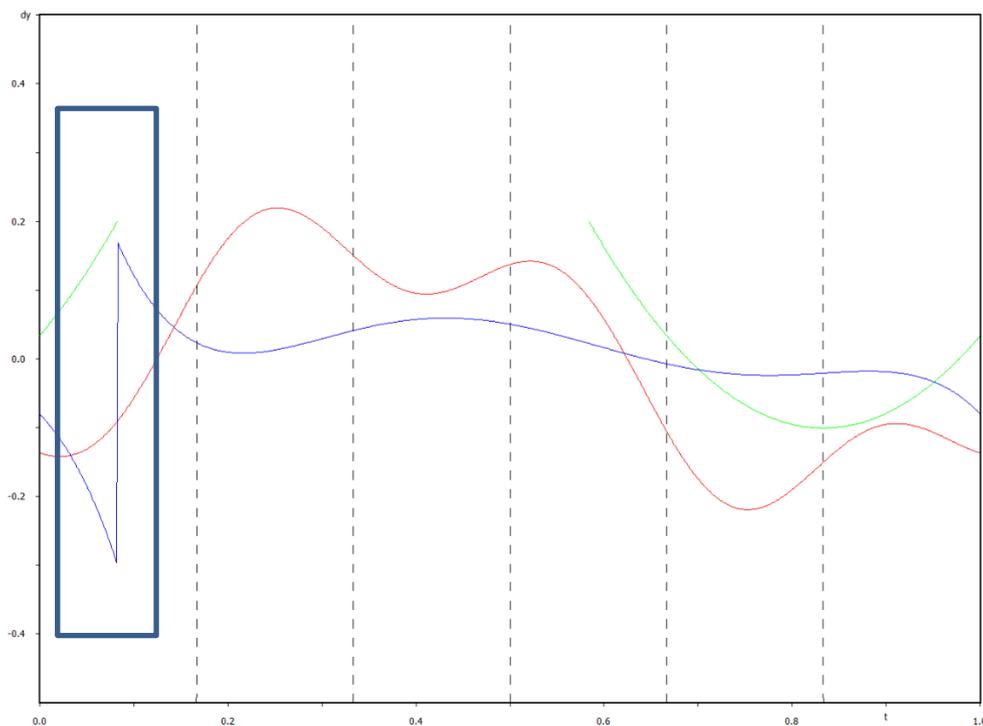
Central atom: P1

Buttons: Previous, Next, New item, Delete item, Esc, Ok

Press “New Item” and define the same for O2 color “Green”;

Press “New Item” and define the same for O3 color “Blue”;

OK to plot; Press the button “Option” and select “Indicate commensurate t sections”:



*In a detailed view, it is clear that the discontinuity in O3 occurs at slightly different  $t$  than the discontinuity in O2. However, this small discrepancy does not make any effect in this commensurate case as only the  $t$  sections indicated by the dashed lines are present in the real supercell and the  $t$  points of discontinuity are far from the dashed lines.*

[Close Graph](#)

## 11. Transformation to supercell

Start “Tools → Transformations → Go to supercell structure”

Follow the wizard for creating refinement reflection file

Continue with the new (supercell) structure

EditM50: check cell parameters (3x1x2 supercell) and symmetry (I2/c)

Refinement commands: set 0 cycles

Refine

*Refinement (with zero cycles) confirms overall R value found previously in the commensurate model*

*Number of structure parameters is 151. This means we were able to get satisfactory results in commensurate refinement saving 46 parameters.*

*Supercell model can be used for plotting of the structure and for calculation of geometry*

“File → Structure → History”: return to the commensurate model

“File → Save As”: make a backup copy

Set three ADP modulation waves to all atoms

Refine – skip warnings

*The number of refined parameters is now much larger but no further improvement of R values occurs. By adding modulation waves and fixing forbidden components to zero we should finally reach the same number of structural parameters in the commensurate and supercell model.*

# Example 7.3: PhenanTin

Commensurate and supercell description of a five-fold superstructure.

Revised: 15 March 2018

**Bis(aquachlorotriphenyltin 1,10-phenantroline),  $C_{150} H_{125} N_{10} O_5 Cl_5 Sn_5, Z=4$**

Single crystal data measured with four-cycle diffractometer SuperNova

Input files:

PhenanTin.hkl, PhenanTin.cif\_od (diffraction data indexed in the supercell - see later)

phenantroline-no-symmetry.m45 (pattern molecule phenantroline)

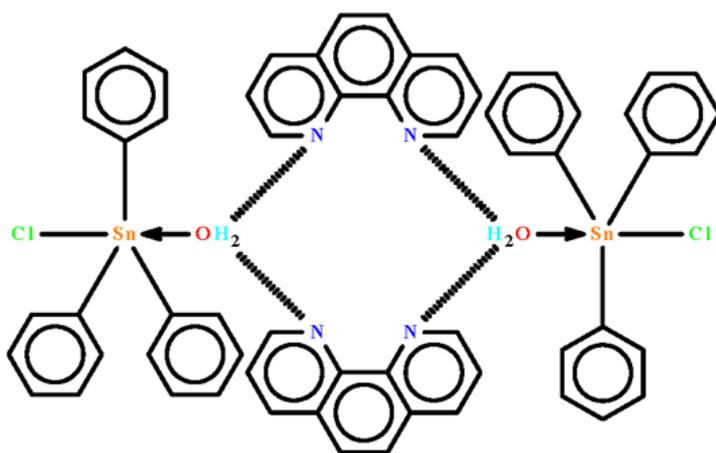
phenantroline-no-symmetry.jpg

phenyl-no-symmetry.m45 (pattern molecule phenyl)

phenyl-no-symmetry.jpg

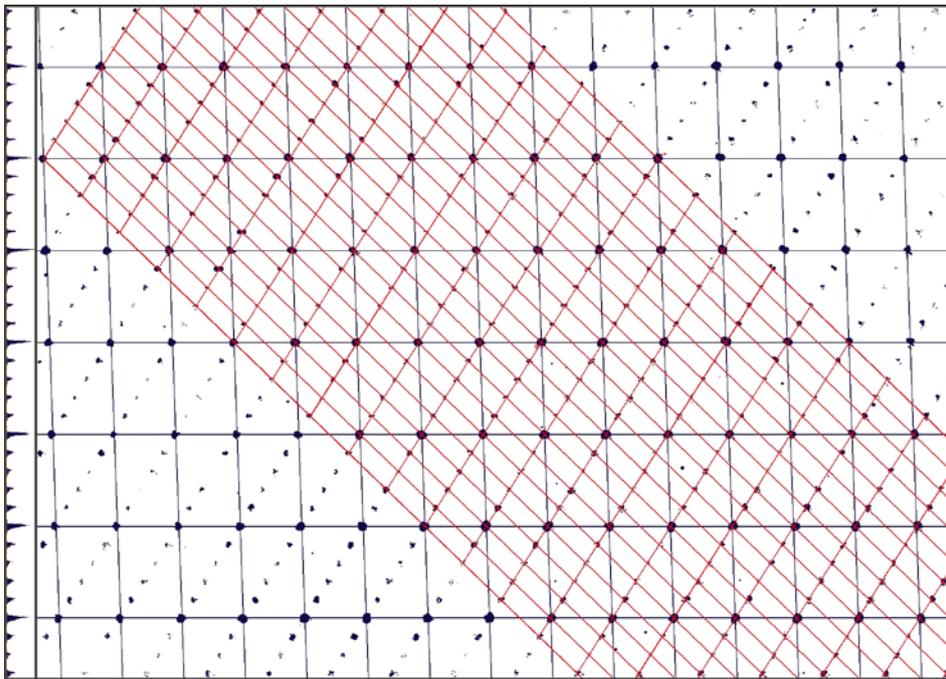
supercell\_keep.txt (pre-prepared keep commands for supercell refinement)

Chemical diagram:



## Introduction

Structure of this compound has been published in *Journal of Science and Technology in the Tropics* (2005), 1, 157-163, as a commensurately modulated structure. The data from Nonius KappaCCD diffractometer contained strong main reflections and weak first and second order satellites with ratio of intensities 1000 : 0.157 : 0.075. Later on the compound was remeasured with much more intensive source of the Rigaku Oxford Diffraction SuperNova. In the new experiment, the satellites were strong and the structure could be solved in a five-fold supercell as a classical three-dimensional structure. This example uses data of SuperNova and compares possibilities of the commensurate and supercell structure refinement.



Reciprocal space with peak positions projected along  $b^*$ . Black: unit cell for commensurate refinement; Red: unit cell for supercell refinement.

Relationship between unit cells in direct space:

$$\mathbf{T}_{\text{comm} \rightarrow \text{sup}} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & -1 & 0 \\ 3 & 0 & -2 \end{pmatrix}; \quad \mathbf{T}_{\text{sup} \rightarrow \text{comm}} = \begin{pmatrix} 2/5 & 0 & 1/5 \\ 0 & -1 & 0 \\ 3/5 & 0 & -1/5 \end{pmatrix}$$

### 1. **Creating new jobname**

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click PhenanTin

### 2. **Import Wizard**

Select "Known diffractometer formats"; NEXT

Select "Oxford Diffraction – CCD"; NEXT

Define basic input file: select Input from "cif\_od" file; OK

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

For absorption correction select "None or done before importing"; NEXT

FINISH

### 3. **Data Repository**

The line in data repository window corresponds to one data set.

OK; YES to accept the data set

### 4. **Symmetry Wizard**

Use default tolerances for crystal system recognition

Select monoclinic Laue symmetry

Select P centering

Select space group  $P2_1/n$

Although it is not first in the list, FOM is almost the same like for  $P2/n$  and the button "Details" shows that the discarded reflections are very weak

Accept the space group transformed into the original cell; FINISH

#### 5. **Creating refinement reflection file**

Follow default steps of the wizard

$R_{int} \sim 4.8\%$  for 24879 reflections

#### 6. **Structure solution wizard**

Type the formula  $C_{150} H_{125} N_{10} O_5 Cl_5 Sn_5$ , four formula units

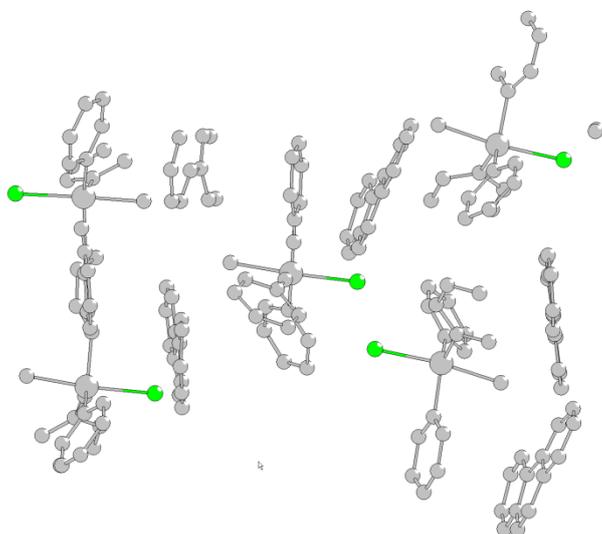
Density should be  $1.53 \text{ g.cm}^{-3}$

Select "Superflip" and "Peaks from Jana2006"; "Run solution"

Superflip converges with  $R$  around 20% and confirms the selected space group

"Accept last solution"

Plot the structure



The structure model returned by charge flipping contains most of the expected structure and it could be finished by adding maxima from difference Fourier and possibly by applying geometry constraints imposed during the refinement. However, we would like to try commensurate refinement in order to see its pros and cons.

#### 7. **Data import for commensurate refinement**

As the structure handled in the 3d supercell cannot be simply transformed to the superspace, we have to re-create the structure. We will use the same job name.

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click PhenanTin

YES to overwrite the existing job name

Select "Known diffractometer formats"; NEXT

Select "Oxford Diffraction – CCD"; NEXT

Define basic input file: select Input from "cif\_od" file; OK

[On the screen: Complete/correct experimental parameters]

Leave all settings unchanged; NEXT

[On the screen: Define the reference cell/split by twinning]

Change target dimension to 4

For "1st modulation vector" type 0.2 0 -0.2

The modulation vector has several possible settings. For instance, the original publication used (0.2,0,0.8). However, the short q-vector as defined here is the most logical selection.

Press "Define transformation matrix"

[On the screen: Define the transformation matrix]

Define the following 3x3 matrix: 2/5 0 1/5; 0 -1 0; 3/5 0 -1/5

"inp" means the input indices; "float" means the transformed indices. They can generally be real numbers, in such case the program tries to index them as satellites

OK

The transformed experimental unit cell parameters should be as follows:

Define the reference cell/split by twinning

Cell parameters: 11.8434 12.0277 17.7796 90.008 91.934 89.998

Target dimension: 4

1st modulation vector: 0.2 0 -0.2

2nd modulation vector: [empty]

3rd modulation vector: [empty]

Max. satellite index: 4

Accuracy: 0.001 0.001 0.001

Twinning Twinning matrices

Number of domains: [empty]

Data related to domain#: [empty]

Multiply input F(hkl)/I(hkl) by: 1

Define transformation matrix

Transformation matrix applied to input indices:

H(float)	=	2/5	0	1/5	*	h(inp)
K(float)		0	-1	0		k(inp)
L(float)		3/5	0	-1/5		l(inp)

NEXT

The wizard transforms indices according to the defined transformation matrix. Resulting integer indices are sorted as main reflections while the others as satellites defined by the q-vector.

For absorption correction select "None or done before importing"; NEXT

FINISH

OK; YES to accept the data set in the Data repository

## 8. Symmetry Wizard

Use default tolerances for crystal system recognition

Select monoclinic Laue symmetry

Select P centering

Select space group P2<sub>1</sub>/c

Although it is not first in the list, FOM is almost the same like for P2/n and the button "Details" shows that the discarded reflections are very weak

NEXT

Select superspace group P2<sub>1</sub>/c(a0g)0s; NEXT

Accept the superspace group transformed into the original cell; NEXT

## 9. Creating refinement reflection file

Follow default steps of the wizard

$R_{int} \sim 4.8\%$  for 24879 reflections

## 10. Structure solution wizard

Type the formula  $C_{30}H_{25}N_2OClSn$ , four formula units

Density should be  $1.53 \text{ g.cm}^{-3}$

Select "Superflip" and "Peaks from Jana2006 – but first run Fourier";

For "Starting model" select "Patterson superposition map"

"Run solution"

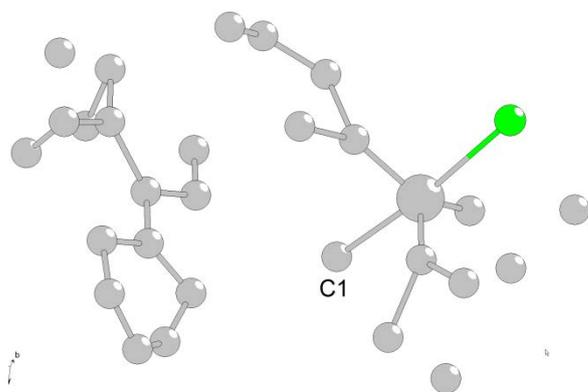
Superflip converges with  $R$  around 22% and confirms the selected superspace group

"Accept last solution" to leave the structure solution wizard

Start "Plot structure"

Select "Draw average structure" and press "Draw+return" or "Draw+continue"

In Diamont start "Build → Get molecules"



The structure model obtained from charge flipping contains fragments of phenyls and phenantroline, Sn, Cl and water oxygen assigned as carbon C1. In commensurate description we have only one symmetry independent Sn.

## 11. Initial commensurate refinement

As the only special position in the superspace group  $P2_1/c(a0g)0s$  is the inversion center, which is not compatible with the assumed shape of the molecule, all atoms should be localized in general positions. Thus one atom in the commensurate structure represents five atoms in the supercell structure, i.e. 15 positional and 30 ADP parameters. Therefore, each atom in the commensurate structure can have maximally two positional (12 parameters) and two ADP (24 parameters) modulation waves (each wave of order  $n$  represents two periodic components –  $\sin 2\pi n x_4$  and  $\cos 2\pi n x_4$ ), which make together with the basic position and the basic ellipsoid  $3+12=15$  positional and  $6+24=30$  ADP parameters.

At this stage all atoms from the charge flipping model already have one position modulation wave interpreted from the electron density map provided by Superflip.

Start "Edit atoms"; change chemical type of C1 (may be also N1) to oxygen and its label to O1;

OK; YES to save changes

Start "EditM50"

Check "Commensurate case"

Clear "Use simple supercell"

Press "Define supercell matrix" and type  $1 \ 0 \ 1 ; 0 \ -1 \ 0 ; 3 \ 0 \ -2$

*This is transformation from commensurate to supercell parameters*

OK

Press "Select supercell group"

*The program lists all supercell space groups, which can be obtained by changing the tzero value. As we know from the preliminary calculations that the symmetry in the supercell should be  $P21/n$ , we should select one of the two equivalent possibilities.*

Select Tzero 0+n/5; OK

OK; YES to rewrite M50; YES to re-create refinement reflection file

Follow steps for merging the reflections; FINISH

*Now we have set up the commensurate refinement. In our case, it means that modulation functions will only have 5 definition points.*

Start refinement

*The refinement converges with  $R_{all} \sim 38\%$ ,  $R_{main} \sim 18\%$  (your numbers can be different)*

Start "Edit atoms"

Double-click Sn1 and change number of position modulation waves to 2

OK; OK; YES to save changes

Start Refinement options; set 100 refinement cycles; OK; YES+START

*The refinement converges with  $R_{all} \sim 24\%$ ,  $R_{main} \sim 14\%$ ,  $R_{sat1} \sim 27\%$  and  $R_{sat2} \sim 31\%$*

*These numbers can be different because Superflip may have returned different number of carbon atoms. However, if R values at this point are significantly larger, for instance  $R_{all} > 26\%$  or  $R_{sat2} \sim 50\%$ , please **do not continue and repeat structure solution (return to the point 10.)**.*

Start "Edit atoms"; Select rejected atoms if exists and delete them;

## **12. Structure completing from difference Fourier**

Start "Edit atoms"; Select rejected atoms delete them (if exist)

Start Fourier options; select the page "Basic" and "Map type" difference Fourier

OK; YES+START

YES to start procedure for including new atoms

Activate "Skip peaks being too close to existing atom" and set 1.1 Å

Include maxima with reasonable C-C distances named C\* (i.e. the next free carbon label).

FINISH; YES to include new atoms

*We don't need a complete structure, just some atomic positions. For correct placement of molecules in next steps, we need to recognize phenantroline and phenyl. For recognizing N atoms of phenantroline, it is useful to plot "ellipsoids" although we refine isotropic ADP: smaller rings will indicate heavier atoms.*

## **13. Preparation for rigid body description**

*Refinement of a commensurate structure with very strong satellites may be difficult. In this example, the refinement could easily finish in a false minimum with distorted geometry of phenyls and phenantroline. Therefore, for the initial refinement we will use fixed rigid bodies pre-defined in M45 files.*

*Atoms used for definition of a rigid body position must belong to the same fragment without need of symmetry transformation. In the next step, we will manage that atoms in M40 are properly transformed.*

Start "Edit atoms"; select all atoms

"Action" → "make symmetry contiguous motifs"

OK; YES to rewrite changes

Start "Plot structure"

Select "Draw average structure"; press "Draw+continue"

In Diamond use "Build → Add all atoms"

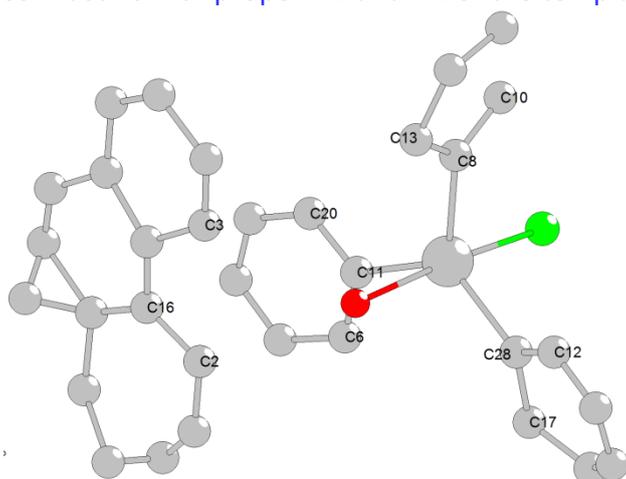
*This adds all atoms from the structure model without applying symmetry.*

Start "Build → Connect atoms"

*The plot may differ for actual solutions but it should display all atoms important for introduction of rigid body of phenyl and phenantroline. In our case, the plot also includes some spurious maxima, but it does not matter.*

For each phenyl and for the phenantroline note labels of three atoms, which will be used for placing complete phenyl and phenantroline templates from m45

In case of phenantroline note also orientation of the fragment because atoms (here) C2 and C3 must fit with proper N1 and N2 of the template



Quit Diamond or let it open for a later reference (depends on style of work)

#### 14. Rigid body templates from M45

Start "File → Structure → Save As"

Make backup copy of the structure

Start "Parameters → Molecule → New molecule"

Select "Model file"

For "Name of molecule" type "Ph"

Press "Browse" and select "phenyl-no-symmetry.m45"

Keep the default scaling distance

Press the button "Show the model molecule"

*[On the screen: Windows opens jpeg plot of the template in a default viewer. Note that the atom labels of the template phenyl end with "p" in order not to mix with any atoms of the structure. Close the jpeg plot.]*

NEXT

*[On the screen: "Specify atomic types in the model molecule:" dialogue for matching chemical types in the template molecule and in the current structure.]*

Keep the suggested chemical types; NEXT

*[On the screen: Define the molecular reference point]*

Select "Geom. center"; NEXT

*[On the screen: Define and complete molecular position #1]*

Pair the following atoms (your labels will differ!)

C1p with C28

C2p with C12

C6p with C17

For "Maximal coincidence distance" type 0.8

Press "Show coinciding atoms"

*The expected coincidence ratio in our example is 6/11 (in case that all carbon atoms were previously localized from the difference Fourier)*

	Model atom	Actual position/atom
1st point	c1p	c28
2nd point	c2p	c12
3rd point	c6p	c17

Options for removing of atoms from atomic block coinciding with those generated from molecular position # 1:

Maximal coincidence distance: 0.8

Molecular parameters:  
Phi = -75.84 Chi = -58.42 Psi = 74.41 determinant = 1  
Translation vector : -0.485510 -0.140775 0.275122  
Occupancy: 1 Coincidence ratio: 6/11

Press "Apply+Next position"

*[On the screen: Define and complete molecular position #2]*

Pair atoms:

C1p with C8

C2p with C10

C6p with C13

*The coincidence ratio (in our example, it may differ) will be 5/11*

Press "Apply+Next position"

*[On the screen: Define and complete molecular position #3]*

Pair atoms:

C1p with C11

C2p with C6

C6p with C20

*The coincidence ratio (in our example, it may differ) will be 6/11*

Press "Apply + End"

Now we continue with phenantroline

Start "Parameters → Molecule → New molecule"

Select "Model file"

For "Name of molecule" type "Trol"

Press "Browse" and select "phenantroline-no-symmetry.m45"

Keep the default scaling distance

Press the button "Show the model molecule"

*[On the screen: Windows open jpeg plot of the template in a default viewer. Note that the atom labels of the template phenantroline end with "t" in order not to mix with any atoms of the structure. Close the jpeg plot.]*

NEXT

[On the screen: "Specify atomic types in the model molecule:" dialogue for matching chemical types in the template molecule and in the current structure.]

Accept suggested chemical types; NEXT

[On the screen: Define the molecular reference point]

Select "Explicit"; type N1t; NEXT

[On the screen: Define and complete molecular position #1]

Pair the following atoms (your labels will differ!)

N1t with C3

N2t with C2

C17t with C16

Be careful with matching the correct orientation of the molecule, interchanging of N1t and N2t would change it

For "Maximal coincidence distance" type 0.8

Press "Show coinciding atoms"

The expected coincidence ratio in our example is 14/22 (depends which carbon atoms were previously localized from the difference Fourier)

Define and complete molecular position # 1:

Apply inversion

	Model atom	Actual position/atom
1st point	<input type="text" value="n1t"/>	<input type="text" value="c3"/>
2nd point	<input type="text" value="n2t"/>	<input type="text" value="c2"/>
3rd point	<input type="text" value="c17t"/>	<input type="text" value="c16"/>

Options for removing of atoms from atomic block coinciding with those generated from molecular position # 1:

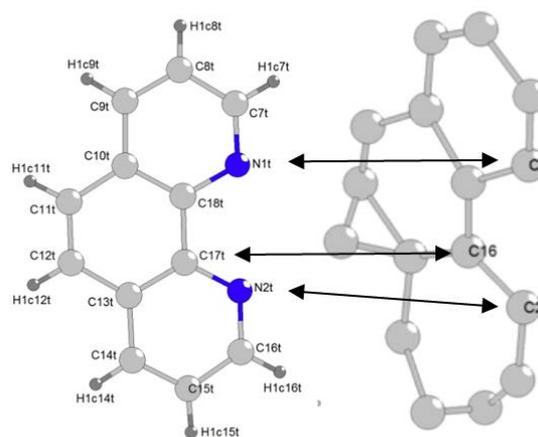
Maximal coincidence distance:

**Molecular parameters:**

Phi = -15.88 Chi = -62.12 Psi = -18.81 determinant = 1

Translation vector : 0.348570 -0.134041 0.021255

Occupancy  Coincidence ratio: 14/22



Press "Apply+End"

Start "Edit atoms"

Delete all carbon atoms, which are not blue (i.e. carbons out of molecules).

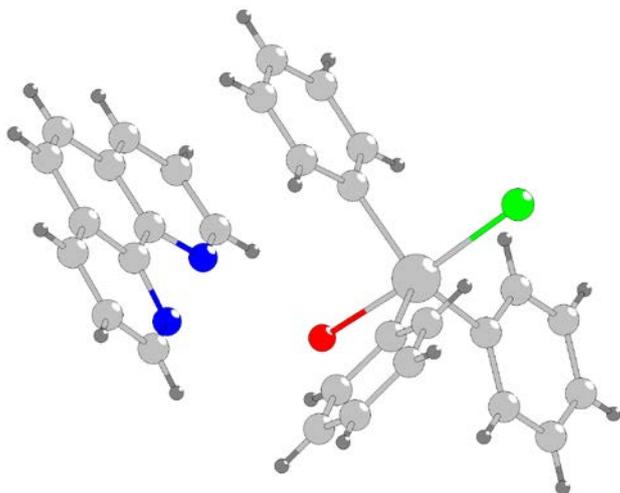
Be careful not to delete chlorine

Press "Select all"

For description of the structure is used 36 atoms

Press "Refresh"; OK; YES to save changes

Plot the structure using "Draw average structure"



Start :File → Structure → Save As" and make a backup copy

### 15. Preparing refinement with fixed rigid bodies

Start "Edit atoms"

Select carbons of phenyl, which have hydrogen: C2p, C3p, C4p, C5p and C6p

Start "Action → Adding of hydrogen atoms"

Check "generate keep command for Refine"

Check "try automatic run ..."

OK

Repeat procedure for carbon atoms of phenanthroline: C7t, C8t, C9t, C11t, C12t, C14t, C15t and C16t

*The procedure for adding hydrogen atoms, applied to already existing hydrogens, generates keep commands, which are necessary for subsequent refinement.*

*After this process number of atoms in the structure must be unchanged, i.e. 36*

Start Refinement options; go to the page "Various"; press "Fixed commands"

Select "All parameters"

For "Atoms/parameters" type "C\*p C\*t N\*t"; Add; OK; OK; YES to save commands without starting Refinement

*This fixes geometry of both phenyl molecules and phenanthroline*

### 16. Refinement with rigid bodies

Start "File → Structure → Save As" and make a backup copy

Start Refinement options; go to the page Basic

Clear "Disable atoms having too large isotropic ADP parameter"

OK; YES+START

*R<sub>all</sub> will be ~28% for 61 parameters*

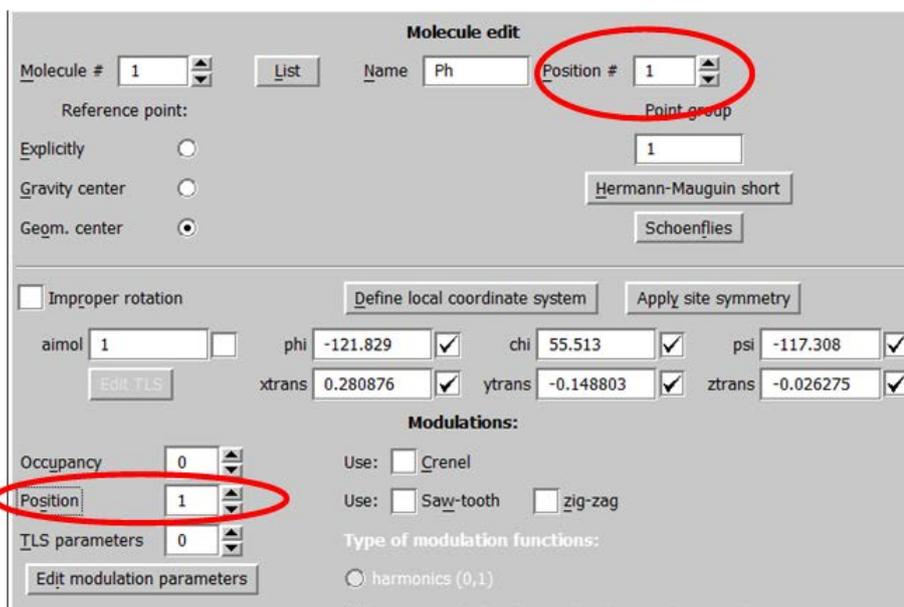
Start "Parameters → Molecules → Edit"

Set 1 position modulation wave for the first position of Ph

Set 1 position modulation wave for the second position of Ph

Set 1 position modulation wave for the third position of Ph

Set 1 position modulation wave for the first position of Trol



Run refinement

$R_{all}$  will be ~22% for 109 parameters

Start "Edit atoms"

For Sn1 set harmonic (anisotropic) ADP

For Cl1 and O1 set 2 position modulation waves and harmonic (anisotropic) ADP

Run refinement

$R_{all}$  will be ~20% for 136 parameters

Start Refinement options; go to the page "Various"; press "Fixed commands"

Disable the command "fixed all C\*p C\*t N\*t "

OK; OK; YES+START

The refinement converges with  $R_{all}$ ~19%,  $R_{main}$ ~11%,  $R_{sat1}$ ~22% and  $R_{sat2}$ ~27% for 204 parameters

Start "Edit atoms"

Set harmonic (anisotropic) ADP for carbons and nitrogens of both molecules

OK; OK, YES to save changes

Start "Parameters → Molecules → Edit"

Set 2 position modulation wave for the first position of Ph

Set 2 position modulation wave for the second position of Ph

Set 2 position modulation wave for the third position of Ph

Set 2 position modulation wave for the first position of Trol

Run refinement

The refinement converges with  $R_{all}$ ~9%,  $R_{main}$ ~6%,  $R_{sat1}$ ~11% and  $R_{sat2}$ ~10% for 352 parameters

Start "Edit atoms"

Set one ADP modulation wave for Sn1, Cl1 and O1

Start "Parameters → Molecules → Edit"

Set one ADP modulation wave (modulation of TLS parameters) for three positions of Ph and one position of Trol

Run refinement

The refinement converges with  $R_{all}$ ~8%,  $R_{main}$ ~6%,  $R_{sat1}$ ~10% and  $R_{sat2}$ ~10% for 548 parameters

Start "Edit atoms"

Set another one ADP modulation wave for Sn1, Cl1 and O1

Start "Parameters → Molecules → Edit"

Set another one ADP modulation wave for three positions of Ph and one position of Trol

Run refinement

*The refinement converges with  $R_{all} \sim 8\%$ ,  $R_{main} \sim 6\%$ ,  $R_{sat1} \sim 10\%$  and  $R_{sat2} \sim 9\%$  for 744 parameters*

*This is the final structure model with molecules*

## 17. Analysis of results

*Considering very good data quality, the results are still not satisfactory. Here we are looking for problems in the structure model*

Start "Edit/View → View of Refine"

*There are no serious warnings*

Plot the supercell structure

*The program does not use the transformation to five-fold supercell. Instead, it expands the structure to 5x1x5 supercell.*

*Geometry seems to be correct.*

Calculate difference Fourier map

YES to start procedure for including new atoms

*Do not include any maxima but look at their distances to atoms of our structure model. The largest difference maxima are close to atoms of phenantroline and phenyl, indicating some problem with the rigid body description.*

Start options for "Dist"

Press "Planes"

For "Atoms defining the best plane" type: C1pa C2pa C3pa C4pa C5pa C6pa; Add

For "Atoms defining the best plane" type: C1pb C2pb C3pb C4pb C5pb C6pb; Add

For "Atoms defining the best plane" type: C1pc C2pc C3pc C4pc C5pc C6pc; Add

*The second and third line can be created with help of the button "Clone"*

OK

Go to the page "Modulation"

Check "Make coordination t-tables"

OK, YES+START

Start "Edit/View → View of Dist"

"Go to" → "List dihedral angles"

Dihedral angle between plane#1 and plane#2 - Average : 60.1(2), Minimum : 56.7(2), Maximum : 68.4(2)										
t	Angle	t	Angle	t	Angle	t	Angle	t	Angle	t
0.000	57.5(2)	0.200	56.7(2)	0.400	68.4(2)	0.600	58.1(2)	0.800	59.9(2)	
Dihedral angle between plane#1 and plane#3 - Average : 42.4(2), Minimum : 21.9(2), Maximum : 59.8(2)										
t	Angle	t	Angle	t	Angle	t	Angle	t	Angle	t
0.000	35.2(2)	0.200	59.8(2)	0.400	21.9(2)	0.600	52.2(2)	0.800	42.7(2)	
Dihedral angle between plane#2 and plane#3 - Average : 66.5(2), Minimum : 55.9(2), Maximum : 89.2(3)										
t	Angle	t	Angle	t	Angle	t	Angle	t	Angle	t
0.000	69.4(2)	0.200	58.6(2)	0.400	89.2(3)	0.600	55.9(2)	0.800	59.3(2)	

*Each "t" value indicates one of the defined commensurate sections, which is realized as one configuration in the five-fold superstructure. We can see that changes of angles between the planes #1, #2 and #2, #3 reach 30 degrees, which cannot be reliably described by rigid body modulation function as used in Jana2006.*

Start "Grapht"

Press "New/edit"

For "Parameter to draw" set "plane"

For "p" set limits from 0 to 90

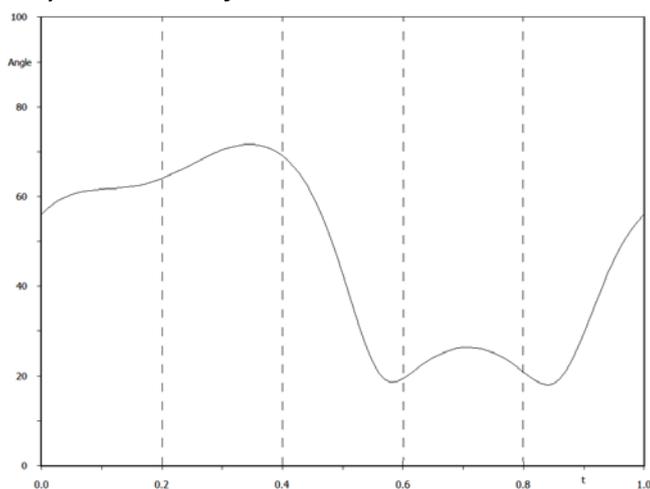
For "Plane #1" type "C1pa C2pa C3pa C4pa C5pa C6pa"

For Plane #2" type "0 0 1"

Grapht now displays angle between the plane through the first position of Ph and the axis c.

Press "Options"; check "Indicate commensurate t sections"; OK

Grapht now also displays the sections, for which the structure is defined. The orientation of the single plane changes by ~40 degrees. Again, this cannot be reliably described by rigid body modulation function as used in Jana2006.



Actual value of t-sections is connected with the origin selection made automatically during solution by Superflip. Also the phenyl molecules can be placed in different order compared with this manual. Thus the actual plot will differ.

### 18. Creating structure model without phenyl molecules

Start "File → Structure → Save As" and make a backup copy

Start "Edit atoms"; Select atoms \*p

Start "Action → Atoms from molecule to atomic part"

The three molecular position have been transformed to atoms with suffixes "a", "b" and "c"

Select H\*pa, H\*pb and H\*pc (it can be also done with H\*p?)

Start "Action → Edit/Define"

Set isotropic ADP

OK; OK; YES to save changes

Start Refinement options

Go to the page "Various"; press "Keep commands"; press "Edit"

Using the text editor:

- change labels \*p to \*pa

- duplicate the commands and change \*pa to \*pb

- create the same commands for \*pc

OK

Go to the page "Basic"; set Damping factor 0.5

OK; YES+START

Run refinement

*The refinement converges with  $R_{all} \sim 5\%$ ,  $R_{main} \sim 4\%$ ,  $R_{sat1} \sim 6\%$  and  $R_{sat2} \sim 6\%$  for 1176 parameters.*

#### **19. Creating structure without phenantroline molecules**

Start "Edit atoms"; Select atoms \*t

Start "Action → Atoms from molecule to atomic part"

*The molecular position have been transformed to atomic part without adding suffix "a", because the molecule had only one position. For this reason, keep commands are still valid and no editing is needed.*

Select H\*t

Start "Action → Edit/Define"

Set isotropic ADP

OK; OK; YES to save changes

Run refinement

*The refinement converges with  $R_{all} \sim 2.7\%$ ,  $R_{main} \sim 2.3\%$ ,  $R_{sat1} \sim 3.2\%$  and  $R_{sat2} \sim 2.9\%$  for 1576 parameters*

#### **20. Geometry of the atomic model**

*The atomic model has excellent R factors. However, we have to ensure that the phenyls are planar and not distorted.*

Start "File → Structure → Save As" and make a backup copy

Start Refinement options

Go to the page "Various"; press "Keep commands"

Select "Geometry" and "Plane"

For "List of atoms" type C1pa C2pa C3pa C4pa C5pa C6pa; Add

For "List of atoms" type C1pb C2pb C3pb C4pb C5pa C6pb; Add

For "List of atoms" type C1pc C2pc C3pc C4pc C5pc C6pc; Add

OK; OK; YES+START

*Change in R values should be very small*

Start Dist

*Commands for best planes prepared previously are still valid*

Start "Edit/View → View of Dist"

"Go to" → "List of best planes"

*Here we can see that the phenyls are almost exactly planar, as expected*

Start Graph

Press "New/Edit"

For "Parameter to draw" select "ADP parameter"

For "p" define "0" as Minimum and "0.1" as Maximum

For type of parameter to plot, select "U(max)"

For Central atom type "N1t"

OK

*[On the screen: plot of U(max) for N1t]*

Press "Options"

Select "Indicate commensurate t sections"; OK

*Now the plot shows the section where the structure is defined*

Press "New/Edit"

Press "New Item"; for "Central atom" type "N2t"

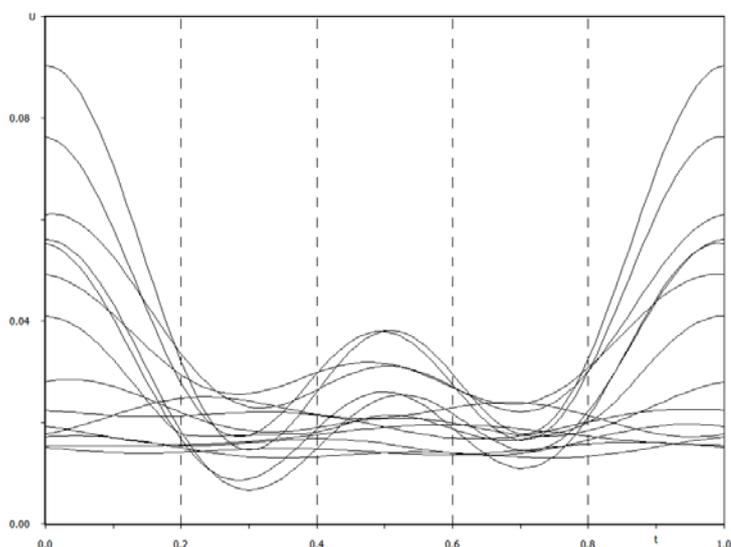
Press "New Item"; for "Central atom" type "C7t"

Press "New Item"; for "Central atom" type "C8t"

Add New items for C8t - C18t

OK

[On the screen: cumulative plot of  $U(\max)$  for all atoms of the phenantroline]



The plot indicates that for one of the sections (here for  $t=0$ ; its actual value is connected with the origin selection made automatically during solution by Superflip) some of the phenantroline atoms are strongly disordered, while the other not.

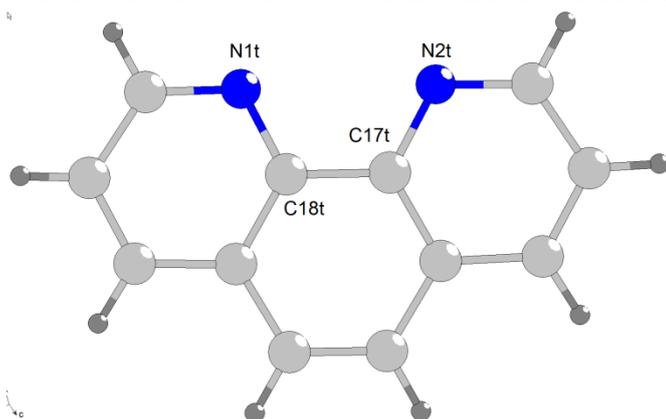
Quit Graph

Draw the average structure, select only the phenantroline molecule

For this Ctrl-M keyboard shortcut of Diamond can be used, which selects molecule belonging to a selected atom

Note atoms N1t, C18t, C17t and N2t.

Phenantroline is often twisted and we will calculate torsion angle of these atoms



Start Dist options

Press "Torsion angles"

For atoms type N1t, C18t, C17t and N2t; Add

OK; OK; YES+START

Open listing of Dist

"Go to" → "List of torsion angles"

```

*****
* List of torsion angles *
*****

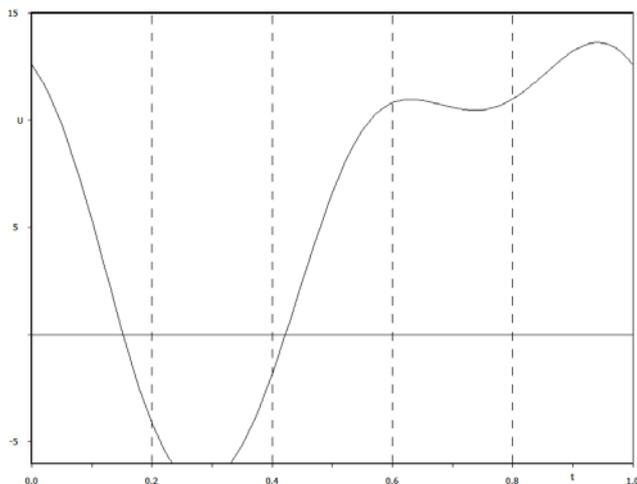
N1t-C18t-C17t-N2t : 5.58(13)

Individual values:
0.000 12.59(17) 0.200 -4.11(17) 0.400 -1.82(16) 0.600 10.82(17) 0.800 10.99(17)
Average : 5.69(17), Minimum : -4.11(17), Maximum : 12.59(17)

```

Here we can see that for five commensurate sections the torsion angle fluctuates between -4 and +12 degrees. This torsion could not be described by the molecular model.

The same torsion angle can be visualized in Graph:  
(Note that only the indicated sections are defined)



## 21. Water

The last missing atoms in our structure model are hydrogens of the water molecule

Start Fourier options

For "Map type" select difference Fourier

Check "Apply sin(th)/lambda limits

define "max" as 0.5

OK; YES+START

YES to start procedure for including new atoms

Add two difference maxima (probably the first two ones) 0.82Å close to O1 and name them H1O1 and H2O1

Start "Parameters → Molecules → New molecule"

Select "Atomic part" and "water" as a name; Next

Select O1, H1O1 and H2O1; OK

For the reference point select "Explicit" and use O1; NEXT

Apply+End

Start "Edit atoms"

Delete all modulation waves for O1, H1O1 and H2O1; OK; YES to save changes

Start "Parameters → Molecules → Edit"

Set one position modulation wave for "water"; OK; YES to save changes

Start Refinement options

In page "Various" define distance restraint 0.82Å for O1-H1O1 and O1-H2O2

In page "Various" define keep command for ADP of hydrogens H1O1, H2O1, to be 1.2 multiple of Ueq(O1).

Run refinement

Add another position modulation wave for the molecule "water"

Run refinement

In "Edit atoms" set one ADP modulation wave for O1

Run refinement

*The refinement converges with  $R_{all} \sim 2.7\%$ ,  $R_{main} \sim 2.2\%$ ,  $R_{sat1} \sim 3.0\%$  and  $R_{sat2} \sim 2.8\%$  for 1584 parameters*

*The first ADP modulation wave improved only slightly R values. Therefore, we will not add the second wave - this is the principle of saving parameters in commensurate refinement comparing with refinement in the supercell.*

In the final step introduce isotropic extinction

Run refinement

*The refinement converges with  $R_{all} \sim 2.6\%$ ,  $R_{main} \sim 2.1\%$ ,  $R_{sat1} \sim 3.0\%$  and  $R_{sat2} \sim 2.8\%$  for 1585 parameters*

*This is the final commensurate model*

## 22. Transformation to supercell

*The final commensurate model can be transformed to the supercell*

Start "Tools → Transformations → Go to supercell structure"

For Name type "sup"; OK

OK to transform molecules

Follow steps of the data processing wizard

YES to continue with the new structure

Set **zero** refinement cycles

Run refinement (skip warnings)

*The R value will be 2.6%, because both descriptions are equivalent*

*In order to refine the supercell structure, keep commands for hydrogens must be re-created.*

*The supercell structure contains 15 independent phenyls:*

C1pa-1, C2pa-1, C3pa-1, C4pa-1, C5pa-1, C6pa-1

....

C1pa-5, C2pa-5, C3pa-5, C4pa-5, C5pa-5, C6pa-5

C1pb-1, C2pb-1, C3pb-1, C4pb-1, C5pb-1, C6pb-1

....

C1pb-5, C2pb-5, C3pb-5, C4pb-5, C5pb-5, C6pb-5

C1pc-1, C2pc-1, C3pc-1, C4pc-1, C5pc-1, C6pc-1

....

C1pc-5, C2pc-5, C3pc-5, C4pc-5, C5pc-5, C6pc-5

*Five independent phenantrolin molecules:*

N1t-1, N2t-1, C7t-1, C8t-1, C9t-1, C10t-1, C11t-1, C12t-1,  
C13t-1, ..., C17t-1, C18t-1

....

N1t-5, N2t-5, C7t-5, C8t-5, C9t-5, C10t-5, C11t-5, C12t-5,  
C13t-5, ..., C17t-5, C18t-5

*Five independent water molecules:*

O1a-1; O1a-2; O1a-3; Oa-4; O1a-5

*Keep commands can be easily expanded and edited according to the above mentioned labels, however, they can be also copied from the pre-prepared file supercell\_keep.txt.*

Start Refinement options

Go to the page "Various"; press "Keep commands"

Press "Edit"

Replace content of the file with content of the supercell\_keep.txt

Save and close the text editor

OK

*Number of keep commands should be 235*

Press "Distance restraints"

Restrain the following distances to 0.82Å: O1a-1 H1O1a-1; O1a-1 H2O1a-1; O1a-2 H1O1a-2; O1a-2 H2O1a-2; O1a-3 H1O1a-3; O1a-3 H2O1a-3; O1a-4 H1O1a-4; O1a-4 H2O1a-4; O1a-5 H1O1a-5; O1a-5 H2O1a-5;

*Some keep commands and distance restraints may be invalid because the atomic positions may be transformed during the commensurate-to-supercell transformation. Such commands would need symmetry codes.*

Start "Edit atoms"

Press "Select all"

Start "Action" → "create symmetrically contiguous motifs"

*After this the keep commands can use labels without symmetry codes*

Start refinement (still with zero cycles)

*The R value will be 2.6%*

Start "File → Structure → Save As" and make a backup copy

Set 100 refinement cycles, damping factor 0.5, and run refinement

*Refinement uses 1611 parameters, which is more than in commensurate refinement, because we did not use full set of parameters for water molecules. However, the resulting R value is still 2.58%*

### **23. Back to the rigid body description**

*Now we can introduce phenyl molecule in 15 positions, which was not possible in the commensurate refinement due to too large rotations. For phenantroline, we can try to use rigid body description using two halves of the phenantroline as independent pattern molecules, in order to describe the torsion of phenantroline. Finally, we can model the disordered phenantroline molecule by partially occupied molecules. All this is routine job, which will not be presented here.*

### **24. Conclusions**

*Commensurate refinement can help to find solution of very large structures, it allows to save parameters by using less than the full set of modulation parameters, and it facilitates interpretation of a superstructure through calculation of various parameters as a function of  $t$ . However, commensurate refinement may be difficult when satellites are too strong, because strong satellites indicate large displacements, which must be described by modulation functions defined only in few points. Despite of this, commensurate refinement was possible for our structure and it helped us to understand its geometry. On the other hand, the phenyl rigid body could be only possible in the supercell refinement, as well as the full description of the disordered phenantroline molecule.*

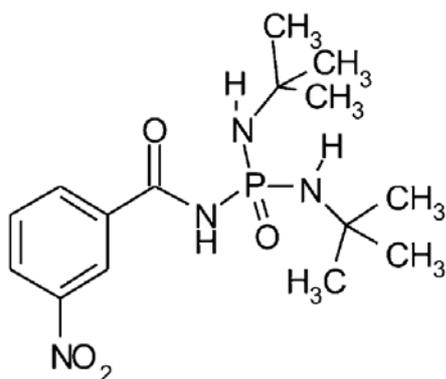
# Example 8.1: TerBut

Application of rigid body groups for disordered parts of crystal structure

Revised: 4 March 2015

N-(3-nitrobenzoyl)-N',N''-bis(tert-butyl)phosphoric triamide

Chemical formula:  $C_{90}H_{150}N_{24}O_{24}P_6$



Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: TerBut.hkl, TerBut.cif\_od

Frame scaling, absorption correction: done with software of the diffractometer

## 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click TerBut

## 2. Import Wizard

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction – CCD”; NEXT

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

For absorption correction select “None or done before importing”; NEXT

FINISH

## 3. Data Repository

Each line in data repository window corresponds to one data set.

OK; YES to accept the data set

## 4. Symmetry Wizard

[On the screen: “Information” about symmetry wizard]

NEXT

[On the screen: "Tolerances for crystal system recognition".]

Leave all settings default; NEXT

[On the screen: Select Laue symmetry]

Select Triclinic; NEXT

Select primitive unit cell; NEXT

[On the screen: Select space group]

Select P-1; NEXT

Accept the space group; FINISH

#### 5. **Creating refinement reflection file**

NEXT to confirm threshold  $3\sigma$

[On the screen: settings for merging of reflections]

Leave all settings default; NEXT

Press "Accept the new DatBlock and calculate coverage"; FINISH

#### 6. **Structure Solution Wizard**

[On the screen: "Information" about Structure solution tool]

OK

[On the screen: window of Structure solution]

In "Formula" textbox type list of chemical elements for TerBut: C15 N4 O4 P H25;

Set "Formula units" to 2 and calculate density;

[On the screen: Calculated density: 0.4242 g/cm<sup>3</sup>]

*This is unrealistic value which indicates that the structure can contain more independent structural motifs. As the density should be larger than 1 the most probable number of independent structural motifs is 6.*

Set "Formula units" to 6;

Select "Superflip", "Peaks from Jana2006"; leave other settings default; "Run solution"

Close listing of Superflip

Press "Accept last solution" to leave the structure solution wizard

#### 7. **Verification of the structure solution**

Start "Plot structure", use either "Draw+return" or "Draw+continue"

[On the screen: window of Diamond]

Start "Build → Get molecules" or use  on the bottom toolbar

Rotate the molecule (  and  on the bottom toolbar) to get an optimal view

[On the screen: plot of the three independent, probably incomplete molecules]

Assignment of chemical types need not be correct and some atoms may be missing.

Chemical types will be corrected later on.

*The three independent molecules are combined with the inversion center. This confirms  $Z=6$  as estimated previously from the density. Correct  $Z$  helps the program to offer proper number of maxima from difference Fourier.*

Quit Diamond;

#### 8. **Refinement**

[On the screen: basic window of Jana]

Right-click the icon of Refine.

*[On the screen: Refinement commands]*

Define 100 of cycles; OK

Choose "YES+START"

*Refinement converges with R(obs) value about 20-22%*

### 9. Completing the structure – difference Fourier synthesis

*[On the screen: basic window of Jana]*

Right-click the icon of Fourier.

*[On the screen: Fourier commands]*

For "Map type" select difference Fourier, make sure that "Weighting of reflections" is checked and "Apply sin(th)/lambda limits" unchecked

OK; YES+START to save commands and run the difference Fourier;

YES to start the procedure for including of new atoms;

*[On the screen: parameters for inserting/replacing of atoms]*

Use default parameters; OK

*[On the screen: the form for inserting of new atoms]*

Go through the list of maxima and include all peaks having reasonable distances (i.e. similar to C-C distance) to already localized atoms. Skip short distances. Do not attempt including H atoms.

After pressing the button "Include selected peak" the form for completing of the new atom appears. For the "Name of the atom" type C\*. For more information what C\* means press the "Info" button.

Repeat the points 8 and 9 till no new atoms are localized. The structure should have 72 non-H atoms

FINISH; YES to include new atoms

Repeat refinement

*Finally R(obs) value should be between 16 and 17%*

### 10. New verification of the structure solution

Start "Plot structure", "Draw+continue" or "Draw+return"

*[On the screen: window of Diamond]*

Start "Build → Get molecules" or use  on the bottom toolbar

Rotate the molecule ( and  on the bottom toolbar) to get an optimal view

*[On the screen: plot of the three independent molecules]*

Activate atom labels

*[On the screen: plot of the molecule with atom labels]*

Compare the plot with the chemical scheme at the beginning of this Cookbook chapter and note labels of atoms which chemical types need to be changed.

*(For Diamond started by "Draw + return" the changes can be done immediately in Jana2006 running alongside.)*

Use  at the bottom toolbar of Diamond to see temperature ellipsoids.

*The large spheres derived from Uiso values for the terminal carbon atoms indicate positional disorder of some tertiary butyl groups.*

### 11. Assignment of correct chemical types

*[On the screen: basic Jana window]*

Start "Edit atoms"

[On the screen: list of atoms]

Highlight one of the atoms you are going to modify

Make left double-click or Start "Action → Edit/define"

Change "Type" to the desired one

Rename the atom. Here you can use again the wild character \* which prevents duplication of atom names.

Repeat this procedure till all atoms have correct chemical types.

*Note: alternatively you can select more atoms and change the chemical type of the selected group. After returning to the list of atoms in Atom/Edit the atoms are still selected and they can be automatically renamed with "Action → Rename selected atoms".*

Check again the chemical types with Diamond

Check number of atoms with "Edit atoms", using the textbox close to "Select advanced", which accepts wildcards as "C\*". The structure contains 3P, 12O, 12N and 45C; 72 atoms altogether.

## 12. Refinement

[On the screen: basic window of Jana]

Double-click the icon Refine.

*Refinement converges with R(obs) value about 16%*

Start "Edit atoms"

[On the screen: list of atoms]

Press "Select all" and "Action → Edit/define"

Choose "harmonic" for ADP parameters. *This defines anisotropic temperature parameters for all atoms. OK, OK, YES to save changes*

Double-click the icon Refine.

*Refinement converges with R(obs) value about 9%*

## 13. Formula check

[On the screen: basic window of Jana]

Run EditM50;

Go to the tab "Composition" and press button "Formula from M40".

*The derived formula should be correct for all atom types except hydrogen.*

## 14. Unifying atom labels

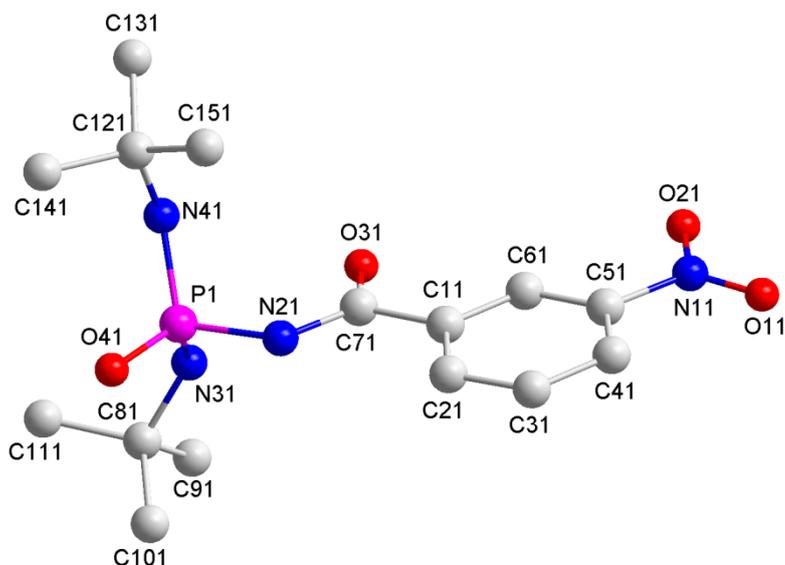
*To follow easily the cookbook we need to re-label the atoms. It would be tedious work and therefore we will use pre-prepared files with correct labelling.*

Start "File → Structure → Copy in", select the structure "TerBut-simple-atomic" and in the next dialogue select files m40 and m50 for the copy.

Double-click the icon Refine.

*Refinement should converge to R(obs) value about 9.4%*

*The labeling of atoms of the first independent molecule is shown in the following figure:*



The last digit in each label is the identifier of the molecule (replaced by 2 and 3 for the second and third independent molecule, respectively).

### 15. Search for split atom positions

Double-click the icon Contour; Click the button “New plot”

[On the screen: options for defining of new maps]

In “New map to draw” select “Fourier map”;

Select “Calculate new ones” and “Draw a general section”; OK

[On the screen: Fourier commands – page Basic]

Set “Map type” to “F(obs) – Fourier”;

Clear “Omit not-matching reflections”;

Clear “Apply sin(th)/lambda limits”;

Select “Use weighting of reflections”; OK

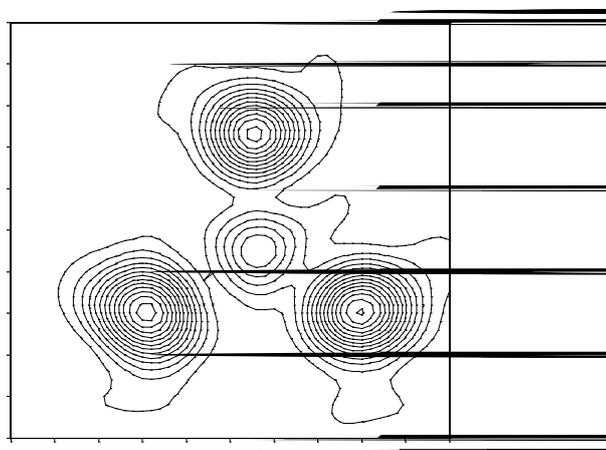
[On the screen: Plane/Volume]

For 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> atom use C91, C101 and C111;

Keep interpolation step 0.1 Å;

Define scope of the section: 5 5 0 and “1<sup>st</sup> point to” 1.5 1.5 0; OK

You should see the following figure:



Click the button “New plot”

*(The definition of the plane has been automatically saved as Plane#1)*

*[On the screen: options for defining of new maps]*

Select “Use old maps” and “Draw a general section” (i.e. default values); OK

*[On the screen: Plane/Volume]*

Select “Use old”

Rewrite 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> atom by C92, C102 and C112;

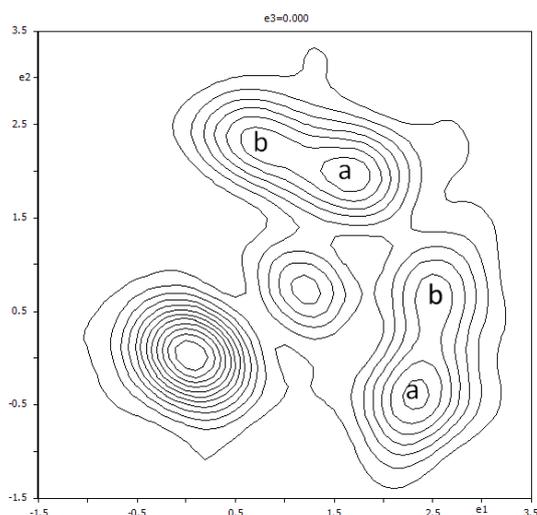
*You should see similar figure like for the previous figure*

Repeat the procedure for C93, C103 and C113;

*Again no clear splitting of atomic positions*

Repeat the procedure for C131, C141 and C151.

*The last map indicates clearly splitting for two atoms:*

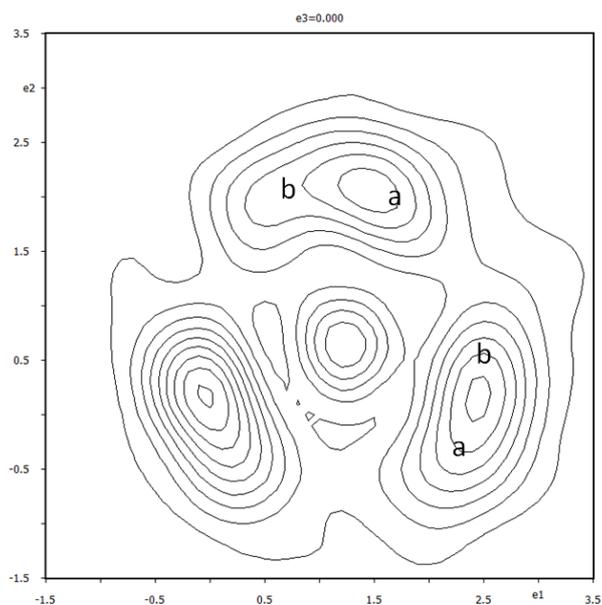


Locate the split positions by clicking at corresponding points of the section and save them for future use by “Save the selected point for future use” button.

*points close to C141 ~ (0.2795, 1.102, 0.2494) and (0.2995, 1.1158, 0.1820)*  
*(they can be named C141a and C141b)*

*points close to C151 ~ (0.2455, 1.111, 0.1117) and (0.1869, 1.0974, 0.1017)*  
*(they can be named C151a and C151b)*

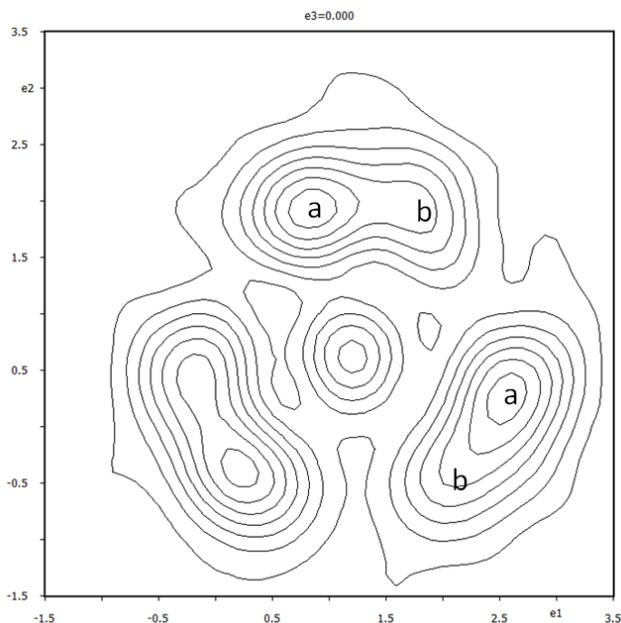
Make the same for the second molecule (the section C132, C142, C152). Here the splitting of atoms C142 and C152 is less pronounced, however we only need some points for initial orientation of rigid bodies.



points close to C142 ~ (0.7732, 0.3731, 0.4747) and (0.8239, 0.4088, 0.4588)  
 (they can be named C142a and C142b)

points close to C152 ~ (0.8695, 0.4942, 0.5074) and (0.8356, 0.5156, 0.5715)  
 (they can be named C152a and C152b)

Make the same for the third molecule (the section C133, C143, C153). Here all positions are clearly split but we only need two pairs of points..



points close to C143 ~ (-0.1854, 0.7837, 0.1733) and (-0.1759, 0.7836, 0.1320)  
 (they can be named C143a and C143b)

points close to C153 ~ (-0.0588, 0.8945, 0.1860) and (-0.1022, 0.8639, 0.2186)  
 (they can be named C153a and C153b)

The split positions localized during preparation of this example were also written to the file "TerBut-points.txt" and can be later to pasted to Jana2006 textboxes.

Quit Contour

YES to save new points in M40 (this does not change structure model)

The points have been stored in M40 in the "Saved points" section

## 16. Defining of rigid-body groups

First we will create a model where one pattern "molecule" – tertiary butyl – is used to create three non-split positions related to N3i, C8i, C9i, C10i, C11i fragments and another six split positions related to N4i, C12i, C13i, C14i and C15i fragments (i=1,2,3).

Start "File → Structure → Save As" and **create a backup copy** "before\_rigid" but **do not continue** with the new structure.

Start "Parameters → Molecules → New molecule";

[On the screen: Wizard for new molecule]

Select "Atoms of the new molecule from" - "Atomic part";

For "Name of the molecule" type, for instance, "Tb"; NEXT;

[On the screen: Select atoms for the molecule]

Select atoms to be used as a *pattern* (elsewhere called *model*) molecule – N31, C81, C91, C101 and C111;OK

[On the screen: Define the molecular reference point]

Select "the molecule reference point" as "Explicit" defined by the atom C81; NEXT

[On the screen: Form for completing of the molecular position #1];

The "Coincidence ratio" says that five atoms of the molecular position #1 coincide with five atoms in the atomic part of M40. This should be true because the pattern molecule is created from five atoms in M40 and the first position coincides with the pattern molecule.

Use the default value for occupancy; Press "Apply+Next Position";

[On the screen: Form for completing of the molecular position #2];

For the position #2 and all consecutive ones we have to define where to put the pattern molecule to get the new actual position. This means that actual positions of three atoms of the pattern molecule, not lying in a line, are to be specified.

Fill "Model atoms" column with N31, C101 and C111 and fill the "Actual position/atom" column with N32, C102 and C112. Press the button "Calculate molecular parameters".

The coincidence ratio should be 5/5. It says that five atoms of the pattern molecule coincide in its actual position with five already existing atoms of the structure. After finishing the molecular position the coinciding atoms will be deleted from the atomic part – for this reason it is important that all of them are recognized by the program. The coincidence can be controlled by the "Maximal coincidence distance".

Press the button "Apply+Next Position";

Repeat the procedure for the third non-split tertiary group (i.e. N33, C103 and C113 for Actual positions); press "Apply+Next position"

[On the screen: Form for completing of the molecular position #4];

For actual positions use N41, % C141a and %C151a. The character "%" refers to saved points.

Press the button "Calculate molecular parameters".

If the "Coincidence ratio" is not 5/5, change the "Maximal coincidence distance" to 0.8 and press again "Calculate coincidence distance"

If the "Coincidence ratio" is still not 5/5, replace the points for the 2<sup>nd</sup> and 3<sup>rd</sup> actual position and press again "Calculate coincidence distance"

The reason for this step is that the selected saved points may define by mistake contradicting rotations of the pattern molecule. This cannot happen when the "a" and "b"

labels have been used as indicated in the plots.

Finally, the "Coincidence ratio" should be 5/5

For "Occupancy" type 0.5.

Press "Apply+Next position";

[On the screen: Form for completing of the molecular position #5];

For actual positions use the same atom N41 and another two split positions % C141b and %C151b.

Press the button "Calculate molecular parameters" and check that the "Coincidence ratio" is 5/5;

Change the occupancy to 0.5;

Press the button "Apply+Next Position";

Repeat the process for the second and third split tertiary butyl:

Position #6: N42, %C142a, %C152a

"Apply+Next Position"

Position #7: N42, %C142b, %C152b

"Apply+Next Position"

Position #8: N43, %C143a, %C153a

"Apply+Next Position"

Position #9: N43, %C143b, %C153b

"Apply+End"

The total number of molecular positions is 9.

## 17. Verification

Use Diamond for verification of proper geometry: each molecule should have one single and one disordered tertiary group.

Use Parameters → Molecules → Edit for verification that positions #4 – #9 have occupancy (i.e. the parameter "aimol") 0.5

Use "EditM50", page "Composition", button "Formula from M40"

If occupancy of molecular positions has been properly defined and the coincidence ratio has been always 5/5 the formula should be C15 N4 O4 P H0 (for Z=6)

Use "Edit atoms" to see changes in the atomic part of M40

Black atoms are the ones not used in molecular description

Blue atoms are the ones defining the pattern molecule

Start "File → Structure → Save As" and create a backup copy "rigid\_ini" but **do not continue** with the new structure.

## 18. Refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine.

[On the screen: Refinement commands]

Change the damping factor to 0.5;

OK, "YES+START"

Refinement converges with R(obs) value about 10.4%

## 19. Refinement of the molecular occupancies

Start "Parameters → Molecules → Edit";

[On the screen: molecule edit]

Allow refinement of the molecular occupancies (aimol) for the positions #4, #6 and #8;

OK; YES to save changes  
 Right-click the icon of Refine; select tab "Various";  
 [On the screen: Refinement commands]  
 Press the button "Restrictions";  
 [On the screen: The tool for defining and editing of restriction commands]  
 Write into the textbox "Atoms/molecules": "Tb#4 Tb#5"  
 Deselect "Coordinates"  
 Select "Occupancies: Keep overall sum"  
 Select "ADP parameters"  
 Press the button "Add";  
*This restriction means that the molecular positions #4 and #5 have independent coordinates, the same ADP and complementary occupation*  
 Select the line: restric Tb#4 Tb#5;  
 Press the button "Clone" and then "Load" and modify the string to "Tb#6 Tb#7"  
 Press the button "Rewrite";  
 Press the button "Clone" and then "Load" and modify the string to "Tb#8 Tb#9"  
 Press the button "Rewrite";  
 OK; OK; Yes+Start;  
*Refinement converges with R(obs) value about 10.3% with 475 parameters*

## 20. Refinement of the molecular TLS tensors

Start "Edit atoms";  
 [On the screen: tool for selection of atoms]  
 Select all atoms of the pattern molecule (before selection they are indicated by blue color).  
 Double-click; Select "Use TLS";  
 OK; OK; Rewrite changes  
*This change means that individual ADP parameters of the pattern molecule are suppressed. Instead, for each actual position independent TLS tensors will be refined.*  
 Run refinement  
*Refinement converges with R(obs) value about 8.6% with 565 parameters*

## 21. Adding hydrogen atoms

Start "Edit atoms";  
 [On the screen: tool for selection of atoms]  
 Select all carbon atoms and nitrogen atoms N21, N22 and N23  
 Press the button "Action"  
 Select the procedure "Adding of hydrogen atoms"  
 [On the screen: parameters for adding hydrogen atom]  
 Use default options (i.e. automatic procedure for C and manual procedure for N);  
 For N21, N22 and N32 select the trigonal coordination with two neighbors (P and C). Then only one H atom will be added.  
*Total number of hydrogen atoms in Atoms edit should be 24*  
 OK; Save changes  
 Use Diamond for verification that all hydrogen atoms have been correctly placed  
 Run refinement  
*Refinement converges with R(obs) value about 6%*

## 22. Drawing of the refined model

Start "Plot structure"

In Diamond, start "Build → Get molecules" or use  on the bottom toolbar

Use  at the bottom toolbar of Diamond to see temperature ellipsoids. For plotting H atoms without ellipsoids switch to "Table of atom groups", select all H atoms and use  again.

*The large temperature ellipsoids for the terminal carbon atoms indicate that there is probably some additional positional splitting of tertiary butyls N3, C8, C9, C10, C11 and also of some oxygen atoms. For teaching purposes, we can stop at this stage, as introducing of additional splitting does not bring any new.*

Quit Diamond

Start "File → Structure → Save as" and save the result as "TerBut\_final\_1" but **do not continue** with the new structure.

## 23. Reset the structure into the atomic model

Start "File → Structure → Copy in", select the structure "before\_rigid" and copy in the m40 and m50 file.

## 24. Defining of rigid-body groups from a known model saved in M45

*M45 may contain coordinates of a rigid-body group. Syntax of M45 is explained in the example 2.3.2-MagCag, where steps how to create M45 from a template found in CSD are shown. Library of frequently used rigid bodies for Jana2006 is under development, see the directory "Molecular patterns" in Jana2006 installation path.*

Start "Parameters → Molecules → New molecule";

[On the screen: Wizard for new molecule]

Select "the new molecule from a model file";

Define "Name of the molecule" Tb;

Define "Model filename" TerButyl-no-symmetry.m45;

Keep the default scaling distance

*With this number the whole object can be shrunk or expanded*

Press "Show the model molecule"

*This will display the pre-prepared figure from the file TerButyl-no-symmetry.jpg*

NEXT

[On the screen: specify atomic types in the model molecule]

Keep the default atomic types; NEXT

[On the screen: Define the molecular reference point]

Select "the molecular reference point" as explicit defined by the atom C81; NEXT

[On the screen: Form for completing of the molecular position #1];

*For creating molecular parameters from a model file we have to specify also the actual coordinates of the first position. Starting from the position #2 we can repeat instructions from the point 16 and 17. Because the pattern molecule contains hydrogen atoms which are not present in the atomic part, the coincidence ratio will be 5/14 or higher for the split positions. This is due to the fact that some hydrogen atoms of the split positions can be close to average carbon positions. This should not have any effect as this message has only informative character. For coincidence lower than 5 please change the "Maximal coincidence distance" to 0.8.*

As follows from the point 16 and 17, the atoms N31, C101 and C111 of the pattern molecule will be associated with the following actual positions present in the atomic part of M40 or from the saved points:

1. N31 C101 C111 (occupancy 1)
2. N32 C102 C112 (occupancy 1)
3. N33 C103 C113 (occupancy 1)
4. N41 %C141a %C151a (occupancy 0.5)
5. N41 %C141b %C151b (occupancy 0.5)
6. N42 %C142a %C152a (occupancy 0.5)
7. N42 %C142b %C152b (occupancy 0.5)
8. N43 %C143a %C153a (occupancy 0.5)C101
9. N43 %C143b %C153b (occupancy 0.5)

Resulting number of atoms: 42 in atomic part (here hydrogens are still missing); 14 in the pattern molecule.

## 25. Refining of the structure with fixed ideal geometry

Start "Parameters → Molecules → Edit";

[On the screen: molecule edit]

Allow refinement of the molecular occupancies (aimol) for the positions #4, #6 and #8;

OK; YES to rewrite files;

Right-click the icon of Refine;

[On the screen: Refinement commands]

Change number of cycles to 100 and the damping factor to 0.5;

Select tab "Various";

[On the screen: Refinement commands]

Press the button "Restrictions";

[On the screen: The tool for defining and editing of restriction commands]

Write into the textbox "Atoms/molecules": "Tb#4 Tb#5"

Deselect "Make identical coordinates";

Select: "Occupancies: Keep overall sum"

Select: "ADP parameters"

Press the button "Add";

*This restriction means that the molecular positions #4 and #5 have independent coordinates, the same ADP and complementary occupation*

Select the line: restric Tb#4 Tb#5;

Press the button "Clone" and then "Load" and modify the string to "Tb#6 Tb#7"

Press the button "Rewrite";

Press the button "Clone" and then "Load" and modify the string to "Tb#8 Tb#9"

Press the button "Rewrite"; OK

[On the screen: Refinement commands]

Press the button "Fixed commands";

Select "Coordinates"; Fill textbox "Atoms/parameters" with

N31 C81 C91 C101 C111 H?c91 H?c101 H?c111

*This fixes coordinates of the pattern molecule. For library molecule we expect correct geometry.*

Press the button "Add"; OK

*[On the screen: Refinement commands]*

Select "Keep commands";

Select "ADP", "Riding";

Central atom: C91; Number of hydrogen atom 3;

Fill hydrogen textboxes by: H1C91, H2C91 and H3C91;

For this button "Select hydrogens" can be used.

Add;

Repeat the process for C101 and C111;

OK; OK; Yes+Start

Refinement converges with  $R(\text{obs})$  value about 10.2% for 441 parameters.

## **26. Refining of the structure with anisotropic ADP for tertiary butyls**

Start "Edit Atoms";

*[On the screen: tool for selection of atoms]*

Select non-hydrogen atoms of the pattern molecule.

Double-click; Select "Harmonic ADP";

OK; OK; Rewrite changes

Start refinement;

Refinement converges with  $R(\text{obs})$  value about 9.4% for 466 parameters

## **27. Refining of the structure with TLS tensors for tertiary butyls**

Start "Edit Atoms";

*[On the screen: tool for selection of atoms]*

Select **all** atoms of the pattern molecule.

Select "Use TLS" using double-click;

OK; OK; Rewrite changes

Start refinement;

Refinement converges with  $R(\text{obs})$  value about 7.5% for 556 parameters

## **28. Adding remaining hydrogen atoms**

Start "Edit Atoms";

*[On the screen: tool for selection of atoms]*

Select all individual (black) carbon atoms and nitrogen atoms N21, N22 and N23

*It is important that carbon atoms of the molecule are not selected. Here the geometric keep commands would contradict with setting of the local symmetry, which will be done later on*  
Press the button "Action"

Select the procedure "Adding of hydrogen atoms"

*[On the screen: parameters for adding hydrogen atom]*

Use default (i.e. automatic run);

For N21, N22 and N32 select the trigonal coordination with the neighbors (P1, C71), (P2, C71) and (P3, C73), respectively.

OK; Save changes

Repeat refinement

Refinement converges with  $R(\text{obs})$  value about 6.6% for 556 parameters. This result can be compared with the previously obtained model *TerBut\_final\_1*, where the shape of the pattern molecule was refined, yielding  $R$  value 5.8 for 565 parameters.

Start "File → Structure → Save as" and save the result as "TerBut\_final\_2" but do not continue with the new structure.

## 29. Introducing of the local symmetry

The tertiary butyl has in an ideal case the point symmetry  $31m$ . Application of the local symmetry can considerably reduce the number of independent atoms. The point group generated by Jana2006 has its three-fold axis directed along the z-axis and the normal of the mirror plane directed along x-axis. As the atoms N31 and C81 are localized at the three-fold axis of the molecule the vector from the central point C81 to N31 can be used to define the z axis. The second x-axis is to be perpendicular to the z axis and it can be located at the plane N31-C81-C91.

Start "Parameters → Molecules → Edit";

Define the point group  $31m$ ; TAB

A dialog window for defining the local coordinate system for the pattern molecule will appear.

The model imported from the m45 file fulfills already the  $31m$  symmetry in the setting as described above and therefore the local coordinate system need not be modified.

OK to close the dialog window; OK; YES to save changes

This process is irreversible because atoms in the pattern molecule are deleted if they become duplicity with respect to the introduced point group

## 30. Check atoms of the model tertiary butyl

Start "Edit Atoms";

The number of independent atoms is now only 5.

Select the first atom of the model tertiary butyl and make double-click;

Switch to Edit to see the site occupancy;

You should get:

N31 0.166667

C81 0.166667

C91 0.500000

H1c91 0.500000

H2C91 1.000000

## 31. Refinement of the structure with local symmetry $31m$ – atomic positions of the tertiary butyl fixed

Start the refinement;

Refinement converges with  $R(\text{obs})$  value about 6.6% for 556 parameters, i.e. the same value like before, because the shape of the pattern molecule is still fixed.

## 32. Refinement of the structure with local symmetry $31m$

Right-click the icon of Refine; select tab "Various";

[On the screen: Refinement commands]

Press the button "Fixed commands";

Disable the fixed command; OK

Start the refinement;

Refinement converges with  $R(\text{obs})$  value about 6.5% for 564 parameters.

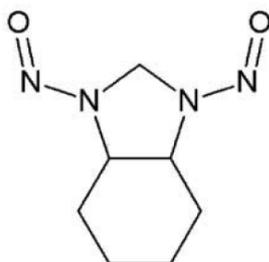
# Example 8.2: Dinitros

Application of rigid body groups for disordered parts of crystal structure

Revised: 27 December 2017

(3aRS,7aRS)-1,3-dinitrosooctahydro-1H-benzimidazole

Chemical formula:  $C_7H_{12}N_4O_2$



Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: dinitros.hkl, dinitros.cif\_od

Frame scaling, absorption correction: done with software of the diffractometer

## 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click dinitros

## 2. *Import Wizard*

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction – CCD”; NEXT

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

For absorption correction select “None or done before importing”; NEXT

FINISH

## 3. *Data Repository*

Each line in data repository window corresponds to one data set.

OK; YES to accept the data set

## 4. *Symmetry Wizard*

[On the screen: “Tolerances for crystal system recognition”.]

Leave all settings default; NEXT

[On the screen: Select Laue symmetry]

Select Monoclinic; NEXT

Select primitive unit cell; NEXT

[On the screen: Select space group]

Select P2/c; NEXT

Accept the space group; FINISH  
[On the screen: define space group window]  
OK to accept the space group P2/c

#### 5. **Creating refinement reflection file**

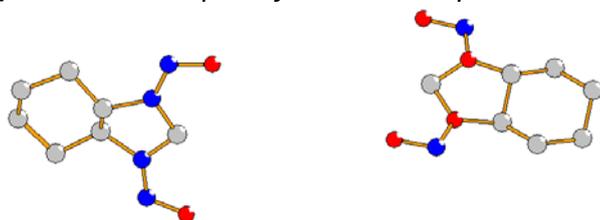
NEXT to confirm threshold  $3\sigma$   
[On the screen: settings for merging of reflections]  
Leave all settings default; NEXT  
Accept the data block and calculate coverage; FINISH

#### 6. **Structure Solution Wizard**

[On the screen: window of Structure solution]  
In "Formula" textbox type list of chemical elements for Dinitros: C7 H12 N4 O2;  
Set "Formula units" to 4 and calculate density;  
The density  $1.393 \text{ g/cm}^3$  looks reasonably so probably  $Z=4$  is correct  
Select "use Superflip", "Peaks from Jana2006"; leave other settings default; "Run solution"  
Close listing of Superflip  
Superflip converges with R value 16% and confirms symmetry P2/c  
Press "Accept last solution" to leave the Structure solution wizard

#### 7. **Verification of the structure solution**

Start "Plot structure"; "Draw + Continue"  
[On the screen: window of Diamond]  
Start "Build → Get molecules" or use  on the bottom toolbar  
Rotate the molecule ( and  on the bottom toolbar) to get an optimal view  
[On the screen: plot of the two independent molecules]



The results may be slightly different for each run of Superflip, because it starts from random phases.

Draw rectangle to select all atoms of the molecule or press Ctrl-A  
Right-click on one of the selected atoms, choose "Add → Atom labels"  
[On the screen: dialogue of Diamond for atom labeling]  
Note incorrect chemical types (using the chemical diagram above);  
Quit Diamond;  
Run "Edit atoms";  
Correct the improper chemical types;  
Rename atoms according to chemical types;  
Make symmetry contiguous motifs;  
Quit "Edit atoms", save the changes

For this structure making the symmetry contiguous motifs is very important. To make sure the motifs have been correctly created:

Return to Diamond;

Use  or “Build → Add all atoms”;

Connect atoms with bonds

This will plot symmetry independent atoms of the structure model without any symmetry transformation. They should create motifs:



If these motifs are not created the atoms must be put to the motif manually using symmetry transformations in “Edit atoms”. **Without proper motifs this example will not work!**

Quit Diamond

## 8. Refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine.

[On the screen: Refinement commands]

Define 100 of cycles; OK

Choose “YES+START”

Refinement converges with  $R(\text{obs})$  value about 13%

Plot the structure

It should be the same like before

Start “Edit atoms” and change ADP of all atoms to “harmonic”

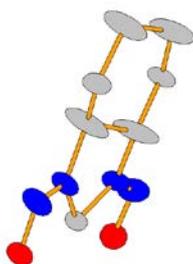
Repeat refinement

Refinement converges with  $R(\text{obs})$  value about 9.4%

Plot the structure

Activate ADP ellipsoids using “Picture → Model and Radii”

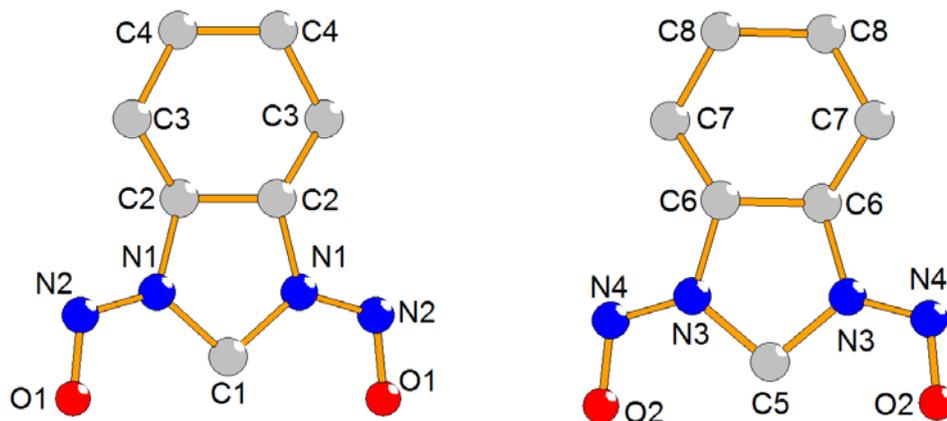
One of the molecules has very large ellipsoids for carbon atoms:



## 9. Labeling

At this point we would need some more practical labeling of atoms. Jana2006 doesn't include tools for graphical renaming. The labels and their changes must be planned in Diamond, noted and realized in “Edit atoms” tool or by direct editing of M40

The desired labeling for the molecule with large ADP's (starts from C1) and the one with smaller ADP's (starts from C5):



(The molecule with large ADP's starts from C1)

Plot the molecules in Diamond; activate atom labels;

EITHER note the desired changes and Quit Diamond;

OR rename atoms in Jana2006 running parallel with Diamond (Diamond started with "Draw+continue")

(You may also keep Diamond window open and type the new labels directly to Edit atoms tool of Jana2006)

Start "Edit atoms"; select all atoms and choose "Rename the selected atoms manually"

Plot the structure and verify the labels

## 10. Splitting positions with large ADP

The largest ADP have been found for atoms C2 and C4

Start "Edit atoms" and split positions of C2 and C4, using default options for splitting

The splitting procedure created pairs C2-C2' and C4-C4', their ADP are isotropic and the same for each pair, partial occupations are  $\frac{1}{2}$  and the sum of occupancies for each pair is kept by a Restriction for the case it would be refined

Run refinement

Refinement converges with  $R(\text{obs})$  value about 10%

Start "Edit atoms" and activate refinement of occupancy for C2 and C4

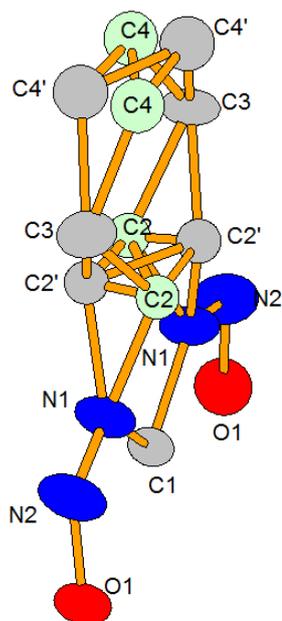
Run refinement

Refinement converges with  $R(\text{obs})$  value about 8.4%

The refined occupancies in both pairs are in the ratio 1:3, i.e. one of the split atoms in each pair is much weaker.

Plot the structure; distinguish by colors the weakly occupied carbon atoms

Activate plotting of ADP ellipsoids and plotting of labels



In the plot C4, C2 have occupancy  $\sim 0.25$ ; C4', C2' have occupancy  $\sim 0.75$ , the other atoms have a full occupancy. We can distinguish two chairs: C4-C4-C3-C2-C2-C3 and C4'-C4'-C3-C2'-C2'-C3, the latter having stronger occupation.

**Warning:** splitting of atomic positions was automatic process. In particular solution, it may happen that the labels of the strongly and weakly occupied atoms (i.e. atoms with and without comma) will be exchanged. In such a case, we recommend relabeling the atoms according to this plot in order to follow easily the cookbook.

### 11. Rigid body description

Refinement of the weakly occupied positions is unreliable because  $\frac{1}{4}$  of carbon is an electron density comparable with hydrogen. In this part, we will describe the disorder with a rigid body. For model molecule, we will take the more occupied version of the molecule.

Start "File  $\rightarrow$  Structure  $\rightarrow$  Save As" and **create a backup copy**

Start "Parameters  $\rightarrow$  Molecules  $\rightarrow$  New molecule"

Choose the name for the molecule, e.g. "molec"

Select "Atomic part"; NEXT

[On the screen: Select atoms for the molecule]

Select O1, N1, N2, C1, C2', C3, C4'

OK

The selected atoms will be removed from the atomic part of the structure model, and they will be used as a pattern molecule. This pattern molecule will be later on transformed to the actual places in the crystal structure by a translation vector and three rotations

[On the screen: Define the molecular reference point]

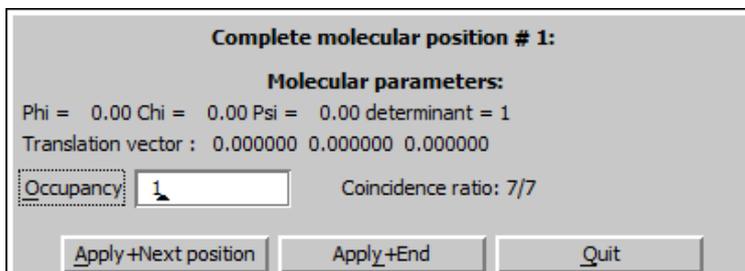
Reference point of the molecule is used for calculation of symmetry restrictions. In our case C1 is located in a special position while the other atoms not. Therefore C1 should be the reference point

Select "Explicit"; for "Reference point" type C1; NEXT

[On the screen: complete molecular position #1]

For the placement of the model molecule to the first actual position the program shows

zero rotations and zero translation. This is because the model molecule has been taken from the existing atoms in the atomic part of the structure model. "Coincidence ratio 7/7" means that 7 atoms of the model molecule placed to the actual position #1 coincides with existing seven atoms in the atomic part. This is correct - the 7 atoms have been used for the model molecule.



For "Occupancy" type 0.75;

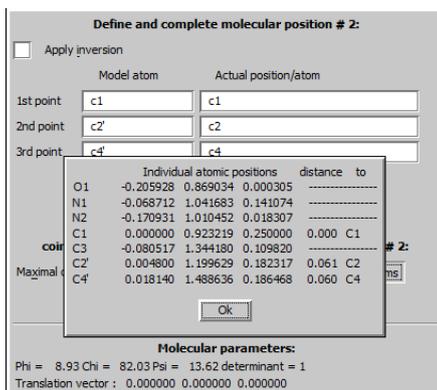
"Apply + Next position"

[On the screen: Define and complete molecular position #2]

In this dialogue we will define rotations and a translation vector for placing the model molecule to the second actual position. This is done by defining three atoms of the model molecule and three atoms in the atomic part of the structure model, which should coincide. In order to get correct placement of the second position the split atom positions must be used.

Use C1, C2', C4' as model atoms and C1, C2 and C4 for the actual position

Press "Show coinciding atoms"



We expected that the 7 atoms in the actual position will coincide with 7 atoms in the atomic part. However, we obtained only 3 coinciding atoms .

OK to quit information window

Select "Apply inversion"; Press "Show coinciding atoms"

Define and complete molecular position # 2:

Apply inversion

	Model atom	Actual position/atom
1st point	c1	c1
2nd point	c2'	c2
3rd point	c4'	c4

	Individual atomic positions	distance to	
O1	0.160020 0.847047 0.138719	0.155	O1
N1	0.060140 1.033941 0.189811	0.193	N1
N2	0.139442 0.991804 0.135700	0.108	N2
C1	0.000000 0.923219 0.250000	0.000	C1
C3	0.093749 1.333709 0.175734	0.096	C3
C2'	0.004800 1.199629 0.182317	0.061	C2
C4'	0.018140 1.488636 0.186468	0.060	C4

Molecular parameters:  
 Phi = 179.52 Chi = -53.10 Psi = -0.70 determinant = -1  
 Translation vector : 0.000000 0.000000 0.000000  
 Occupancy 1 Coincidence ratio: 3/7

Now we have seven coinciding atoms. Thus to get the second position the rotation must be combined with inversion. The inversion centre is the reference point.

For "Occupancy" type 0.25

"Apply + End"

Start "Edit atoms"

The atoms of the model molecule are blue

Rename C2' to C2 and C4' to C4

Change occupancy of C2 and C4 to 1 (the model molecule has the full occupancy)

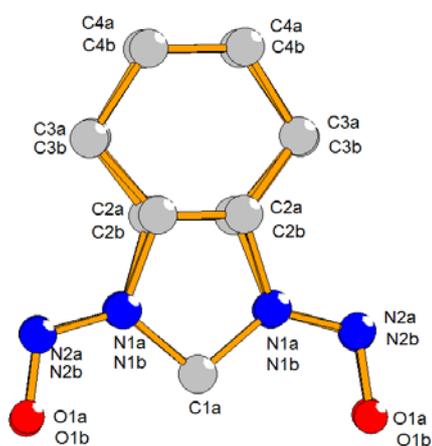
Change ADP of C2, C4 to "harmonic"

Quit "Edit atoms"

Plot the structure

Before starting Diamond Jana transforms the molecular positions back to the atomic part.

Atoms of the first position will obtain the suffix "a", the second position has the suffix "b"



Note that all positions except C1 are now more or less split. Close positions in the rigid body model are not problematic because the individual atomic parameters will be refined only once for the model molecule.

Start "Parameters → Molecules → Edit"

Select refinement of "aimol" (this is occupancy of the molecular position)

OK; YES to save changes

Start Refinement options

In page "Various" go to "Restrictions"

Define a new restriction command between Molec#1 and Molec#2: coordinates and ADP parameters will not be restricted but molecular occupancies will keep the overall sum.

OK; OK; Yes+Start

Refinement converges with  $R(\text{obs})$  value about 8%  
The  $R$  value is still rather high but in a light structure missing hydrogen atoms may play an important role

## 12. Local coordinate system

Atoms in the atomic part are generated according to the space group symmetry. In order to generate atoms within a model molecule, we have to define local symmetry of the molecule. After the placement of the model molecule to the final position in the unit cell, the local symmetry and the space group symmetry are combined.

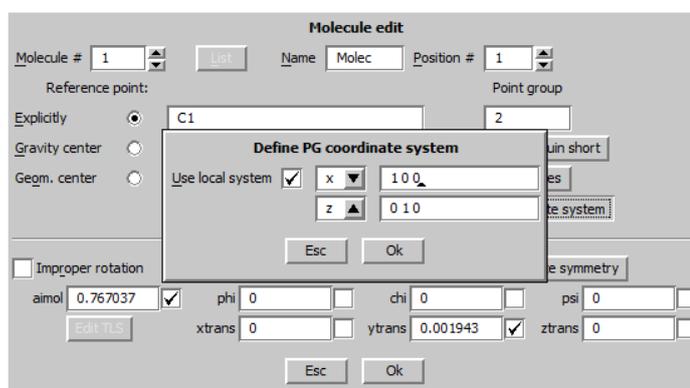
In our case, if we define the local symmetry 1, still keeping only one half of atoms in the model molecule, the molecule would be completed after correct placement on a two-fold crystallographic axis. However, we could not keep hydrogens of the carbon C1 in geometrically expected positions because the keep command applies to the model molecule and hydrogen positions need to be generated by symmetry. For this reason, we have to define the local symmetry.

In our case, the model molecule has a two-fold axis along  $b$  and its point group will be 2. Because the internal definition of the point group expects rotation along  $c$  we have to define the point group 2 and change the local coordinate system.

Start "Parameters → Molecules → Edit"

For "point group" type "2"; TAB

Check "use local system" and define "1 0 0" for x and "0 1 0" for z



OK; OK; YES to save changes

Run refinement – the results should be the same like without the local symmetry

## 13. Hydrogen atoms

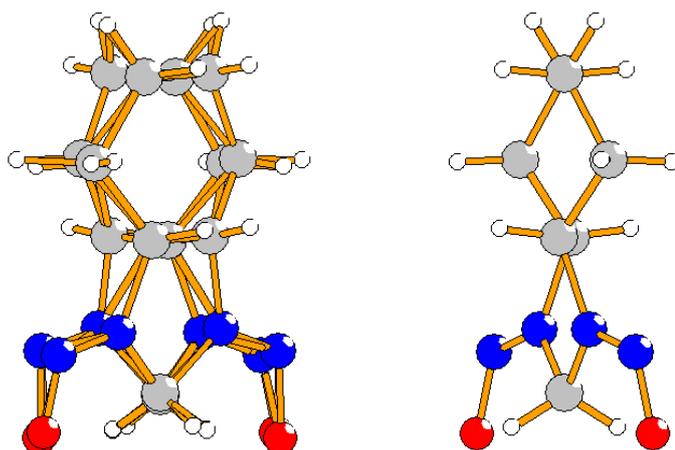
Start "Edit atoms"

Select all carbon atoms including the ones of the model molecule

Add hydrogen atoms in automatic mode

Verify by plotting placement of hydrogen atoms

For suppressing one of the disordered positions its molecular occupapcy can be temporarily set to zero through "Parameters → Molecules → Edit". In such case, do not forget to set it back after the plotting.



### Run refinement

R value drops to 3.9%, GOF=2.6.

### Start EditM50

Go to the page "Composition"

Press "Formula from M40"

*It should print C7 H12 N4 O2 for Z=4*

Start Refinement options, page Basic

Change Instability factor from 0.01 to 0.02

### Run refinement

*Refinement converges with  $R(\text{obs})=3.9\%$ , GOF=2.0.*

*Ideally, the instability factor should be determined for a given instrument. In the practice we know that it ranges between 0.01 and 0.02.*

*GOF about 2.0 may indicate that disorder is not described exactly. It may also indicate that the data contains information about bonding effects.*

### Start Fourier options

In page Basic define "Map type" "Fobs-Fcalc difference Fourier"

Run difference Fourier

In the listing of Fourier check list of maxima and minima

*The residua are small like for fully solved structure*

*Last step, which is skipped in this example would be comparison of the molecular model with a model built from split atom positions. The resulting R value would be very similar to that of the molecular model.*



# Example 8.3: DFerrocene

Simple disordered structure from neutron single crystal data

Revised: 5 April 2018

## DFerrocene

Single crystal data measured with SXD ISIS diffractometer

Input file: DFerrocene.int

### 1. Creating new jobname

**Start Jana2006**

[On the screen: Basic Jana window]

**"File → Structure → New" opens a file manager**

[On the screen: New : Select name of the structure]

**Left pane: locate directory with input files**

**Right pane: double-click dferrocene**

### 2. Import Wizard

[On the screen: Specify type of the file to be imported]

**Select "Single crystal: known diffractometer format", NEXT**

[On the screen: Data reduction file from]

**Select "ISIS SXD"; NEXT**

File name is automatically set to "hurea.int".

[On the screen: Complete/Correct experimental parameters]

**Modify temperature to 200; NEXT**

[On the screen: Define the reference cell/split by twinning]

**NEXT; FINISH**

[On the screen: Data repository]

**OK; Yes, to accept changes**

### 3. Creation of the refinement reflection file

**Leave the form unchanged; NEXT; OK; Finish**

*SXD, the single-crystal diffractometer at the ISIS spallation neutron source, uses an array of two-dimensional position-sensitive detectors and the neutron time-of-flight technique to measure diffraction data throughout very large volumes of reciprocal space for each fixed orientation of a single-crystal sample. [from: D.A.Keen, M.Gutmann and C.C.Wilson Journal of Applied Crystallography, (2006), 39, 714-722.].*

*The "int" file contains all necessary information to create Jana reflection file for multi-wave data. As intensities of reflections are measured by TOF method with more than one detector the step of merging data and symmetry test in Jana is skipped.*

### 4. Structure solution

[On the screen: Structure solution]

**Type formula C10 D10 Fe; Formula units 2**

**Press "Change the space group";**

[On the screen: Define space group]

File the space group P21/a, monoclinic axis “b” (P 1 21/a 1)  
 Go through the dialog for creation of the refinement of the reflection file;  
 Select “Use Superflip”  
 For peak interpretation select EDMA – fixed composition  
 Check “Repeat Superflip: Number of runs”  
 Set “Maxcycles” to 2000 and Number of runs 10;

**Structure solution**

use SIR 2011
Formula C10 D10 Fe

use Superflip
 Formula units 2 Calculate density

use Shexl
 Actual space group: P21/a Change the space group

---

allow manual editing of the command file before start  
 use previously prepared input file for Superflip  
 use old solution and reinterpret it Biso: 0  
 Repeat Superflip: Until the convergence detected Maxcycles: 2000  
 Repeat Superflip: Number of runs => 10  
 Use local normalization  
 Use a specific random seed  
 Define explicitly delta value

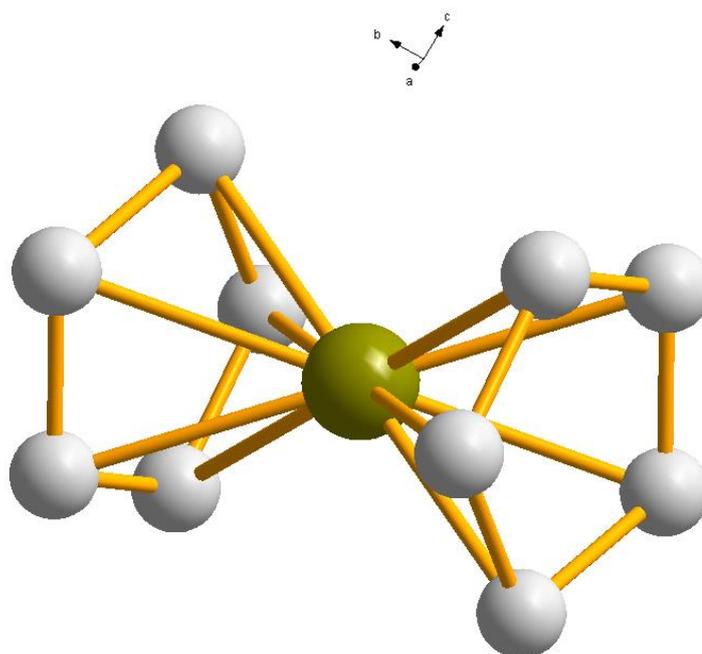
Iteration scheme:  CF For peak search use:  EDMA - fixed composition  
 LDE  EDMA - fixed number of atoms    
 AAR  EDMA - peak interpretation by Jana2006

Starting model:  Random phases  Peaks from Jana2006  
 Patterson superposition map  Peaks from Jana2006 but first run Fourier

Run solution
Open the listing
Draw structure
Draw 3d map

Accept last solution
Quit

Press “Run solution” to start Superflip  
 Press “Draw structure”



The model seems to be correct the D atoms will be localized in the next step.  
[Accept last solution.](#)

#### 5. Refining the structure

[On the screen: basic window of Jana]

[Start Refine](#)

Refinement converge with  $R(obs)$  about 42%

#### 6. Completing the structure

[On the screen: basic window of Jana]

[Start Fourier option](#)

In the page "Basic" define "F(obs)-F(calc) – difference Fourier)

[OK; YES+START](#)

[OK to start procedure for including new atoms](#)

[Go through the list of found peaks to add missing D atoms:](#)

List of peaks			Equivalent coordinates			Distance	Atom
Max1	Min3		0.577309	0.140873	0.613336	- as typed in	
Max2	Min4		-0.077309	-0.359127	0.386664	1.13	C2
Max3	Min5		0.077309	0.359127	0.613336	2.17	C5
Max4	Min6		0.077309	0.359127	0.613336	2.56	C3
Max5	Min7		0.077309	0.359127	0.613336	2.83	Fe1
Max6	Min8		-0.077309	-0.359127	0.386664	2.83	Fe1
Max7	Min9		-0.422691	0.140873	0.613336	2.90	C1
Max8	Min10		0.077309	-0.640873	0.613336	2.97	C2
Max9							
Max10							
Min1							
Min2							

Peak : Max1 Charge : 4.710

Include selected peak

No peaks included  
No atom modified

Finish

**Complete information for the new atom**

Name of the atom:

Uiso:

Site symmetry order: 1

Occupancy reduction:

Atomic type:

Finish; Yes to include new atoms;  
 Start Editm40; Select all carbon and deuterium atoms;  
 Press Action and select "Make symmetrically contiguous motifs";  
 Yes to save changes;

## 7. Refinement of the structure

[On the screen: basic window of Jana]

Start Refine

Refinement converge with  $R(\text{obs})$  about .1%

Press "Select all" and "Action → Edit/define"

Choose "harmonic" for ADP parameters. This defines anisotropic temperature parameters for all atoms. OK, OK, YES to save changes

Start Refine

Refinement converge with  $R(\text{obs})$  about 25.5%

## 8. Extinction correction

[On the screen: basic window of Jana]

Go to “Parameters → Extinction”

The screenshot shows the 'Extinction model' dialog box in the Jana software. It contains several radio button options for selecting an extinction model: 'None', 'Isotropic - Becker & Coppens', 'Anisotropic - Becker & Coppens', and 'SHELX model'. There are also radio buttons for 'Type 1', 'Type 2', and 'Mixed'. Additionally, there are radio buttons for 'Gaussian' and 'Lorentzian'. A text input field for 'Radius [cm]' is set to '0.1' with a note 'used only if tbar not present on M90 file'. Below this is the 'Extinction parameters' section with a 'Giso' input field set to '0.01' and a checked checkbox. At the bottom, there are buttons for 'Refine all', 'Fix all', 'Reset', 'Esc', and 'Ok'.

Results:

Isotropic – Becker & Coppens, Type 1, Gaussian  $R(\text{obs})=18.3\%$

Isotropic – Becker & Coppens, Type 1, Lorentzian  $R(\text{obs})=18.5\%$

Isotropic – Becker & Coppens, Type 2,  $R(\text{obs})=18.4\%$

Continue with the best fitting model Isotropic – Becker & Coppens, Type 1, Gaussian

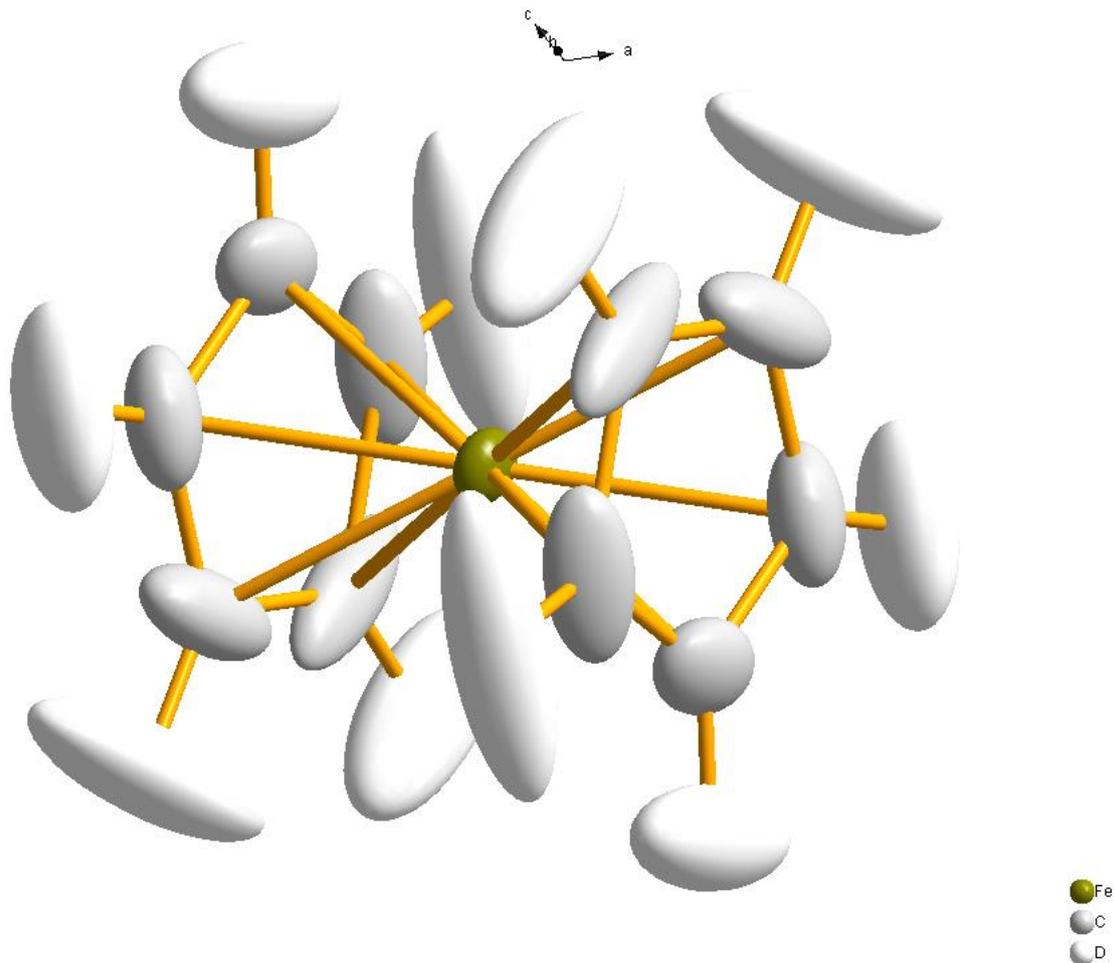
## 9. Disorder in the structure

[On the screen: basic window of Jana]

Start “Plot structure” with Diamond

Plot the structure with 

Use  at the bottom toolbar of Diamond to see ADP ellipsoids.



*The ellipsoids of C and D atoms are strongly prolonged in way, which clearly demonstrate a rigid body disorder.*

Quit Diamond

#### 10. **Atom split model**

[On the screen: basic window of Jana]

Start Edit atoms

Select all C and D atoms; Press Action and run "Split atom position"

**Split atomic position for : C1**

Name of the split atom:

Atomic type:  ▼

Relative occupancy of the split atom:

Shift of the split atom:

defined manually ->

derived from ADP

Reset ADP to isotropic

Generate restrict commands for REFIN

Restrict the split atoms to have identical positions

*The atomic position will be split into two positions with a shift which is derived from the ADP ellipsoid. The above choice means newly created atoms will have identical isotropic ADPs and their occupancies will be restricted to keep a constants sum.*

OK; Yes to save changes

Right-Click on "Refine"

[On the screen: Refine commands]

Set "Number of cycles" to 30

OK; Yes+start

*Refinement converge with R(obs) about 23.7% for 83 refined parameters*

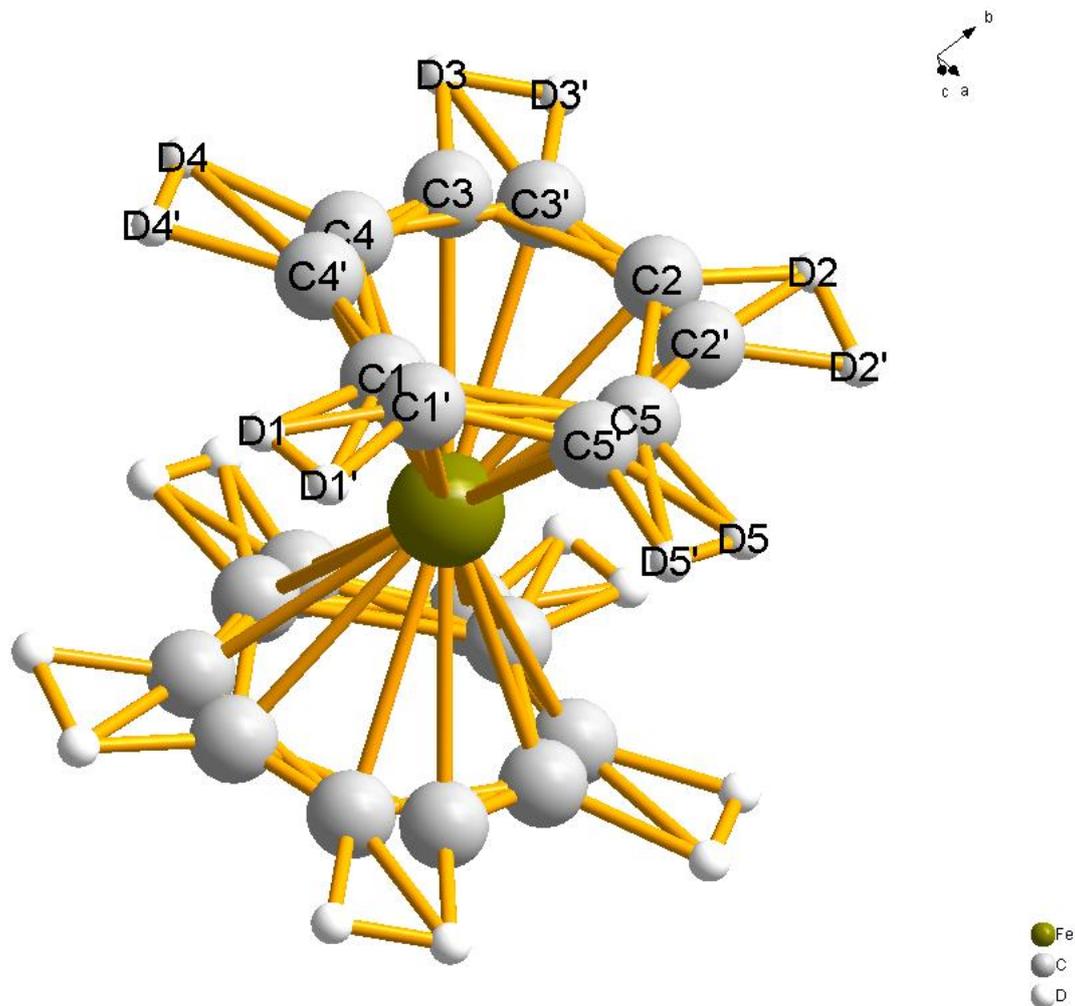
*The fit is considerably worse that we got from the simple anisotropic model. The split model can help us to get a starting positions for two split molecular fragments C5D5*

## 11. Rigid body model

[On the screen: basic window of Jana]

Start "Plot structure" with Diamond

Plot the structure with 



Two molecular fragments make the atoms: C1,D1,C4,D4,C3',D3',C2',D2',C5',D5' and C1',D1',C4',D4',C3,D3,C2,D2,C5,D5.

“Parameters → Molecule → New molecule” starts the procedure for building a new molecule

[On the screen: Atoms of the new molecule from]

Select from Atomic part;

Type in the name of molecule “Cp” (cyclopentadienyl) ;NEXT

[On the screen: Select atoms for the new molecule]

Select C1,D1,C4,D4,C3',D3',C2',D2',C5' and D5'; OK

[On the screen: Define the molecular reference point:]

Check “Gravity center”; OK

[On the screen: Complete molecular position #1:]

Press “Apply+Next Position”;

[On the screen: Complete molecular position #2:]

Fill the three model atoms – C1, C2' and C3';

Any three atoms can be used as in cyclopentadienyl none of three atoms lay on the line;

Fill the three model atoms – C1', C2 and C3;

Change the maximal coincidence distance to 0.5; Press “Show coinciding atoms”

The coincidence ration should be 10/10;

**Define and complete molecular position # 2:**

Apply inversion

	Model atom	Actual position/atom
1st point	C1	C1'
2nd point	C2'	C2
3rd point	C3'	C3

**Options for removing of atoms from atomic block  
coinciding with those generated from molecular position # 2:**

Maximal coincidence distance

---

**Molecular parameters:**

Phi = -4.92 Chi = 15.12 Psi = -19.65 determinant = 1  
Translation vector : -0.017939 -0.012244 -0.009167

Occupancy  Coincidence ratio: 10/10

Press Apply+End;

## 12. Refining the rigid bode model

[On the screen: basic window of Jana]

Start Refine

Refinement converge with  $R(\text{obs})$  about 24.52% for 59 refined parameters

"Parameters → Molecule → Edit"

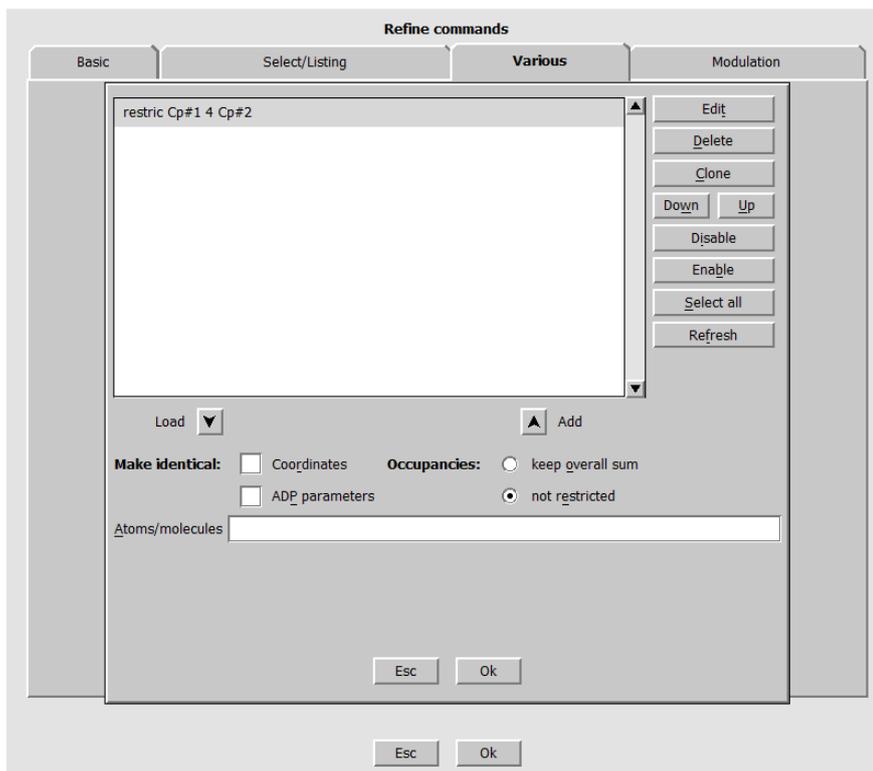
Activate refinement of "aimol" i.e. relative occupancy of the first molecular position;

Right-Click on "Refine"

[On the screen: Refine commands]

Go to "Restrictions"

Define two molecular positions Cp#1 and Cp#2 and check "keep overall sum"; Add; Ok; Ok



### Yes+Start

*Refinement converge with  $R(\text{obs})$  about 24.47% for 60 refined parameters. This means almost no change – two positions are equally occupied.*

### Run Edit atoms

Select all atoms of the molecule (blue ones); Double click with mouse;

Activate "Use TLS"; Ok; Ok; Yes to rewrite changed files;

Run Refine;

*Refinement converge with  $R(\text{obs})$  about 10.6% for 90 refined parameters*

## 13. Corrected structure

[On the screen: basic window of Jana]

*Multi-wave data collected with several detectors cannot be merged by a usual data reduction procedure and therefore all  $R$  values are considerably worse than for other diffraction techniques. For this reason a special option which creates so called "corrected" structure has been included into the Jana software. This method uses the refined scales and extinction parameters to correct the measured intensities.*

Go to "Tools → Special tools → Creation of "corrected" structure"

[On the screen: Create a corrected structure]

Define name for the corrected structure "\_corrected"; OK

After the creation of the refinement reflection file continue with the corrected structure

[On the screen: basic window of Jana]

Start Refine

*Refinement converge with  $R(\text{obs})$  about 8.81%*

# Example 8.4: Boroncage

Revised: 8 March 2019

Data	Topic	Level
X-ray single crystal data	Structure with disorder solved from a non-merohedric twin	Intermediate

## Tasks

Disordered structure solved with help of rigid body

- creating new jobname
- reading input file in the hklf5 format with twinning
- determination of symmetry
- solving a structure with charge flipping
- completing the structure
- basic refinement
- identification of disorder
- description of disorder with several positions of one molecule

## Initial data

### Data

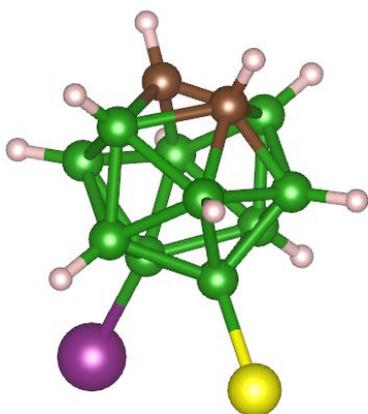
Single crystal data measured with Oxford Diffraction four-circle diffractometer

### Input files:

Cage\_hklf5.hkl, cage\_hklf5.cif\_od

### Additional information:

Chemical formula: B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>IS



Frame scaling, absorption correction: done by the diffractometer software

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## Instructions

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### I. Data import

#### Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files; Right pane: double-click cage\_hklf5 (Step2)

#### Import wizard

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction → CCD”; NEXT

Select “Input from “cif\_od” file”; OK

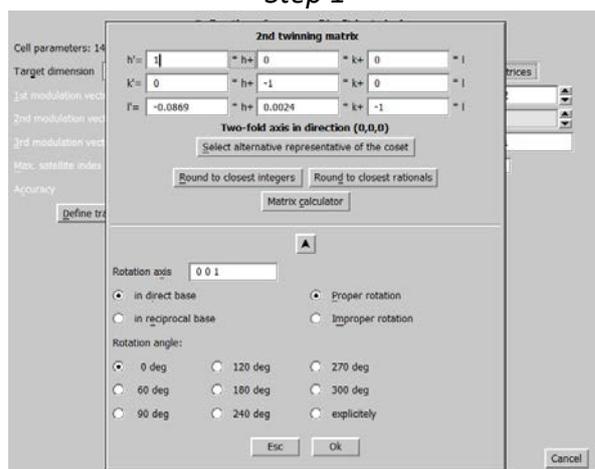
Leave all settings unchanged; NEXT

In the next window, click the button “Twinning matrices” to check that the twinning was properly read from the cif\_od file; (Step1)

OK; Yes to accept the twinning matrix and close the window; NEXT

The program reads 10823 reflections from the hkl file

#### Step 1



For the absorption correction select “None or done before importing”; NEXT; FINISH

OK to accept data repository; NEXT to start symmetry wizard

### II. Symmetry and data merging

#### 5. Symmetry wizard

[On the screen: “Tolerances for crystal system recognition”.]

Leave all settings default; NEXT

“Continue with the basic cell”; NEXT

[On the screen: Select Laue symmetry]

Select Monoclinic Laue symmetry; NEXT

Note

Note the high  $R_{int}$  for both Laue classes and low redundancy. This is the consequence of the twinning in the data.

[On the screen: Select cell centering]

Select primitive unit cell; NEXT

[On the screen: Select space group]

#### Notes

The window shows possible space groups. In this case all statistics show zeroes and all space groups have the same FOM (figure of merit). This is due to the twinning described with the *hklf5* format, which prevents the detection of systematic absences from the data. No distinction between the space groups can thus be done and we need to guess. We select  $P2_1/n$ , because it is a very common space group. The space group will later be independently checked by structure solution in Superflip (see part III – Structure solution).

Select  $P2_1/n$ ; NEXT

Accept the space group in the original cell setting; FINISH

Symmetry is saved in file *cage\_hklf5.m50*.

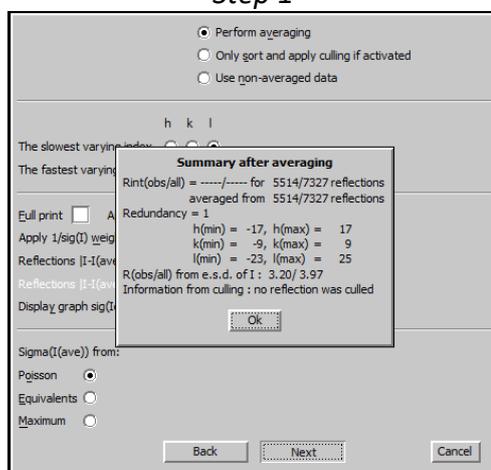
Creating refinement reflection file

#### Notes

In this step the program creates file *cage\_hklf5.m90* containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.

NEXT to confirm threshold 3sigma; OK (to confirm Information windows); NEXT (Step1)

#### Step 1



#### Notes

Due to the twinning described with the *hklf5* format, no merging can be performed and no  $R_{int}$  is calculated.

OK; Select "Accept the new DatBlock and calculate coverage"; FINISH

### III. Structure solution

#### 6. Structure solution wizard

[On the screen: Structure solution]

In "Formula" textbox type list of chemical elements: C B I S H

#### Notes

Superflip as well as SHELXT does not need exact information about chemical elements because it is required only for analysis of the resulting electron density. Other solution methods like SIR may need the correct formula and number of formula units. In this example, usage of SHELXT is not possible because we would lose the twinning information.

Select "Use Superflip"

Leave other settings default; press "Run solution"

[On the screen: window of Superflip is replaced after reaching the convergence with the listing of Superflip](Step2)

#### Notes

Superflip converges (after noise suppression) with R value ~24%. The space group suggested from the symmetry search in the electron density map is P21/n and it thus confirms our initial guess.

#### Step 1

```
5 cycles of noise suppression follow:
R: 24.337  charge: 0.00  Peaks: 8.93

#####
# Checking the density for symmetry #
#####

Symmetry operations compatible with the lattice and centering:

Symmetry operation      agreement factor
n(0,1,0):      1/2+x1      -x2      1/2+x3      0.641      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
2_1(0,1,0):      -x1      1/2+x2      -x3      8.748      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
-1:      -x1      -x2      -x3      9.501      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
2(0,1,0):      -x1      x2      -x3      43.765      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
a(0,1,0):      1/2+x1      -x2      x3      52.472      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
c(0,1,0):      x1      -x2      1/2+x3      53.690      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
m(0,1,0):      x1      -x2      x3      62.353      XXXXXXXXXXXXXXXXXXXXXXX

-----
Space group derived from the symmetry operations:
-----
HM symbol: P21/n
Hall symbol: -P 2yn
Fingerprint: 3300220n{03}27 (0,0,0)
Symmetry operations:
1:      x1      x2      x3
2_1(0,1,0):      1/2-x1      1/2+x2      1/2-x3
-1:      -x1      -x2      -x3
n(0,1,0):      1/2+x1      1/2-x2      1/2+x3
```

Press CLOSE to leave the listing

Verification of the structure solution from the structure solution wizard

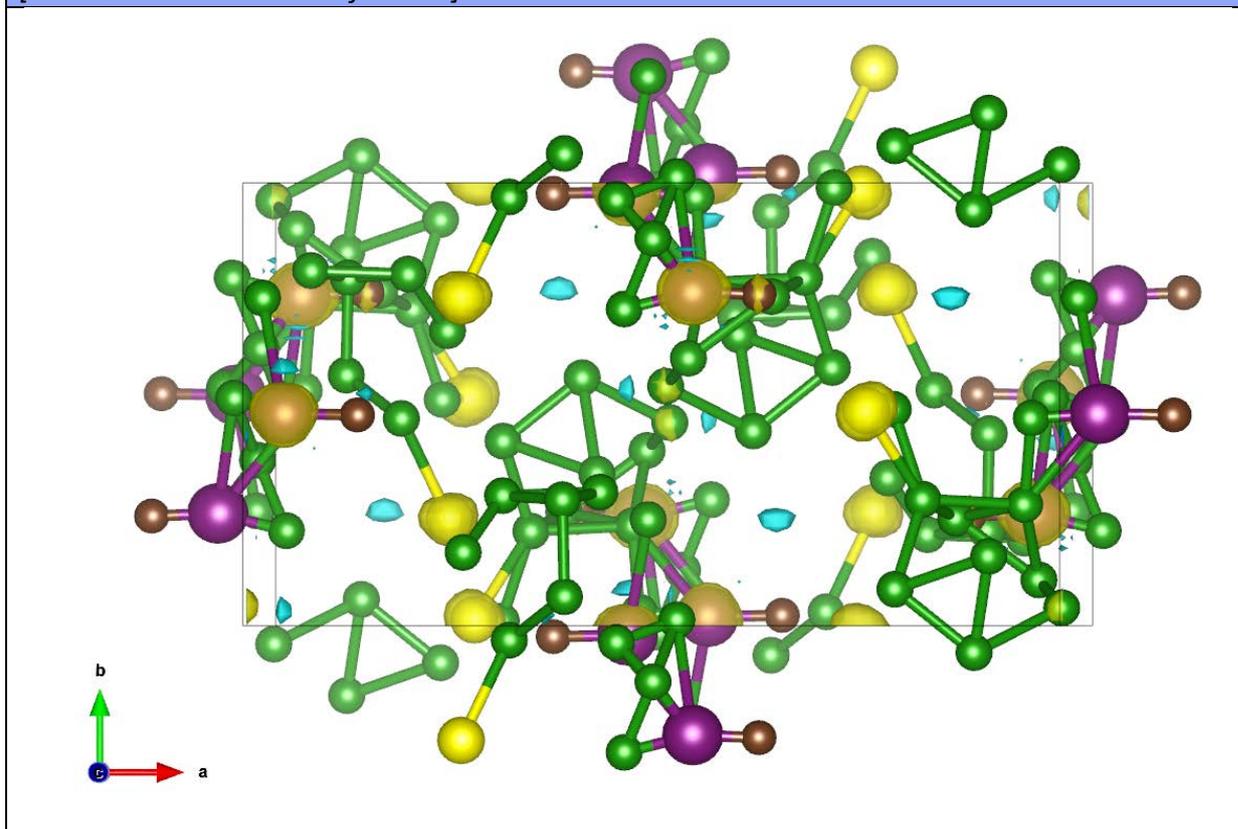
[On the screen: Structure solution]

Press "Draw 3D map"

#### Notes

This button starts Vesta (requires path to Vesta set in Tools Programs), which plots the electron density produced by Superflip together with atomic positions found by Jana2006.

[On the screen: window of VESTA]



#### Notes

Look closely at the structure. Compare with the expected molecule shown at the beginning of the tutorial. You will see that large part of the structure is present, but some atoms are spurious and quite a few atoms are missing.

Close VESTA; Do not save the changes in VESTA;

Click "Accept last solution"

Completing and correcting the structure

[On the screen: basic Jana window]

Start Refine

Refinement converges with R value ~13%

Start Edit Atoms; Press Select rejected; Action → Delete selected atoms

Start Refine

Refinement converges with R value ~13%

Right click on Fourier; select "F(obs)-F(calc) – difference Fourier"; OK; Yes+Start

Yes to start adding new atoms; OK

[On the screen: dialog for adding new atoms]

Add all maxima with reasonable (~1.7 Å) distance of some existing carbon or boron:

In the left pane, select the maximum to be added

In the right pane, check the distances and press "Include selected peak"

Name of atom: B\*; OK

Repeat the process for other maxima

FINISH; YES to include new atoms

Start Refine

*Refinement converges with R value ~9.5% with 113 refined parameters*

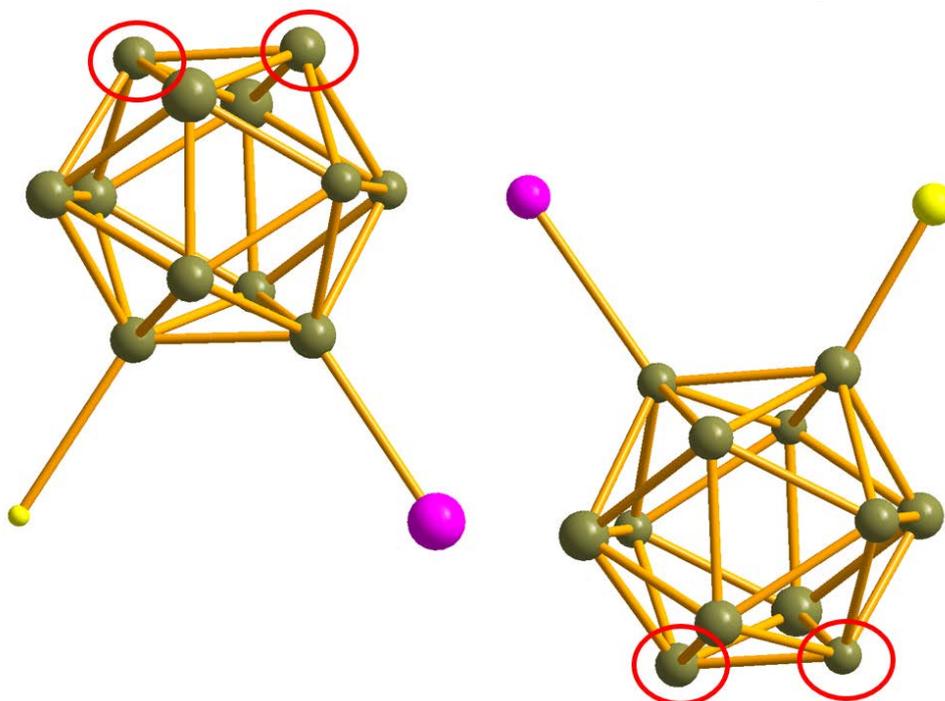
*In case of less parameters, something is missing and difference Fourier must be repeated.*

*The resulting number of atoms is 28.*

*[On the screen: basic Jana window]*

Double click the icon "Plot Structure"; "Draw + Continue"

In Diamond, press "Get Molecules directly" and activate plotting of ellipsoids



#### Notes

*We can see two complete cages, and the only issue is assignment of carbons. From chemistry, it follows that in each cage carbons are the two atoms opposite the boron atoms with I and S. These atoms are highlighted in the figure.*

*Another remarkable feature is rather small  $U_{iso}$  of Sulphur and rather large  $U_{iso}$  of iodine in one of the cages.*

In Jana2006, Edit Atoms, change the highlighted atoms to carbon and all other atoms of the cage to boron

Still in Edit atoms, select all atoms and press Action → "Rename atoms to atom type + number"

Select I1, I2, S1, S2; Action → Edit/define atoms

Select harmonic (anisotropic) ADP; OK; OK; YES to save changes

Run Refine

*Refinement converges with R value ~7% and 133 refined parameters*

*Some ADP are negative*

YES to open the refinement listing

Press Go to; select "List of serious warnings"

*We can see that one of S atoms has non-positive ADP. Together with the fact of strange  $U_{iso}$*

*if Sulphur and iodine, this is clear we should try refinement of their occupancy*

Close the refinement listing

Start Edit Atoms

Select I1, I2, S1, S2; Action → Edit/define atoms → Page Edit

Activate refinement of “ai”; OK; OK; YES to save changes

Run Refine

*Refinement converges with R value ~5% and 137 refined parameters*

*No serious warning are present*

Start Edit Atoms

Select I1; Action → Edit/define atoms → Page Edit

Look at “ai” (site occupancy) of I1

Using arrows close the List button, look at “ai” of I2, S1 and S2

Quit Edit atoms

#### Notes

*We can see “ai” (site occupancy) of I1 and I2 is decreased while occupancy of sulphur is significantly increased in one case and slightly increased in the second case. **This can be explained by assuming the disorder of the molecule between the two positions, in which all the boron and carbon atoms are essentially in the same position, but iodine and sulphur are exchanged.** In the following, we will describe this disorder using the rigid body approach.*

#### IV. Setting up molecules and molecular positions

##### 1. Preliminary work

Start File → Structure → Save As and create a backup copy

Start Edit atoms; Select all; Action → Make symmetrically contiguous motifs

Still in Edit atoms: Select I1, I2, S1, S2;

Action → Edit/define → Edit; double-click “ai” textbox and change its value to 1, and disable its refinement

Change ADP of I1, I2, S1, S2 to isotropic

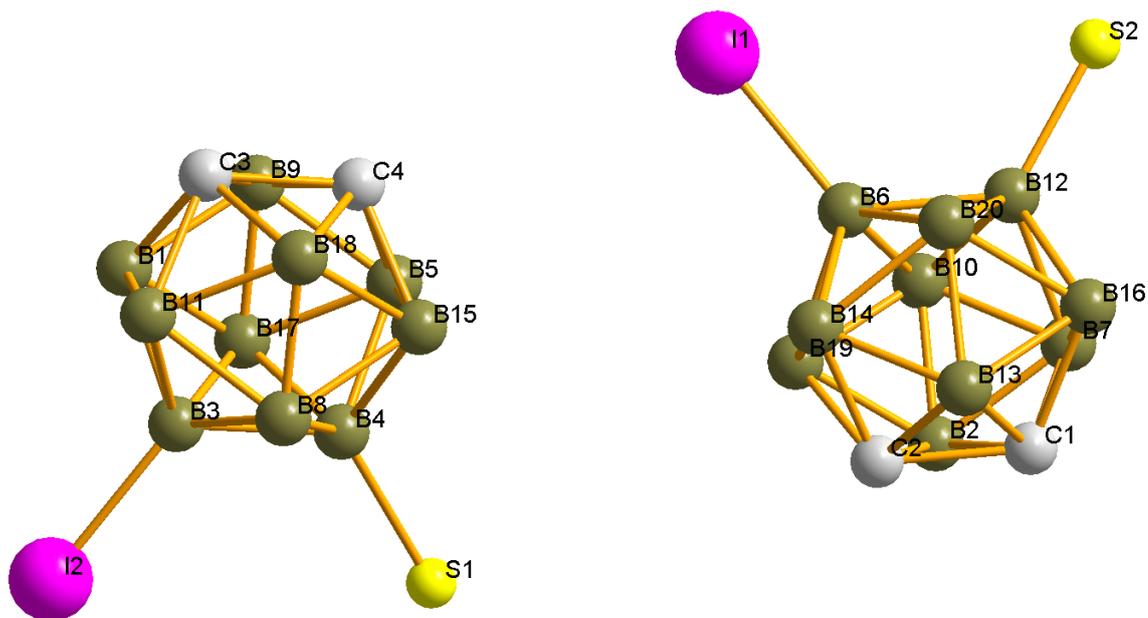
OK; OK; YES to save changes

Plot structure: in Diamond, use the button  (Add all atoms and bonds), which adds atoms like they are in M40 (i.e., without symmetry transformation). Connect atoms with bonds.

#### Notes

*If you see two complete cages that means the previously used command “Make symmetrically contiguous motifs” has been working correctly. The properly connected sets are necessary for work with rigid body.*

Still in Diamond, plot labels of atoms



Note labels of three atoms from the first cage and three corresponding atoms from the second cage.

#### Notes

*In our example, the possible three pairs of atoms are I2-I1, S1-S2, C4-C1 (in your solution, labels might be different). In next steps, the procedure for transforming the first cage to the second one will use atoms I2, S1 and C4 of the first cage and create a transformation matrix + translation vector for transforming these three atoms to positions of I1, S2 and C1.*

Note labels of all atoms of the first cage (in our case, I2, S1, C3, C4, B1, B11, B3, B8, B4, B17, B18, B5, B15, B9, 14 atoms)

2. Defining the molecule from atomic part

[On the screen: basic window of Jana]

Go to "Parameters → Molecules → New molecule"

Name the molecule "cage"; NEXT

Select the previously noted 14 atoms belonging to the first molecule; OK

Select gravity center as the molecular reference point; NEXT

Leave all setting default, click "Apply + Next position"

To define the second position, identify three pairs of corresponding atoms between the first and second instance of the molecule in the structure. In our example, the pairs are I2-I1, S1-S2, and C4-C1. In your case, labels might differ.

**Define and complete molecular position # 2:**

Apply inversion

	Model atom	Actual position/atom
1st point	I2	I1
2nd point	S1	S2
3rd point	C4	C1

Select the actual atom

Fill by a saved point

**Options for removing of atoms from atomic block coinciding with those generated from molecular position # 2:**

Maximal coincidence distance: 0.3

---

**Molecular parameters:**

Phi = -3.34 Chi = 12.40 Psi = 150.54 determinant = 1  
 Translation vector : 0.498649 0.372604 0.009049

Occupancy: 1 Coincidence ratio: 14/14

Click "Show coinciding atoms" to convince yourself that all atoms of the second molecule were correctly identified with the atoms in the reference molecule.  
 Click "Apply+End" to apply the changes.

### Start Edit Atoms

Atoms which are part of a rigid body are blue. No black atoms should be present

Select all; Action → Rename selected atoms to "atom type"+number

OK; YES to rewrite changes

### Notes

*With this procedure, we generated one reference molecule from the first of the two independent molecules, and placed this molecule in two positions, corresponding to the two molecules in the structure. We will now run a check refinement to see if we did not make any serious mistake with this modification of the structure model.*

### Checking refinement

[On the screen: basic window of Jana]

Make a backup copy of the structure through "File – Structure – Save as"

Start Parameters → Twin fractions and activate refinement of twvol2

The initial value was determined by the diffractometer software. This step could have been done sooner but the initial value is correct.

Double click the icon "Refine"

The refinement converges to an R-value of about 11.7%

```
R factors : [7327=5514+1813/64], Damping factor: 1.0000
GOF(obs)= 5.79 GOF(all)= 5.06
Number of reflections excluded due to refinement options: 0+0
R(obs)= 11.71 wR(obs)= 13.09 R(all)= 13.82 wR(all)= 13.21
Last wR(all): 14.48 13.24 13.21 13.21 13.21
Maximum change/s.u. : -0.0149 for phi[Cage#2]
```

## Notes

11.7% is a larger value than 9.5% from the previous refinement. However, the number of parameters is also much lower (64 instead of 114 of the free-atomic isotropic model with refined twvol2). The reason for the increased R-value is the fact that now atoms in both molecules have identical displacement parameters and identical mutual positions, while before the two molecules were refined independently. Given this strong restriction, the increase in R-value is not so large and we may proceed with the current model.

Set up the disordered positions of the molecules

## Notes

To place second position of the molecule that describes the disorder of Sulphur and iodine, we may either use some of the available transformation tools, or we need a set of atoms to align the new position with. In the current case the transformation between the positions is difficult to express in crystallographic coordinates, and we will therefore use the second option. In Jana, new molecular position can be aligned only to atoms in atomic part. We will thus first create duplicates of three atoms in each molecule, move it to atomic part and then use them to define the new position.

[On the screen: basic window of Jana]

Click "Edit Atoms"

Select atoms I1, S1, C1

Click "Action -> Split atomic position" (Step1)

Uncheck "Generate restrict commands for REFIN";

Set Relative occupancy of the split atom to 0 (we are making a dummy atom) (Step2)

"Apply-> Go to next";

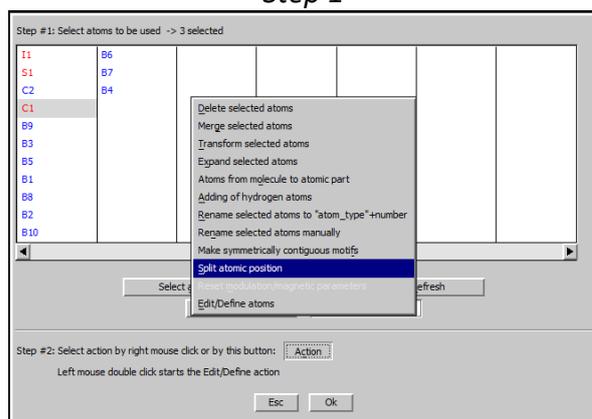
Repeat with the remaining two atoms

Select the newly created atoms I1', S1', C1'

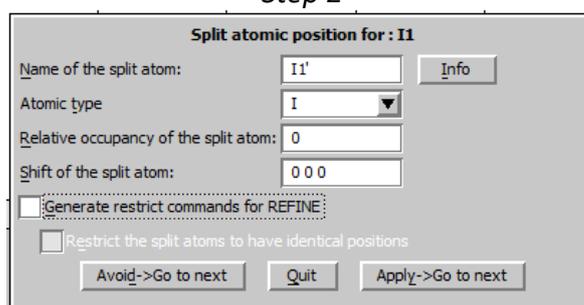
Click "Action -> Atoms from molecule to atomic part" (Step3)

"OK+Yes" to apply changes

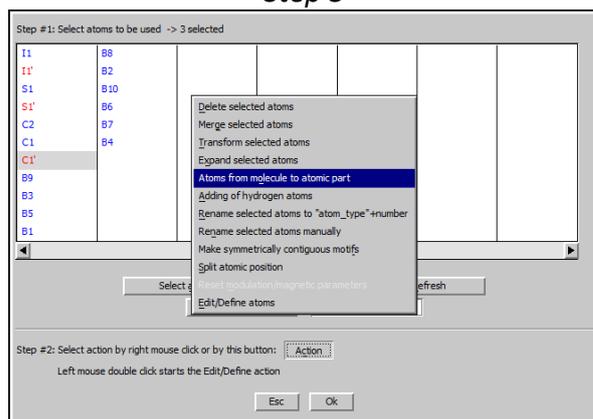
### Step 1



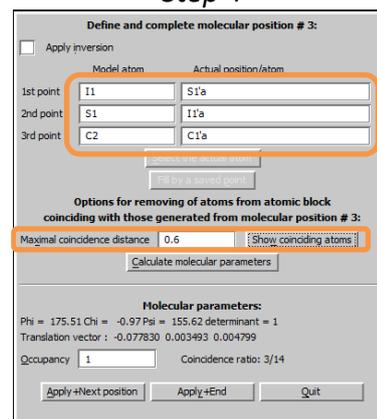
### Step 2



### Step 3



### Step 4



### Notes

We now generated six new atoms I1'a, I1'b, S1'a, S1'b, C1'a, C1'b. To place a molecular position with I1 and S1 exchanged, we will identify the model atom I1 with S1'a, S1 with I1'a and C2 with C1'a, and similarly for the second molecule.

[On the screen: basic window of Jana]

Go to "Parameters → Molecules → New position"

Type in model atoms I1, S1, C2 and actual position/atom S1'a, I1'a, C1'a Increase "maximum coincidence distance" to 0.6 (Step4)

Click "show coinciding atoms" to ensure that all three pairs have been correctly matched "Apply+Next position"

Repeat with model atoms I1, S1, C2 and actual position/atom S1'b, I1'b, C1'b "Apply+End"; "Yes" to confirm changes and rewrite files

[On the screen: basic window of Jana]

Go to "Parameters → Molecules → Edit"

Set the molecular occupancy aimol of the first position to 0.5; check the check box next to it to refine it (Step5)

Repeat for the remaining three positions

OK; "Yes" to confirm the changes

Right-click the icon Refine

[On the screen: basic window of Jana]

Go to tab Various click on "Equations" (Step6)

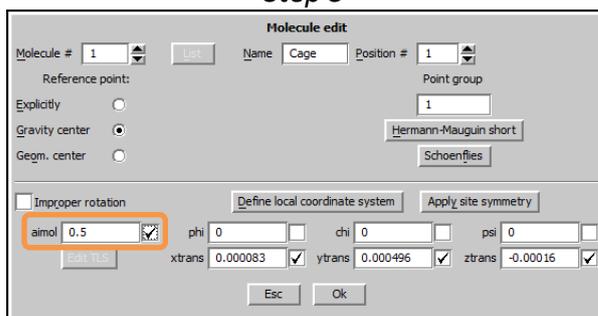
In the Equation line type "aimol[cage#3]=1-aimol[cage#1]"

Click the arrow "Add" (Step7)

In the same manner define the second equation aimol[cage#4]=1-aimol[cage#2]"

OK+OK+Yes to confirm and save new commands.

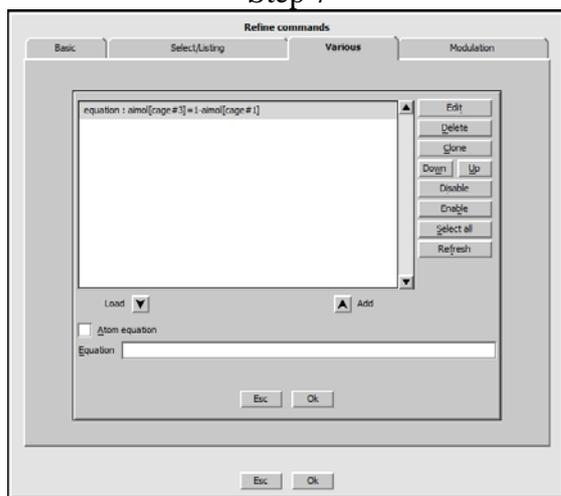
### Step 5



### Step 6



### Step 7



### Notes

Let us summarize what we did in this long series of commands. We have

- 1) Placed two new positions of the molecule that almost superimpose with the original positions except for a rotation by 180 degrees, which exchanges iodine with sulphur.
- 2) Reset the occupancies to 0.5, so that the occupancies of the superimposed molecular positions sum up to 1.
- 3) Asked Jana to refine the occupancies.
- 4) Defined equations that ensure that the sum of the occupancies of overlapping positions will remain 1.

Now we are ready to start refinement. You may first plot the structure to better understand the changes and appreciate the complexity of the created structure model.

Refine the disordered model

[On the screen: basic window of Jana]

Double click the icon "Refine"

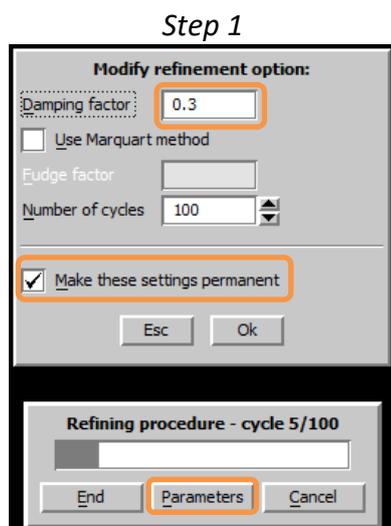
The refinement first converges quickly to relatively low R-values, but then oscillates. We need to damp the refinement

Click the button "Parameters" in the refinement window during the refinement

Set the Damping factor to 0.3; check the checkbox "Make these settings permanent; OK (Step1)

The refinement stabilizes and converges to an R-value of about 6.9%

*This is an important improvement showing that the disordered model was a good direction  
(The iodine and sulfur atoms are still isotropic)*



*[On the screen: basic window of Jana]*

Go to “Parameters → Molecules → Edit”

Check the refined occupancies of the molecular positions.

#### Notes

*The occupancy of position 1 refines to 77% and position 2 to 95%. Thus, the occupancy of the minor orientation of molecule 2 is only 5%. However, the esd of this value is 0.2% (this can be found in the refinement listing), i.e. the occupancy is small, but strongly significant. At this point it is good to check the difference Fourier map to see if the problem with the large maxima on iodine and sulphur atoms disappeared.*

#### Add hydrogen atoms

*[On the screen: basic window of Jana]*

Double click the icon “Edit atoms”

Select all atoms except I1, S1 and the two boron atoms bonded to I and S

Go to “Action → Adding of hydrogen atoms” (Step1)

Uncheck the check box “try automatic run for carbon atoms”; OK (Step2)

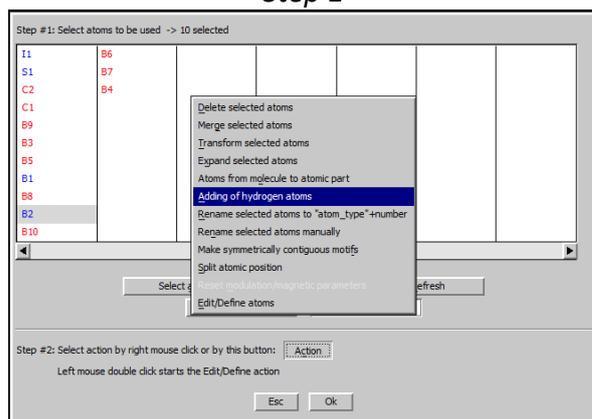
Set the hydrogen distance to 0.96Å if the title atoms is carbon, and 1.06 for boron (Step3ab)

Leave other settings default; “Apply -> Go to next”

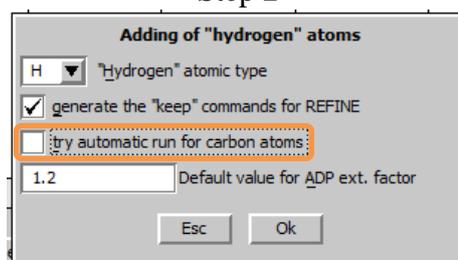
Repeat for all atoms

OK; “Yes” to confirm changes

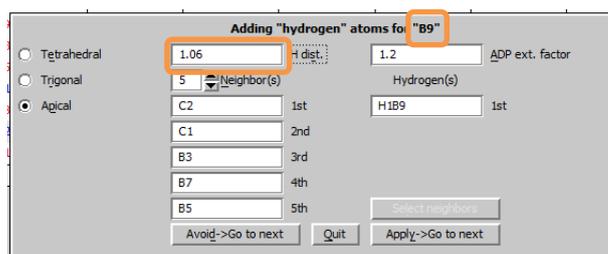
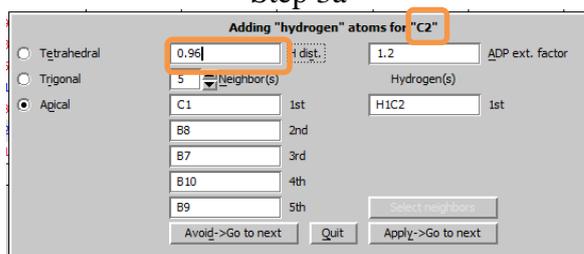
### Step 1



### Step 2



### Step 3a



[On the screen: basic window of Jana]

Double click the icon "Refine" to refine the model with hydrogen atoms

The refinement converges to an R-value of about 6.6%. Thus, the improvement by adding hydrogen atoms is only minor, which is not surprising given the presence of iodine and sulphur in the structure.

### Apply TLS tensors

#### Notes

So far all corresponding atoms in the four positions of the molecules had the same (isotropic) displacement parameters. This is quite a coarse approximation. If we change ADP of all non-hydrogen atoms to anisotropic, we will increase number of parameters from 78 to 148 but the decrease in R value will be only 0.6 %. More logical seems to be refinement of the displacement parameters of each position separately using the concept of TLS tensors. TLS tensors are a generalization of displacement parameters to groups of atoms which are assumed to undergo collective displacement.

[On the screen: basic window of Jana]

Create backup copy of your structure

Double click the icon "Edit atoms"

Select all atoms and double click any of them

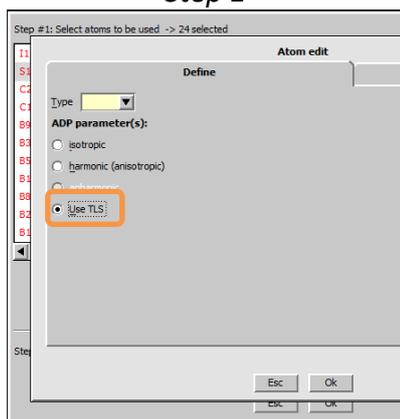
Choose "Use TLS" (Step1)

OK+OK+Yes

Double click the icon "Refine" to refine the new model

The refinement converges to an R-value of about 4.5% (Step2)

## Step 1



## Step 2

```
R factors : [7327=5514+1813/145], Damping factor: 0.3000
GOF(obs)= 2.30 GOF(all)= 2.01
Number of reflections excluded due to refinement options: 0+0
R(obs)= 4.47 wR(obs)= 5.15 R(all)= 5.62 wR(all)= 5.22
Last wR(all): 5.22 5.22 5.22 5.22 5.22 5.22 5.22 5.22
Maximum change/s.u. : 0.0484 for psi[Cage#3]
```

## Notes

*The improvement of the fit with the TLS tensors is dramatic, despite of the increase of the number of refined parameters to 144. Unfortunately, TLS tensors tend to generate physically meaningless displacements on some atoms, especially on those at the periphery of the molecules. This can be checked in the refinement listing (check for negative eigenvalues of the ADP parameters in the list towards the end of the file) or by visual inspection of the structure with ADP ellipsoids. In the current case the main molecular positions (position a and b) refine to largely acceptable displacement parameters (although a few hydrogen atoms and two non-hydrogen atoms also have non-positive ADP), but the minority positions have some of the displacement tensors non-positive definite. This not surprising especially for the position with 5% occupancy. To solve this problem, some of the TLS parameters would have to be set to zero or restrained between the two positions.*

*The most often case is that "S" tensors are the cause of the troubles. In the next step, we will set "S" tensor components to zero*

Start refinement options → page Various → fixed commands

Check "set individual"

In the Atoms/parameters textbox type s??[Cage#?]; Add

OK; OK; YES+Start

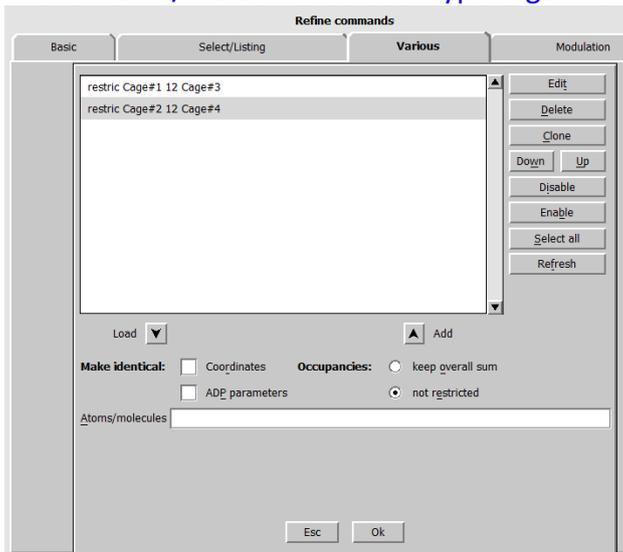
*The refinement converges to an R-value of about 4.6% with 112 parameters. This shows the S components could be omitted*

*In the next step, we will define a constraint that TLS parameters are the same for "a" and "c" cage (i.e. cage#1 and cage#3), and also for "b" and "d" cage (i.e. cage#2 and cage#4)*

Start refinement options → page Various → Restrictions

Delete three already present restrictions defined previously fro already not existing dummy atoms I1', S1' and C1'

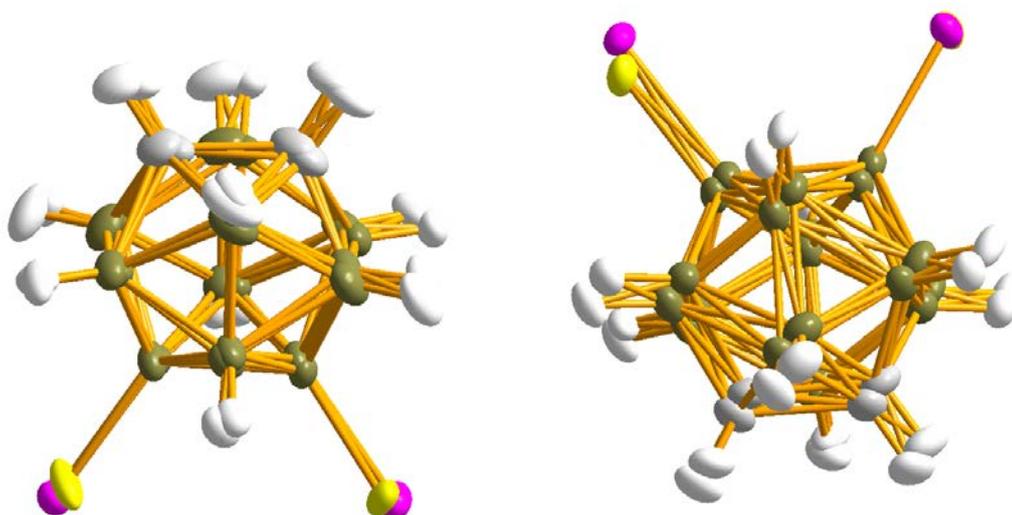
In the Atoms/molecules textbox type cage#1 cage#3; check “ADP parameters”; Add



OK; OK; YES+Start

*The refinement converges to an R-value of about 4.8% with 88 parameters.*

*The list of eigenvalues in the refinement listing as well as a plot with ellipsoids show that everything is correct.*





# Example 9.1: L9A

Getting familiar with the output of Superflip. Some useful tricks.

Revised: 15 September 2014

Single crystal data measured with Oxford Diffraction four-circle diffractometer  
Input files: L9A.m40, L9A.m50, L9A.m90, L9A.m95

The purpose of this exercise is to understand the log-file of Superflip, point out the most important information to check, and to learn some basic tricks for the case Superflip does not converge with default parameters. The structure used for the exercise is an organic structure with symmetry  $Pna2_1$ .

## 1. Load the structure

*The structure is already prepared in Jana format for your convenience.*

Start Jana2006;

“File → Structure → Open” opens a file manager;

Left pane: locate directory with input files;

Right pane: double-click L9A;

*Plot the structure, if you wish, check EditM50 to see the composition and symmetry.*

## 2. Run Superflip.

Double click the icon Structure solution 

[On the screen: Structure solution]

Select “use Superflip”;

Start “Run Solution”;

*Superflip starts, and after a few moments you will see the Superflip’s log-file open in the window of Jana. It should be very similar to the commented file below. It will not be exactly the same, because the iteration starts from random starting point, but the differences should be minor. Please take your time to go through the text below, read the comments, try to understand the listing both in this exercise and on your screen. Are the two listings different in any important manner?*

*The first part is the header of the file, with information about the version. If you encounter strange behavior of Superflip, make sure in <http://superflip.fzu.cz> you have the newest version. The executable of Superflip downloaded from this web page should be copied to the SUPERFLIP directory of Jana2006 installation.*

```
*****
                          Superflip
                          Version: 12/04/13  7:57
Palatinus, L. & Chapuis, G.(2007): J. Appl. Cryst. 40, 786-790
                          http://superspace.epfl.ch/superflip
*****
```

*Next part is a review of input parameters and crystallographic information. Superflip currently writes only the matrix-vector representation of the space group, and not the space group symbol.*

```
-----
Start of the calculation: 28.JAN 2014, 14:29:49
-----
```

```
#####
# Following data were read from the input file or set as default: #
#####
```

```
Job title: L9A
```

```

Information about files:
-----
Name of the input file: L9A.inflip
Density will be written in following files:
  L9A.m81, with type jana
  L9A.m80, with type m80
Warning: If the outputfile exists, it will be overwritten by the new density.
Logfile will contain only basic information about the calculation.
Logfile will contain information about the data coverage.

-----
Crystallographic information:
-----
Superspace dimension:          3
Dimension of the physical space: 3
Direct cell parameters:      15.3079   9.2915  13.8059  90.0000  90.0000  90.0000  Volume:  1963.65942
Reciprocal cell parameters:   0.0653   0.1076  0.0724  90.0000  90.0000  90.0000  Volume:   0.00051
Wilson plot will be based on this composition: C84H104N8O16
4 symmetry operations found, their list follows:

  1:  1  0  0  0.0000   2:  -1  0  0  0.0000   3:  1  0  0  0.5000
     0  1  0  0.0000       0  -1  0  0.0000       0  -1  0  0.5000
     0  0  1  0.0000       0  0  1  0.5000       0  0  1  0.0000

  4:  -1  0  0  0.5000
     0  1  0  0.5000
     0  0  1  0.5000

The structure is non-centrosymmetric.

-----
Settings of the algorithm:
-----
Number of voxels:              40   24   36   Total:   34560
Number of voxels for polishing: 80   48   72   Total:   276480
The density modification method will be charge flipping.
Delta will be determined automatically.
The iteration will be stopped when the convergence is detected or after ***** cycles.
After the regular iteration 5 cycles of "density polishing" will be applied.
The random number generator will be initialized automatically.

Random initial phases will be assigned to the structure factors.
Isotropic Debye-Waller factor: 0.000
Proportion of reflections to be treated as weak: 0.000
All reflections with sin(th)/lambda < 0.400 not present in the input data set will be treated as missing.
The amplitudes of the missing reflections will be left unconstrained.

The resulting density will be shifted and averaged according to the symmetry operations given above.
Following symmetry operations will be used to locate the origin of symmetry: 3 4

```

*Most of the information above is just diagnostic and is not important for ordinary user. However, the number of reflections treated as weak might be changed, if Superflip does not converge with default parameters. See below for more discussion on this parameter.*

*Next part is an overview of reflection import. "Number of reflections treated as missing" is the number of low-resolution reflections that are not present in the input data. By default, Superflip lets their value vary freely during the iteration. However, if this number is large (say more than 10% of all reflections), the iteration may fail. In such a case a more sophisticated treatment of reflections (or a more complete dataset) may be necessary. See manual of Superflip, keyword `missing` for more information.*

```
#####
# Information about reflections: #
#####

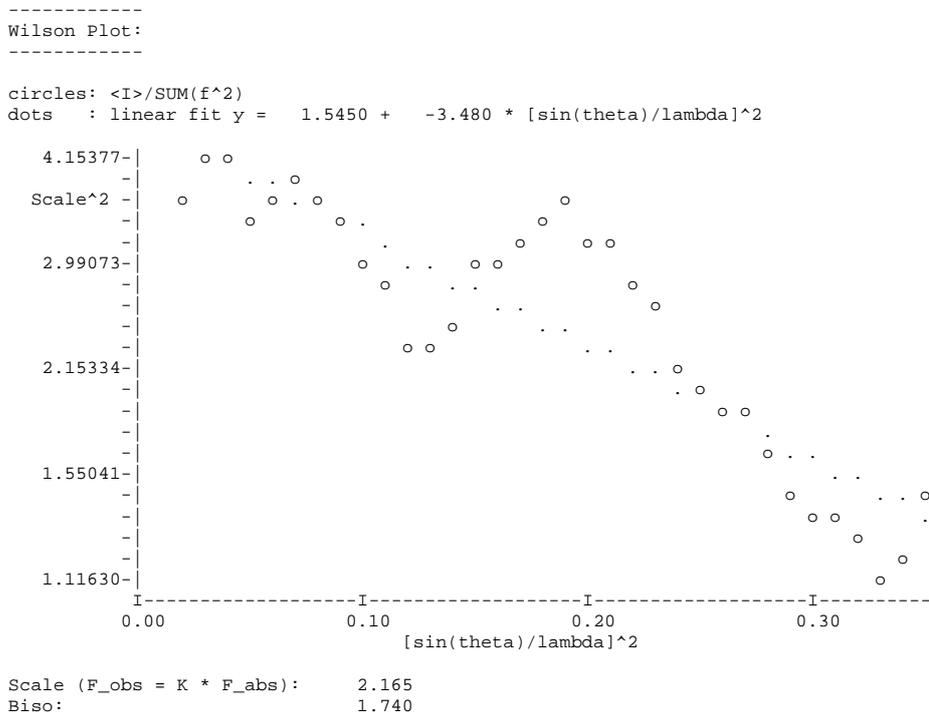
Number of reflections in the input file: 1624

-----
Averaging of reflections:
-----
Redundancy : 1.000
Rint       : -----

Maximum indices in expanded reflection set: 17 10 15

Number of reflections treated as missing: 6
```

*Wilson plot is always a useful indicator of the data quality and consistency. If you encounter problems with your structure, do not forget to check the Wilson plot and make sure it does not show anomalies. The value Biso is the Wilson-plot based estimate of the average Debye-Waller factor. If it is larger than 2, a correction of the input data might be needed. We will learn how to make this correction later in this exercise.*



*Coverage statistics shows the coverage as a function of resolution. The coverage should be high (optimally more than 90%) up to a reasonable resolution ( $d_{min} < 1.1$  or better). If one of these conditions is not fulfilled, Superflip may fail. Very low coverage at low resolution is especially dangerous.*

```
-----
Coverage statistics of the expanded reflections by shells:
-----
```

Resolution (sin(th)/l):	0.050	0.100	0.150	0.200	0.250	0.300	0.350	0.400
Resolution (d_min):	10.000	5.000	3.333	2.500	2.000	1.667	1.429	1.250
Obs. refl. in shell:	0	25	69	139	238	349	515	655
Total refl. in shell:	0	27	73	139	238	349	515	655
Coverage in shell:	0.0%	92.6%	94.5%	100.0%	100.0%	100.0%	100.0%	100.0%
Commulative coverage:	0.0%	92.6%	94.0%	97.5%	98.7%	99.3%	99.6%	99.7%
Resolution (sin(th)/l):	0.450	0.500	0.550	0.575				
Resolution (d_min):	1.111	1.000	0.909	0.870				
Obs. refl. in shell:	876	1093	1323	708				
Total refl. in shell:	876	1093	1323	730				
Coverage in shell:	100.0%	100.0%	100.0%	97.0%				
Commulative coverage:	99.8%	99.8%	99.9%	99.5%				

Iteration record shows some most important quantities during the iteration process. At the beginning the program tries to estimate the value of delta automatically. This procedure is very reliable, and only in very rare cases a manual selection of delta is necessary. The four quantities shown in every line are as follows:

- R: The R-value between the observed structure-factor amplitudes, and the amplitudes calculated after flipping. This value usually lowers at the convergence.
- Charge: Total charge in the current density. This value progressively lowers during the whole iteration, but drops down abruptly at the convergence
- Peaks: The third central moment of the density – a measure of “peakiness” of the density. This value grows at the convergence.
- Score: A combined “Figure of merit” calculated from the three quantities above as well as from their derivatives. If the score grows above 0.8, Superflip considers the iteration as converged.

*Note: An automatic detection of convergence is an extremely difficult task, because it must cover a wide range of cases. Therefore, despite of a substantial effort invested into the detection, Superflip occasionally fails to detect convergence. It is therefore always worth checking whether the structure is solved, even if the iteration does not seem to converge.*

```
#####
# Iteration #
#####

Estimated delta:  2.2715
Random seed:     131727704

Searching for a proper delta:
Current delta =   2.27153 (k_ed =  1.00000)
Total/flipped ratio =  1.021. Increasing delta.

Current delta =   2.43053 (k_ed =  1.07000)
Total/flipped ratio =  0.856.
Criterion for delta fulfilled, continuing iteration.
 20 R: 49.925 Charge:  1220.10 Peaks:  1.26 Score:  ---
 30 R: 48.103 Charge:  1149.05 Peaks:  1.36 Score:  ---
 40 R: 49.758 Charge:  1128.06 Peaks:  1.47 Score:  ---
 50 R: 49.224 Charge:  1120.09 Peaks:  1.53 Score:  ---
 60 R: 49.160 Charge:  1067.55 Peaks:  1.58 Score:  ---
 70 R: 49.279 Charge:  1092.28 Peaks:  1.62 Score:  ---
 80 R: 48.642 Charge:  1088.73 Peaks:  1.70 Score:  ---
 90 R: 48.457 Charge:  1063.52 Peaks:  1.74 Score:  ---
100 R: 48.313 Charge:  1065.67 Peaks:  1.74 Score:  ---
200 R: 46.931 Charge:  1057.27 Peaks:  1.89 Score:  ---
300 R: 38.686 Charge:   972.57 Peaks:  2.09 Score:  0.15

Calculation successfully converged after  390 cycles.
Last iteration record:
 390 R: 23.891 Charge:    878.59 Peaks:  2.23 Score:  0.91

  5 cycles of noise suppression follow:
  5 R: 14.793 Charge:     0.00 Peaks:  2.71
```

At this moment the calculation is converged (or the maximum number of iteration cycles was reached). Superflip has the capacity to check the resulting density for symmetry. It is advisable to always check this part of the log-file, and to make sure that the detected symmetry corresponds to your expectations. Derived space group P1 in cases where higher symmetry is expected usually indicates that the structure is not solved. Superflip lists all symmetry operations compatible with the lattice. Each line in the listing corresponds to one symmetry operation. The symbol of the operation is followed by a one-line representation as used in International Tables for crystallography. Next is the “symmetry agreement factor”. This number indicates quantitatively, how well the operation is present in the electron density. Numbers below 10 indicate a very good match, number between 10 and 25 are still probable symmetry operations of the density, and numbers above 25 usually mean that the corresponding symmetry operation is not present. In the



```
#####  
# Search for the origin of the space group #  
#####
```

```
Position of the origin in the CF map:  
  0.6641  0.6559  0.0000  
Agreement factors of individual generators:  
Number smb agreement  
  3  a      0.07  
  4  n      0.02
```

```
Overall agreement factor:  0.06
```

*These are the final notes in the log file with information about the file with the output:*

You can obtain more information about the reconstructed reflection phases by using 'expandedlog yes'.

Electron density written to file L9A.m81.

```
-----  
End of the calculation: 18.JAN 2010, 13:17:29  
-----
```

```
Superflip version: 07/16/09 09:12
```

Press “Close” to close the listing and return to the Structure solution dialogue

### 3. View the output of Superflip and resulting structure model

*[On the screen: Structure solution]*

*After closing the listing of Superflip, Jana2006 automatically interprets the resulting density in terms of atomic positions and types. For chemical types, only the ones available in “Formula” are considered.*

Press “Draw structure” to visualize structure model interpreted by Jana2006 from the density provided by Superflip

*Note that the structure model has the symmetry originally det by the user. If the symmetry suggested by Superflip is different and you want to use it, it must be set by the “Change the space group” button, and the interpretation of the density map or complete charge flipping must be repeated.*

*“Return to previous” loads the previous structure model. Note that there is only one step back possible.*

*If everything goes well, the structure model correctly describes the density produced by Superflip. However, in some cases this can lead you to the wrong impression that this is what Superflip produces. In case of problems (typically disorder or wrong chemical types in the formula) viewing the density may be very helpful.*

Press “Draw 3d map” to view the 3D isosurface representation of the raw density produced by Superflip

*The crystallographic (not only) viewer VESTA must be installed on your computer and enabled it in Jana. If not, consult the installation notes and install the program first. Jana passes the volumetric data to VESTA along with the structure model. VESTA shows an overlay of both, with the density represented by isosurfaces, and atoms by spheres. In this case the density shows nice spherical maxima at the positions of atoms. All maxima are “occupied” by an atom. Thus, the structure model is likely to be complete and ready to be refined.*

By default, the density from Superflip is saved in the file `jobname.m81`. That means that you can directly view it even after quitting the Structure solution dialogue as long as you do not overwrite it by calculating another Fourier map. M81 can be viewed with Contour program.

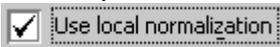
By default, the structure factors from Superflip are saved in the file `jobname.m80`. That means the Fourier map can be recalculated by Jana2006 as long as `m80` is not overwritten by refinement.

#### 4. Modify the default settings for Superflip

The default settings passed to Superflip by Jana are applicable to most standard cases. However, under some circumstances the change is necessary. The most useful changes will be listed here.

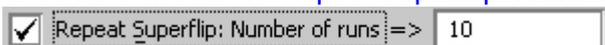
Hint 1: use normalized intensities:

For more difficult structures using normalized intensities helps enormously.

Check the checkbox next to Use local normalization: 

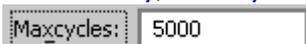
Hint 2: Run Superflip several times with a limited number of cycles:

Check the checkbox “Repeat Superflip: number of runs”



You may select a different number of repetitions than the default 10.

If necessary, modify the maximum number of cycles per run, for example to 5000:



This option may help if the solution appears unstable or if it gets trapped in a local minimum. Some of the repeated runs may escape from the local minimum. Superflip selects the best of all attempts for the output.

Hint 3: Use a non-random starting model

Select the option “Patterson superposition map” from the list named “Starting model”:



With this option Superflip first calculates a Patterson superposition map and then uses this map as a starting model for the iteration. Very often this option speeds up the convergence, and sometimes it makes the difference between solved and non-solved structure. However, sometimes – especially for simpler structures – the convergence is so rapid that it cannot be detected and Superflip keeps running. This option saves time only for larger structures, ideally with at least one non-light atom.

Hint 4: use the AAR algorithm:

Select the AAR iteration scheme from the list of options at the bottom of the window:

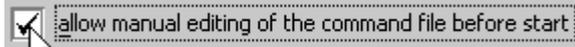


The AAR algorithm appears to perform better than the standard algorithm for very incomplete data or for low-resolution data. However, it is less stable than the standard algorithm and it is more difficult to detect its convergence. AAR is the default algorithm for electron diffraction data.

*Try one or more of the above hints and see how they affect the speed of convergence. You should come to the conclusion that for this simple structure there is hardly any difference between the options, but most of them speed up the convergence., However, combination AAR + local normalization is too aggressive and does not lead to the solution.*

*Superflip offers a large number of other options, which are described in detail in the manual. If you want to use any of these advanced options, then:*

[Check the checkbox “Allow manual editing of the command file before start:](#)



[Click Run solution](#)

*Before Superflip starts, the input file opens in a text editor and you may edit the file and include whatever additional options you wish.*

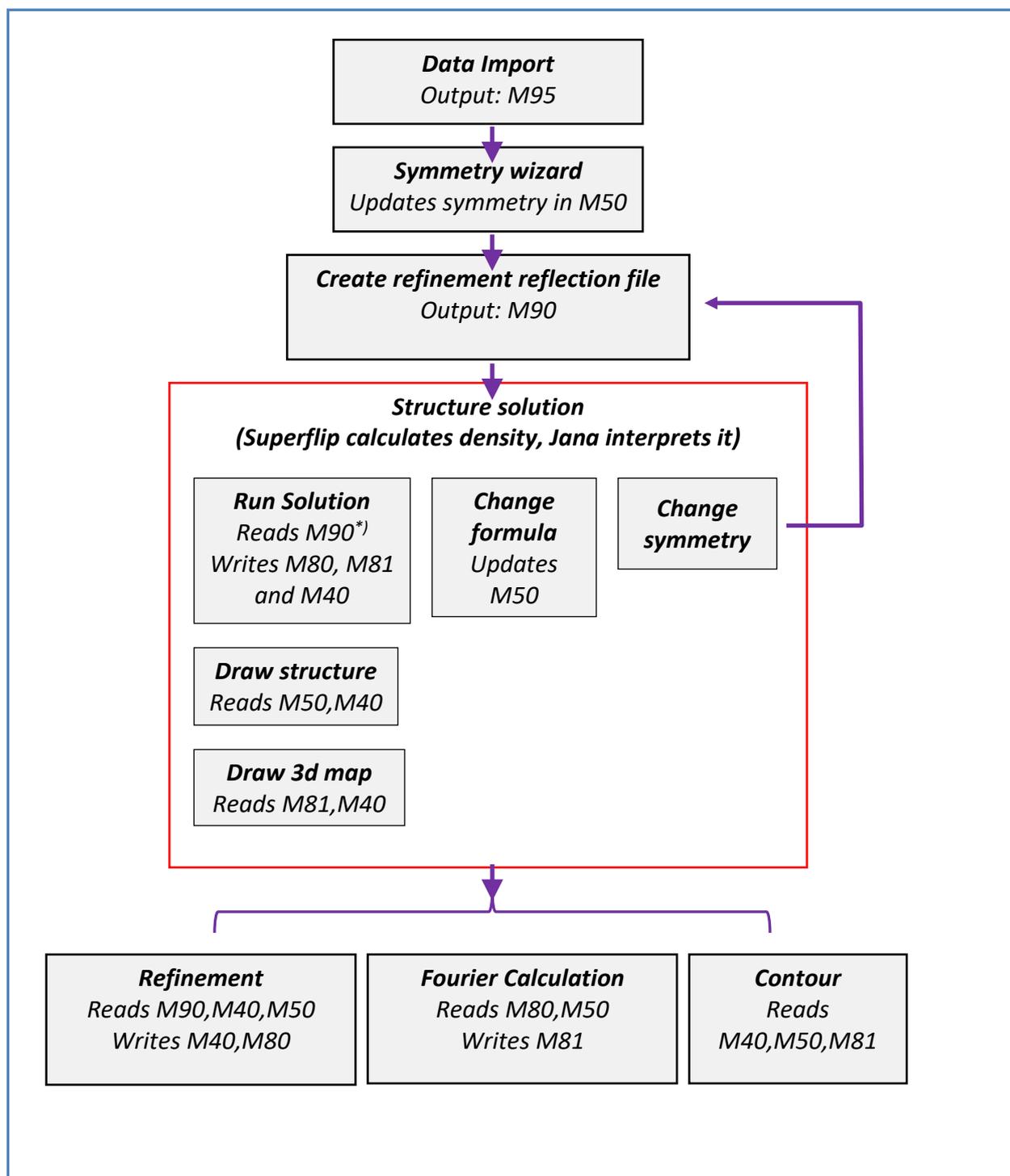
*The price to pay for faster convergence is the increased noise in the result, and sometimes more difficult detection of convergence. Because the default parameters work usually quite well and yield the best densities, we recommend using them for first attempts. Only if the iteration does not converge, try modifying the parameters according to the hints described above.*

[Press “Quit” to close the Structure solution tool](#)

*Note that there is no “escape” option. The original M40 which might be present before starting this tool is being overwritten after each “Run solution” process and the only way how to retain it is to use in proper time the “Return to previous” button.*

## 5. Integration of Superflip to Jana2006

The following scheme shows how Superflip communicates with the rest of Jana2006. M95 contains raw data; M90 is refinement reflection file (merged reflections without extinct reflections); M40 is structure model; M50 is basic crystal information; M80 are structure factors from refinement or charge flipping; M81 is density map



\*) Superflip expands M90 to P1 symmetry. However, its results are to some extent influenced by the symmetry set by the user with the Symmetry wizard, because M90 contains merged reflection and systematically extinct reflections are omitted

# Example 9.2: pArNO2

## Solving the centro-noncentro ambiguity with Superflip

This relatively simple structure illustrates the advantages of using Superflip to determine the space group.

**Revised: 16 September 2014**

Single crystal data measured with Oxford Diffraction four-circle diffractometer  
Input files: pArNO2.hkl, pArNO2.cif\_od

### 1. Create new structure

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click pArNO2

### 2. Import Wizard

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction – CCD”; NEXT

Leave all settings unchanged; NEXT

OK to confirm the name of the basic input file

Leave all settings unchanged (note the cell parameters and thus the probable crystal system); NEXT

Finish the import wizard with all settings default

### 3. Symmetry Wizard

*[On screen: Information about the symmetry wizard.]*

NEXT to start the wizard;

Leave all settings default; NEXT; OK;

*[On screen: Select Laue symmetry]*

*Jana2006 suggests orthorhombic symmetry based on  $R_{int}$ . In this case the choice appears clear.*

Keep the suggested selection; NEXT

Select primitive unit cell; NEXT

*[On screen: Select space group]*

*You are now offered a list of candidate space groups sorted by their likelihood. Note that the first two space groups  $Pnma$  and  $Pn2_1a$  differ only by the presence of inversion center and they have the same FOM:*

Select space group			
Space group	obs/all	ave(I/sig(I))	FOM
Pnma	33/1780	4.720/0.530	0.00174
Pn21a	33/1780	4.720/0.530	0.00174
Pmma	19/1193	4.345/0.458	0.00201
Pm2a	19/1193	4.345/0.458	0.00201
P21ma	19/1193	4.345/0.458	0.00201
Pnmm	14/587	5.229/0.675	0.00802
Pnm21	14/587	5.229/0.675	0.00802
Pn21m	14/587	5.229/0.675	0.00802
P21212	3/46	6.782/1.041	0.04581

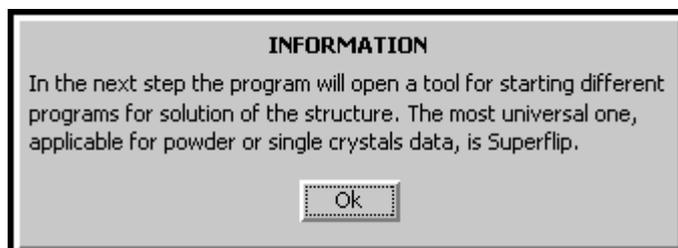
*Jana by default does not use the distribution of E-values to estimate, if the structure is centrosymmetric or not. The main reason is that the same information can be obtained from Superflip with higher reliability. At this point the space group choice can be made either randomly or based on chemical knowledge. The choice of one of the two space groups has no impact on the structure solution by Superflip.*

Select Pnma; NEXT

Accept the space group; FINISH

#### 4. Creating refinement reflection file

Proceed with the creation of refinement reflection file, leaving all settings default until you see the following screen:



#### 5. Consulting the intensity statistics

*At this point we will interrupt the standard flow of the solution process to check the E-statistics and estimate the presence or absence of the inversion center.*

OK; Quit to escape the structure solution dialog.

[On screen: Main window]

*First we have to define the chemical composition. The crystallized molecule has sum formula C<sub>42</sub> H<sub>43</sub> N<sub>1</sub> O<sub>6</sub> S<sub>4</sub> (see the end of the exercise for the picture of the molecule), number of molecules per unit cell: 8. The solvent was acetonitrile – we do not know the number of solvent molecules per formula unit, but we may ignore the solvent contribution for now.*



Double click the icon EditM50

Select the page "Composition"

Enter "C<sub>42</sub> H<sub>43</sub> N<sub>1</sub> O<sub>6</sub> S<sub>4</sub>" in the first field;

Keep 8 for the number of formula units; OK; Yes;

[On screen: Main window]

Go to Run → Intensity statistics

[On screen: Wilson plot]

Check the Wilson plot. Click anywhere in the plot to continue;

Yes to open the listing;

[On screen: listing of intensity statistics]

This listing contains a large number of statistics related to intensity normalization. We will focus only on the following table (found around the middle of the listing):

Value	Experimental					Theoretical		
	All data	hk1	0k1	h01	hk0	Acentric	Centric	Hypercen.
mod(E)	0.801	0.804	0.779	0.499	0.867	0.886	0.798	0.718
E**2	1.000	1.003	1.086	0.473	1.095	1.000	1.000	1.000
E**3	1.690	1.694	2.131	0.630	1.773	1.329	1.596	1.916
E**4	3.556	3.570	5.127	0.997	3.433	2.000	3.000	4.500
E**5	8.781	8.832	13.989	1.728	7.628	3.323	6.383	12.260
E**6	24.409	24.611	41.363	3.164	18.939	6.000	15.000	37.500
<b>mod(E**2-1)</b>	<b>0.983</b>	<b>0.981</b>	<b>1.177</b>	<b>0.905</b>	<b>0.985</b>	<b>0.736</b>	<b>0.968</b>	<b>1.145</b>
(E**2-1)**2	2.556	2.565	3.955	1.051	2.244	1.000	2.000	3.500
(E**2-1)**3	15.740	15.908	28.239	0.592	10.922	2.000	8.000	26.000

This table shows the numbers typically used to estimate the centrosymmetry. If you compare the column All data with the theoretical values, you can see that all numbers indicate a centric or hypercentric distribution. Our guess Pnma thus appears to be strongly supported by the statistics

Click the button “Close” to close the listing and return to the main window.

## 6. Structure Solution



Double click the icon Structure solution

[On screen: window of Structure solution]

Leave all settings default;

Click the button “Run solution” to start Superflip

Superflip converges smoothly and the listing of the solution procedure opens in Jana.

[On screen: listing of Superflip]

Locate the symmetry analysis in the listing. It should look very similar to this (rows of XXXX are omitted here to save space):

```
#####  
# Checking the density for symmetry #  
#####
```

Symmetry operations compatible with the lattice and centering:

	Symmetry operation		agreement factor	
a(0,0,1):	1/2+x1	x2	-x3	0.229
n(1,0,0):	-x1	1/2+x2	1/2+x3	0.651
2_1(0,1,0):	-x1	1/2+x2	-x3	0.714
2_1(0,0,1):	-x1	-x2	1/2+x3	51.947
-1:	-x1	-x2	-x3	52.037
2(0,0,1):	-x1	-x2	x3	66.366

m(0,1,0):	x1	-x2	x3	71.723
2_1(1,0,0):	1/2+x1	-x2	-x3	72.620
c(0,1,0):	x1	-x2	1/2+x3	72.643
2(0,1,0):	-x1	x2	-x3	78.403
m(1,0,0):	-x1	x2	x3	78.485
2(1,0,0):	x1	-x2	-x3	78.709
n(0,1,0):	1/2+x1	-x2	1/2+x3	78.768
m(0,0,1):	x1	x2	-x3	82.199
b(1,0,0):	-x1	1/2+x2	x3	82.308
a(0,1,0):	1/2+x1	-x2	x3	83.217
c(1,0,0):	-x1	x2	1/2+x3	89.079
n(0,0,1):	1/2+x1	1/2+x2	-x3	126.255
b(0,0,1):	x1	1/2+x2	-x3	131.166

-----  
Space group derived from the symmetry operations:  
-----

HM symbol: Pn21a  
Hall symbol: P -2ac -2n  
Fingerprint: 33002241Y40qY3 (3/4,0,3/4)  
Symmetry operations:  
1: x1 x2 x3  
a(0,0,1): 1/2+x1 x2 1/2-x3  
n(1,0,0): 1/2-x1 1/2+x2 1/2+x3  
2\_1(0,1,0): -x1 1/2+x2 -x3

*Look at the table. You can see that the first three operators belonging to the Pn2<sub>1</sub>a space group have very low agreement factors (less than 1%) indicating a very good match. All other operators have agreement factors above 50%, which is very poor. In particular the mirror plane perpendicular to **b** has agreement factor 71.7%. It is thus clearly absent in the structure. The space group is without doubt Pn2<sub>1</sub>m.*

## 6. Insert the correct space group and solve the structure

*Although the solution by Superflip is correct, the space group in Jana is still wrong, and the solution is thus not usable. We have to set the correct space group and rerun Superflip.*

*Close the view of the log file;*

*Click “Change the space group” in the “Structure solution” form;*

*Type “Pn21a” in the upper left box; OK; YES;*

*As the symmetry changed, the refinement reflection file must be recreated. Create the new file with default settings.*

*Press “Run solution” to start Superflip again with the correct symmetry;*

*Superflip starts, and should again converge smoothly to a solution.*

*Close the log-file viewer;*

*Click “Draw 3D map”;*

*View the resulting electron density and the interpreted model. The structure is correctly solved, but quite a few peaks have not been assigned an atom. We know the expected composition and we may thus use the alternative peak-interpretation option – use of an external program EDMA:*

*Close VESTA;*

*Select the radiobutton “EDMA – fixed composition”:*

For peak search use:  EDMA - fixed composition  
 EDMA - fixed number of atoms   
 EDMA - peak interpretation by Jana2006  
 Peaks from Jana2006

Check the checkbox "Use old solution and reinterpret it:

use old solution and reinterpret it

Click "Run solution" to interpret the previous solution with the new setting.

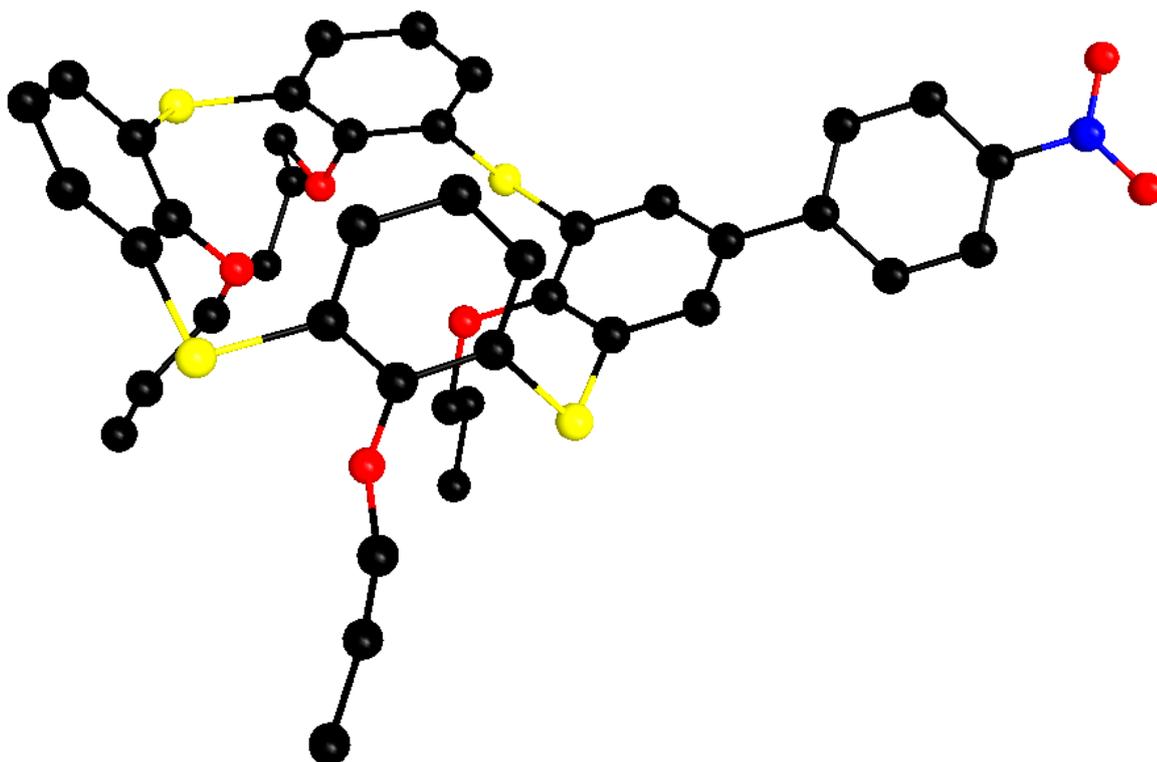
A new screen appears with the run-time information from EDMA: When EDMA finishes, a listing of Superflip opens.

Close the listing and return to the structure solution dialog

Double click "Draw 3D map"

This time you should see all maxima in the map occupied by an atom. Most atoms should have a correctly assigned atomic type, although carbon, nitrogen and oxygen may be occasionally swapped.

Here is the correct molecule for reference (hydrogens omitted for clarity):





# Example 9.3: flo19

## A challenging case of difficult symmetry and difficult convergence detection

Revised: 18 February 2014

Input files: flo19.cif, flo19.hkl. The structure is an organic molecule built by four aromatic rings bridged by one or two nitrogen atoms.

### 1. Load the structure from CIF

Start Jana2006;

“File → Structure → New”;

Locate the input files, and double click the name flo19 in the right pane;

Select the radiobutton “Structure: from CIF”; NEXT; OK to confirm the file flo19.cif

OK to the warning that the CIF does not contain symmetry information;

*At this moment you loaded the basic crystallographic information. You can check the composition and unit cell dimensions by double clicking the EditM50 icon and consulting the card Cell and Composition.*

### 2. Import the reflection file

“File → Reflection file → Import/modify the reflection file”

Select “Single crystal: reflection file corrected for LP and absorption”; NEXT;

Check that the filename is flo19.hkl and that the file type is SHELX on I; NEXT;

2x NEXT for the two following screens; OK; Finish; OK; YES to finish the import wizard

### 3. Estimate the symmetry

*When the reflection import finishes, you are automatically offered the symmetry determination form<sup>1</sup>.*

NEXT to start the wizard;

NEXT to confirm the default settings of the test;

OK to the information about no higher metric symmetry;

*On the screen with Rint for different Laue groups make sure you understand Jana’s choice of the mmm Laue group.*

NEXT;

*On the screen with centering statistics make again sure that you understand the meaning of the numbers and the choice Jana2006 made.*

NEXT;

*At this moment you are presented with the list of possible space groups. The upper part of the list looks like this:*

---

1. <sup>1</sup> If you accidentally close the wizard or if you want to repeat the test, you can access the symmetry determination procedure through the EditM50 icon, card Symmetry.

Space group	obs/all	ave(I/sig(I))	FOM
P21221	3/48	3.993/0.820	0.03190
P2221	3/43	3.993/0.886	0.03891
P212121	4/50	5.722/1.015	0.04050
P22121	4/45	5.722/1.100	0.05127
P2122	0/5	0.000/0.252	0.16973
Pmmn	8/41	5.230/1.644	0.79129
Pm21n	8/41	5.230/1.644	0.79129
P21mn	8/41	5.230/1.644	0.79129
P21212	1/7	10.911/1.804	0.94732
Pmmm	0/0	0.000/0.000	1.00000
Pm2m	0/0	0.000/0.000	1.00000
P2mm	0/0	0.000/0.000	1.00000
Pmm2	0/0	0.000/0.000	1.00000
P222	0/0	0.000/0.000	1.00000

Select the space group P21221 and click “Details”;

In the listing you can find basic information about the space group and the list of observed reflections that violate the rules for systematic absences. Check the details for several space groups. Which space groups would you consider possible and which would be the most likely?

Because the solution in Superflip is not sensitive to the choice of the space group symmetry, we will choose just one of the space groups without any systematic absences to keep the solution unbiased.

Select the space group Pmmm; NEXT; FINISH; OK; YES to finish the space group selection

We selected the space group Pmmm not because it is the most likely choice, but because it does not induce any systematic absences. We will now process the reflections, and ask Superflip to estimate the space group. If we selected a space group with systematic absences, some reflections would be excluded from the reflection file, and the result from Superflip could be biased.

#### 4. Create refinement reflection file

When the space group determination finishes, you are automatically offered the “Create refinement reflection file” tool. If you accidentally exit it, you can always return to it through “File → Reflection file → Create refinement reflection file”

NEXT; OK; NEXT; OK; FINISH to create the refinement reflection file with all settings default

#### 7. Run Superflip.

Next Jana offers you the dialog for structure solution. If you want to open this dialog later, just double click the icon “Structure solution” in the main window of Jana.

Make sure Superflip is selected;

Leave other settings default; Click Run solution;

Superflip starts and runs for many thousand cycles. No convergence is detected.

Press “Interrupt” to stop Superflip;

The log file of Superflip opens. Check the symmetry determination part. You will see that no symmetry operation has agreement factor lower than 25% and thus the derived space group is P1. Because we expect higher symmetry (although we do not know the exact space group), it is a sign that the calculation did not converge.

Inspection of the log file does not reveal any serious problem, but a series of hints shows that the structure can be difficult to solve. The potential problems are that the coverage starts dropping already at  $d_{min} \approx 1.1 \text{ \AA}$ , and that the coverage at low resolution is very low (only 21% at  $d_{min} \approx 5 \text{ \AA}$ ). It can be assumed that quite a few strong reflections are missing in the dataset. The first change to try is to use normalized intensities. When using normalized intensities, Superflip also automatically treats the missing reflections in a special way that improves the performance in case of data with missing low-order reflections.

[Close the view of the log file;](#)

[Check the checkbox "local normalization"](#)

[Click "Run solution"](#)

Superflip starts and probably runs again for many thousand cycles without detecting convergence<sup>2</sup>.

If you look at the evolution of the convergence indicators, you will most probably see behavior similar to this<sup>2,3</sup>:

20	R: 56.175	Charge:	20.84	Peaks:	1.11	Score:	---
30	R: 57.537	Charge:	20.13	Peaks:	1.16	Score:	---
40	R: 58.291	Charge:	19.03	Peaks:	1.15	Score:	---
50	R: 58.075	Charge:	19.08	Peaks:	1.22	Score:	---
60	R: 57.460	Charge:	18.65	Peaks:	1.22	Score:	---
70	R: 59.161	Charge:	18.79	Peaks:	1.32	Score:	---
80	R: 57.279	Charge:	18.88	Peaks:	1.33	Score:	---
90	R: 59.624	Charge:	18.89	Peaks:	1.39	Score:	---
100	R: 56.954	Charge:	18.29	Peaks:	1.41	Score:	---
200	R: 55.838	Charge:	18.37	Peaks:	1.29	Score:	0.15
300	R: 57.292	Charge:	18.12	Peaks:	1.35	Score:	0.15
400	R: 55.889	Charge:	17.89	Peaks:	1.32	Score:	0.15
500	R: 55.456	Charge:	18.50	Peaks:	1.32	Score:	0.15
600	R: 55.902	Charge:	18.88	Peaks:	1.22	Score:	0.15
700	R: 53.192	Charge:	18.50	Peaks:	1.24	Score:	0.15
<b>800</b>	<b>R: 53.102</b>	<b>Charge:</b>	<b>18.23</b>	<b>Peaks:</b>	<b>1.27</b>	<b>Score:</b>	<b>0.15</b>
<b>900</b>	<b>R: 50.902</b>	<b>Charge:</b>	<b>17.41</b>	<b>Peaks:</b>	<b>1.23</b>	<b>Score:</b>	<b>0.15</b>
<b>1000</b>	<b>R: 45.968</b>	<b>Charge:</b>	<b>18.16</b>	<b>Peaks:</b>	<b>1.19</b>	<b>Score:</b>	<b>0.15</b>
<b>2000</b>	<b>R: 43.139</b>	<b>Charge:</b>	<b>18.59</b>	<b>Peaks:</b>	<b>1.12</b>	<b>Score:</b>	<b>0.15</b>
3000	R: 42.466	Charge:	18.12	Peaks:	1.11	Score:	0.15
4000	R: 43.158	Charge:	19.33	Peaks:	1.16	Score:	0.15
5000	R: 43.369	Charge:	18.80	Peaks:	1.11	Score:	0.15
6000	R: 44.689	Charge:	18.11	Peaks:	1.12	Score:	0.15

Note the bold part. We can see a clear drop in R-value accompanied by no change in the charge and a small decrease (instead of expected increase) of the Peaks indicator. Although the change in R-value is clearly visible, together with the decrease in Peaks it is not enough to trigger automatic convergence detection. However, it is likely that the iteration converged.

[Press "Interrupt" to stop Superflip;](#)

[In the log file locate the symmetry determination part.](#)

You will see a listing similar to this:

<sup>2</sup> Occasionally it may detect convergence, but in most cases it does not.

<sup>3</sup> Rarely the calculation does not converge even after several thousand cycles. In that case interrupt Superflip and run it again.

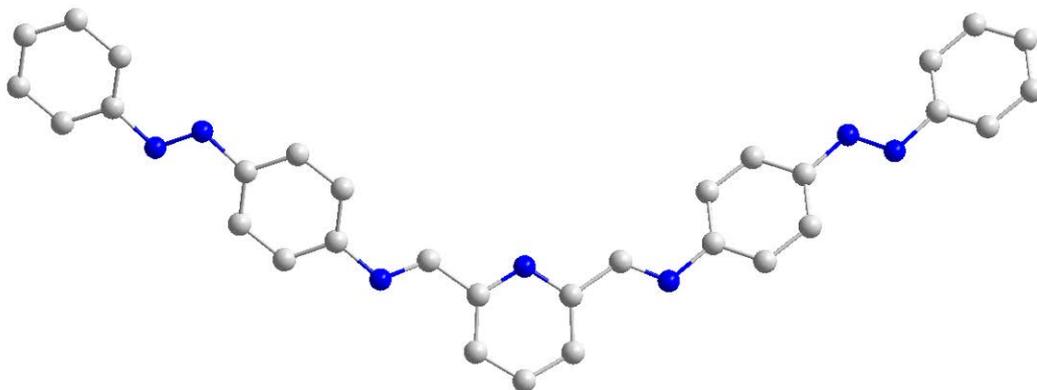


Press “Run solution” to start Superflip again with the correct symmetry;  
*Superflip starts, and should again converge smoothly to a solution. You may again need to interrupt the iteration, when you see the drop of the R-value. Check that the derived symmetry is again  $P2_122_1$ .*

Close the log-file viewer;

Double click “Plot structure”; Draw+continue

In Diamond click the “Get molecules directly”  button in the bottom toolbar. The molecule should look like this, possibly with a few carbon and nitrogen atom types interchanged:



Close Diamond;

Double click the icon “Refine”

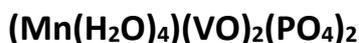
*The refinement will converge to an R-value around 10% or less depending on the number of incorrectly identified atoms. The structure is solved. Now the atoms must be correctly assigned to chemical types, and the structure refined in the standard manner.*



# Example 9.4: MnVPO

A difficult case for symmetry determination

Revised: 12 February 2014



Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: MnVPO.m50, MnVPO.m95

## 1. Opening the structure

Start Jana2006

“File → Structure → Open” opens a file manager

Left pane: locate directory with input files

Right pane: double-click MnVPO\_start

You opened a structure which contains crystal information about the compound and hkl-data. There is no structural information present yet. To preserve the original files, save the structure under another name:

“File → Structure → Save as” opens a file manager

Type “MnVPO” in the line under the right pane and press Enter

“YES” to the question if you want to continue with the new structure

## 2. Symmetry Wizard

“File → Reflection file → Make space group test”

Proceed with the space group test. Check the table of the Laue groups, and note  $R_{int}$  for Laue groups 4/m and 4/mmm. Continue until the screen with the title “Select space group”. You should see this output:

Select space group			
Space group	obs/all	ave(I/sig(I))	FOM
I4/m	0/0	0.000/0.000	1.00000
I-4	0/0	0.000/0.000	1.00000
I4	0/0	0.000/0.000	1.00000
I41	2/3	19.872/13.855	798.18793

In this case it is impossible to determine the space group only from systematic absences.

Select the space group I4/m, NEXT, FINISH

## 3. Creating refinement reflection file

Answer YES to the question if you want to create refinement reflection file

Leave all settings default; NEXT; OK; NEXT; OK;

Accept the data block; FINISH



“Parameters → Atoms → Edit”

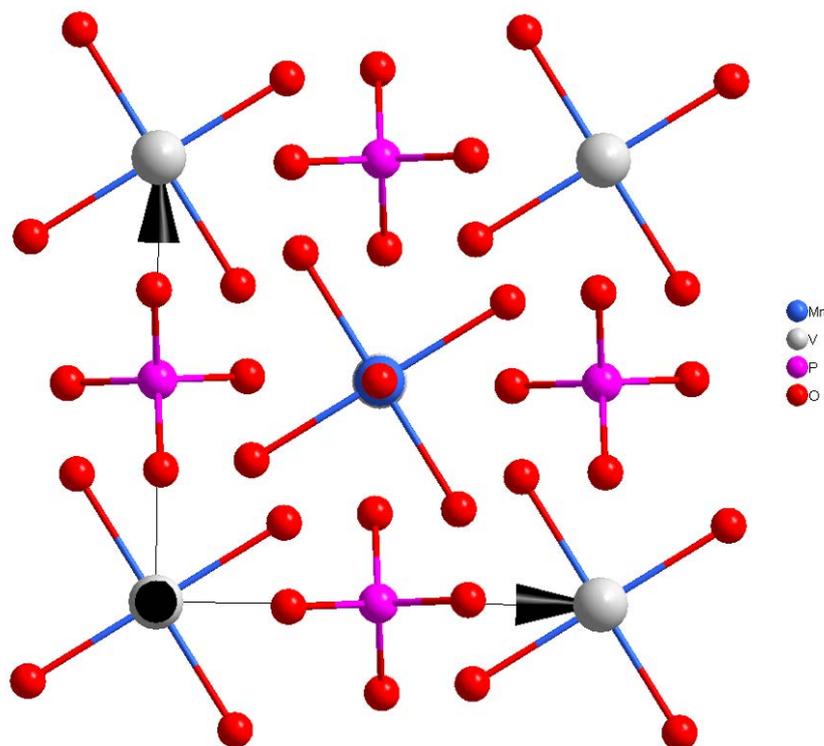
Check that the list of atoms contains one Mn, V and P atom and three oxygens. The peak search sometimes does not assign all atoms at once. In practice the missing atom would be located among the Fourier peaks. For the purposes of this example, however, make sure the solution contains 6 atoms immediately to keep your files compatible with the rest of the exercise. If it does not, rerun Superflip again.

### 5. View the structure

Double click the icon “Plot structure”; Answer NO to question about Fourier peaks;

In Diamond click the button for filling one unit cell  and for filling coordination spheres ;

You should get a view similar to this:



The structure looks correct. To convince yourself that the cations have correct coordinations, rotate the structure and increase the accepted V-O bond length to 2 (“Build → Connectivity”). Try to understand, why Superflip suggested a wrong space group before you go to the next page and read the solution.

*The reason Superlip gets confused by this structure is the strong pseudosymmetry. All atoms except for one oxygen (the in-plane oxygen coordinated to Mn) obey the I4/mmm symmetry. The contribution of the oxygen to the total density is not sufficiently strong to indicate the deviation from the higher symmetry.*

*If you look closely at the list of symmetry operators and their agreement factors, you will see indeed that the symmetry operators of the space group I4/m are all at the beginning of the list with the lowest agreement factors. But the difference in agreement factors between the true operators and the remaining operators of the I4/mmm space group is too small to be detected by the program.*

## **6. Refine the structure**

Run Refine by double clicking the icon Refine

*Refinement should immediately converge to an R-value around 5%*

“Parameters → Atoms → Edit → Select all → Action → Edit/Define atoms → harmonic”

*Change the type of displacement parameters of all atoms from isotropic to harmonic*

Run Refine again

*Refinement should converge to an R-value around 3.8%*

*This exercise demonstrates that the best approach to determining the space group is to combine the information from diffraction pattern and the symmetry determination of Superflip. In most cases the two approaches yield the same result. If the results differ, the structure or data usually exhibit some non-standard features. It can be a strong pseudosymmetry (as in this example), problem in the evaluation of systematic absences, or twinning. The two approaches are complementary, and have different weaknesses. Their combination gives the best result.*

## **7. Additional exercises**

- a) *Try to solve and refine the structure in I4/mmm. Apart from the high  $R_{int}$ , would you be able to recognize that something is wrong with the structure model? What R-value do you get?*
- b) *For training purposes you can try to finish off the structure – check for the presence of hydrogen atoms, define them and refine.*

# Example 9.5: 8rings

Very large structure – use of non-random starting point in Superflip

Revised: 12 February 2014

Input files: 8rings.hkl, 8rings.p4p. This is a huge organometallic structure with three eight-membered and one three-membered ring containing chromium, nickel, iron and cobalt. Cell volume 67312 Å<sup>3</sup>.

Reference: G. F. S. Whitehead, F. Moro, G. A. Timco, W. Wernsdorfer, S. J. Teat and R. E. P. Winpenny, *Angewandte Chemie International Edition*, 2013, 52, 9932-9935.

## 1. Load the data

Start Jana2006;

“File → Structure → New”;

Locate the input files, and double click on the green name 8rings in the right pane;

Select the radiobutton “known diffractometer formats”; NEXT;

Select the format Bruker-CCD; OK

OK to skip the warning about incomplete information;

Continue with the data import wizard, leaving all setting default, until the screen with the information about the symmetry wizard

*At this moment you loaded the basic crystallographic information and intensity data.*

## 2. Determine the symmetry

*When the reflection import finishes, you are automatically offered the symmetry determination form. If you accidentally close this card, you can access the same functions through the EditM50 icon, card Symmetry.*

NEXT to start the wizard;

NEXT to confirm the default settings of the test;

OK to the information about no higher metric symmetry;

*On the screen with Rint for different Laue groups make sure you understand Jana’s choice for the 6/m Laue group.*

NEXT;

*On the screen with centering statistics make again sure that you understand the meaning of the numbers and the choice Jana2006 made.*

NEXT;

*At this moment you are presented with the list of possible space groups. Based on the analysis of systematic absences Jana suggests the space group P65. You may click the button “Details” to get a detailed listing with the absent reflections. In this case there is little doubt that the correct space group is indeed P6<sub>1</sub>/P6<sub>5</sub>.*

## 3. Create refinement reflection file

*Now you will filter and merge the raw reflection data to produce the final reflection file ready for solution and then refinement. In this case all settings can be left default:*

Answer YES to the question if you want to create refinement reflection file  
Leave all settings default; NEXT; OK; NEXT; OK;  
Accept the data block; FINISH

#### 4. Structure Solution

As the next step the wizard suggests starting the structure solution. When you accept the suggestion, a form with options for structure solution opens.

This is a large structure, and normalizing the intensities is most likely necessary.  
Check the checkbox "Use local normalization".

It is also necessary to give some composition. It is not used for solution but for interpretation. It is sufficient to enter just a list of present atoms. Iron, cobalt and nickel will most probably be indistinguishable in the solution, but we may enter them anyway, so that we do not have to add them later during the refinement process. The same holds for hydrogen.

In the files Composition enter "Cr Fe Co Ni C H F N O"

Leave other settings default.

Click "Run solution"

Superflip starts and tries to solve the structure with default options for the charge flipping algorithm. You may let the iteration run for a few hundred cycles and you will see that there are no signs of convergence in the three indicators (R-value, total charge and peakiness).

There is still a chance that the structure is solved – sometimes the convergence is just not visible. We will interrupt the iteration and check the result.

In the window of Jana click the button "Interrupt"

Superflip finishes the calculation and the log-file opens in the main window of Jana. Check the symmetry analysis. The final part will look like this:

```
-----  
Space group derived from the symmetry operations:  
-----
```

```
HM symbol:      P1  
Hall symbol:    P 1  
Fingerprint:    33001041a0 (0,0,0)  
Symmetry operations:  
      1:          x1          x2          x3
```

It is most unlikely that the structure really has symmetry P1. Together with the lack of indicators of convergence this means that the structure is not solved.

The structure contains moderately heavy atoms. It is thus sensible to start the iteration with Patterson superposition map instead of the random map.

Click the button "Close" in the upper row to close the viewer of the log file;

In the selection list labeled "Starting model" select the radiobutton "Patterson superposition map":

Starting model:  Random phases  
 Patterson superposition map

Run the solution again

Typically the iteration converges within a few hundred cycles. The space group determination part of the log file looks like this:

-----  
Space group derived from the symmetry operations:  
-----

```
HM symbol:      P61
Hall symbol:    P 61
Fingerprint:    3300163Xx01 (0,0,0)
Symmetry operations:
      1:          x1          x2          x3
6+_1(0,0,1):    x1-x2        x1          1/6+x3
3+_1(0,0,1):    -x2         x1-x2        1/3+x3
 2_1(0,0,1):    -x1         -x2          1/2+x3
3-_2(0,0,1):    -x1+x2      -x1          2/3+x3
6-_5(0,0,1):    x2          -x1+x2       5/6+x3
```

*This time the solution has the correct symmetry and it is a strong indication that the structure is solved.*

Close the log-file viewer;

Wait until Jana performs the peak search (be patient, it is a large structure...)

Click the button “Draw 3D map” to view the resulting electron density

*The density and the interpreted model are shown overlaid in VESTA. The structure is large and it is not easy to understand the density. Nevertheless, after a while it becomes clear that the structure is correctly solved and the main expected motifs are well visible. It is also visible that some of the peaks present in the electron density were not interpreted as atoms by the peak-searching routine. These peaks are saved as “Fourier maxima” in Jana and you may change them to regular atoms when you go to Parameters → Atoms → New → Peaks from the last Fourier calculation. To see which maxima are interesting, we will plot the strongest peaks together with the structure:*

Close VESTA;

Click the button “Draw structure”;

In the next dialog click “Add Fourier peaks”;

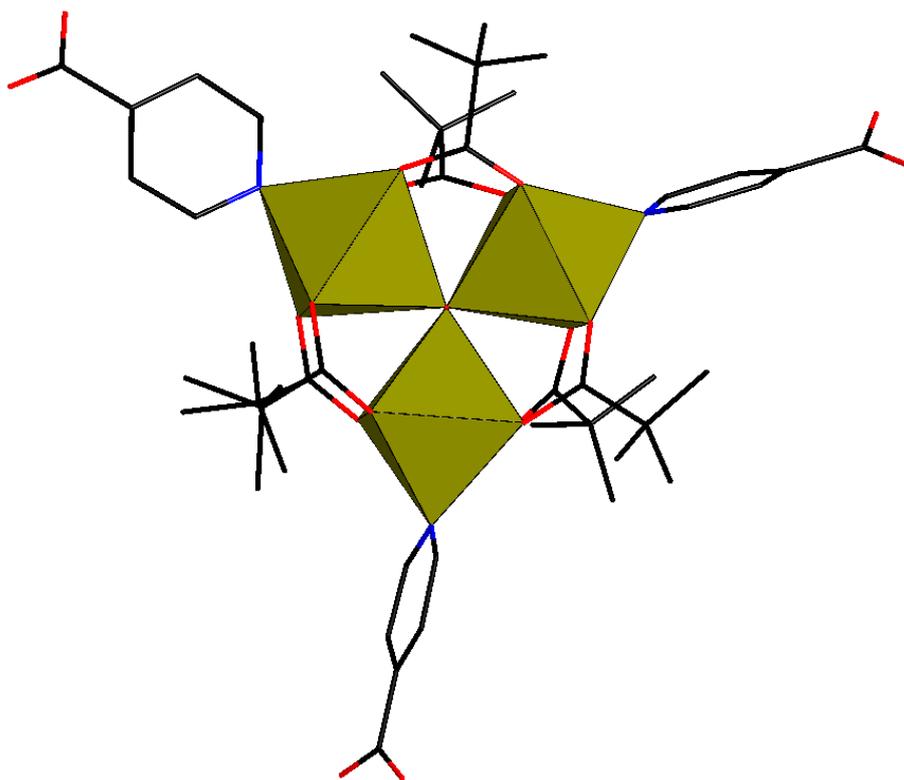
*A dialog with a long list of maxima opens. First about 100 maxima are deselected, because they represent existing atoms. Then a large number of maxima are selected (typed in red).*

OK to include all maxima;

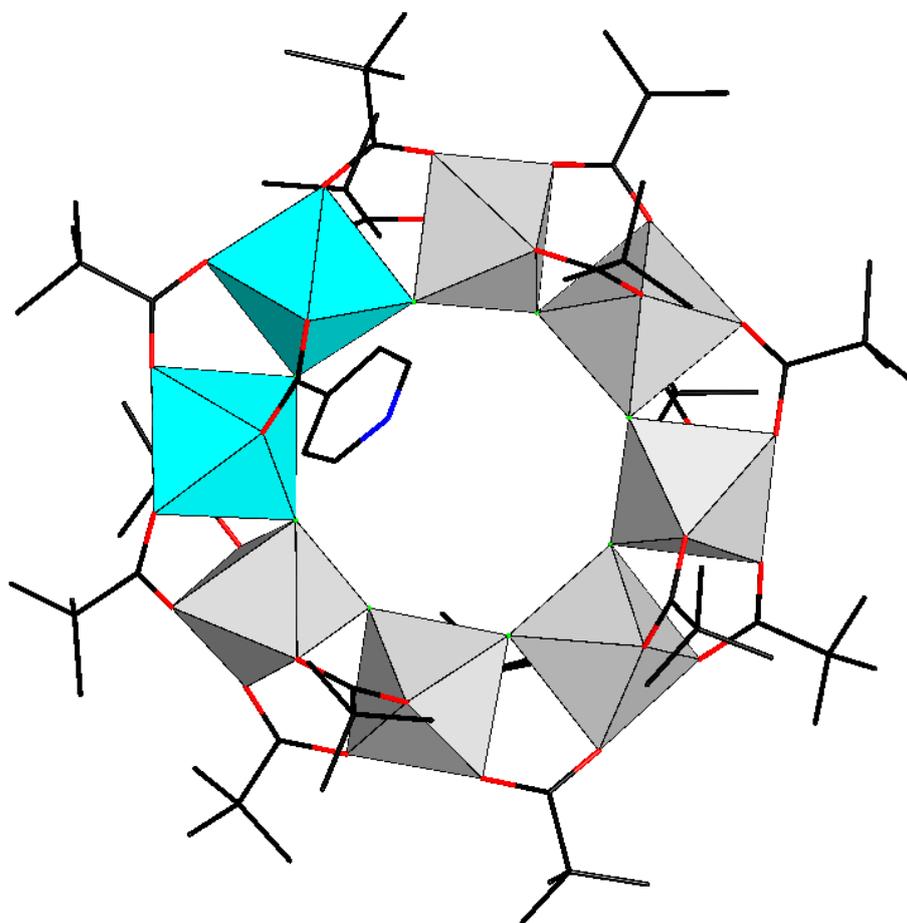
*The structure-plotting program (typically Diamond) opens and you may view the structure. The added maxima are shown as the lightest element from the element list. In this case it is hydrogen. You can see that a large number of these maxima are just artifacts close to the heavy atoms, but among the added maxima you can also find most of the missing atoms. This illustrates the fact that often the raw solution – the electron density – is more complete and informative than the structure interpretation, and it is worth checking the electron density after the solution, if the interpreted structure appears incomplete or otherwise wrong.*

*Here is for reference the image of the two chemically different entities found in the structure:*

*The three-ring with mixed iron-cobalt sites:*



*The eight-ring with chromium and nickel:*



# Example 10.1: AgSbS

## Refinement of anharmonic ADPs in Jana2006.

**Chemical formula:** Ag<sub>3</sub>SbS<sub>3</sub>

**Reference:** F. Laufek, J. Sejkora & M. Dušek (2010). Journal of Geosciences, 55, 161–167

Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: agsbs.hkl, agsbs.cif\_od

Frame scaling, absorption correction: done with software of diffractometer

*In this example we shall need installation of VESTA for visualization of electron density associated with anharmonic ADP. VESTA is supplied as a zip archive which can be unpacked to arbitrary location (with simple path – not to Desktop). Then the path to VESTA.exe must be defined in “Parameters → Programs”.*

### 1. **Creating new jobname**

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate the directory with input files

Right pane: double-click agsbs

Right pane detects possible Jana files and shows one jobname for each group of files

### 2. **Import Wizard**

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction – CCD”; NEXT

Select “Input from “cif\_od” file”; OK

*The used diffractometer software splits reflection file and another information (cell parameters, wavelength ...). There are several output formats for both cases.*

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

*The program reads 11948 reflections from hkl file*

For absorption correction select “None or done before importing”; NEXT

FINISH

### 3. **Data RepositoryOK;**

*Each line in data repository window corresponds to one data set converted to Jana format.*

*In our case we use only one data set.*

OK; YES to accept the data set

### 4. **Symmetry Wizard**

*[On the screen: “Tolerances for crystal system recognition”.]*

*Symmetry wizard can be started separately by “File → Reflection file → Make space group test.*

Leave all settings default; NEXT

*[On the screen: Select Laue symmetry]*

Select Trigonal -3m1 Laue symmetry; NEXT

Select R-obverse cell; NEXT

[On the screen: Select space group]

Select R3c; NEXT

Selecting the non-centrosymmetric space group is a shortcut. It will be explained at "Verification of structure solution".

Accept the space group transformed into the original cell; FINISH

Symmetry is saved in file agsbs.M50.

#### 5. **Creating refinement reflection file**

In this step program creates file agsbs.M90 containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.

NEXT to confirm threshold 3sigma

[On the screen: settings for merging of reflections]

Leave all settings default; NEXT

The program reports Rint 1.88% for 430 observed reflections merged from 3577 observed reflections.

Accept the new data block and calculate coverage; FINISH

#### 6. **Structure Solution Wizard**

[On the screen: window of Structure solution].

In "Formula" textbox type list of chemical elements: Ag Sb S

Select "Use Superflip", "Peaks from Jana2006";

Select "Use a specific random seed" and use "222"

Fixing the random seed to 222 guarantees for most processors that the Superflip returns exactly the same results like described in this cookbook. Otherwise each run of Superflip may return different equivalent origin. For normal work random seed should be automatic because the convergence of charge flipping is not guaranteed for every value of random seed.

Leave other settings default; OK

[On the screen: window of Superflip replaced after reaching the convergence with listing of Superflip]

Superflip converges (after noise suppression) with R value (after noise suppression) 16%.

Press CLOSE to leave the listing

Press "Accept the result"

#### 7. **Verification of the structure solution**

Start EditM50, go to page Composition, enter 6 for "Formula units", press "Formula from M40"

It displays formula Ag<sub>3</sub> Sb S<sub>3</sub> (for Z=6). This is the same as expected composition.

[On the screen: Information about formula]

OK; YES for updating the formula.

In next steps we shall verify with Superflip that centre of symmetry is not present.

Start "File → Structure → Save As"

Save the structure with jobname "testspg"

YES to continue with the new structure

Start "Run → Solution"

Select "Use Superflip" and press button "Change the space group"

For the "Space group" type R-3c; OK; YES to rewrite M50  
Follow steps for creating the refinement reflection file  
*Merging the data yields Rint 2.11% and the program returns to the structure solution wizard*  
[On the screen: Structure solution wizard]  
OK to start structure solution  
[On the screen: listing of Superflip]  
At the end of the listing we can see unsatisfactory agreement factor for the symmetry operator "2". This indicates the space group is probably wrong.  
Press "Accept the result"  
Start EditM50, go to page Composition, enter 6 for "Formula units", press "Formula from M40"  
*It displays formula Ag0 Sb S6 (for Z=6) which is also wrong*  
Return to the basic window of Jana2006  
Start "File → Structure → History" and open the previous structure (with space group R3c)

## 8. Refinement

[On the screen: basic window of Jana]  
Right-click the icon of Refine.  
[On the screen: refinement options]  
Define 100 of cycles, damping factor 0.5; OK  
Choose "YES+START"  
*Refinement converges with R value about 12%*  
Start "Edit atoms"  
[On the screen: list of atoms]  
Press "Select all" and "Action → Edit/define"  
Choose "harmonic" for ADP parameters. *This defines anisotropic temperature parameters for all atoms.* OK, OK, Yes to save changes  
Double-click the icon Refine.  
*Refinement converges with R value about 4%.*

## 9. Extinction correction

*The results seem to be OK, but:*  
[On the screen: basic window of Jana2006]  
Open listing of Refine (by "Edit/View → View of Refine")  
Press "Go to" and select "Statistics Fo, sin(th)/lambda after refinement"  
*R value should decrease with increasing intensity or with lowering the diffraction angle. Here the R value for the strongest reflections as well as for the low angle reflections is higher than in the previous shell. This suggests that extinction correction is required.*  
Close the refinement listing  
"Parameters → Extinction"  
Select "Isotropic"; OK  
*Refinement of extinction coefficient is enabled by default*  
Double-click Refine and refine the final structure  
*Refinement converges with R factor 3.67 %.*  
Check the extinction coefficient through "Parameters → Extinction"  
View listing of Refine; Go to "Statistics"; check improved R value for strongest reflections.

## 10. Anharmonic refinement

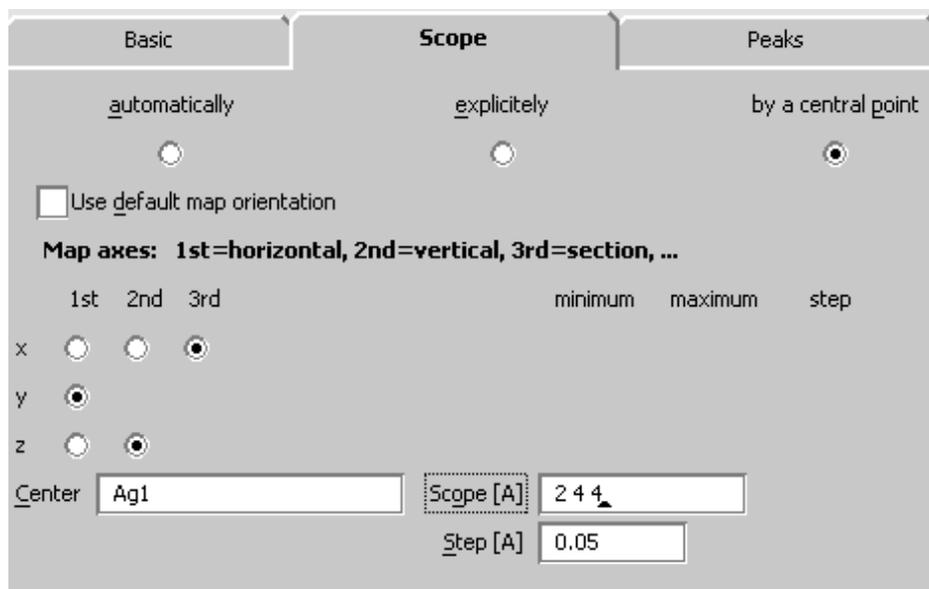
Run Contour, start "New plot" – "Calculate new ones" + " Draw maps as calculated".

Here no previous map exists and therefore "Calculate new ones" will be disabled

[On the screen: Fourier commands]

In Basic thumbnail select "F(obs)-F(calc) – difference Fourier"; leave other settings default

screenshot; OK

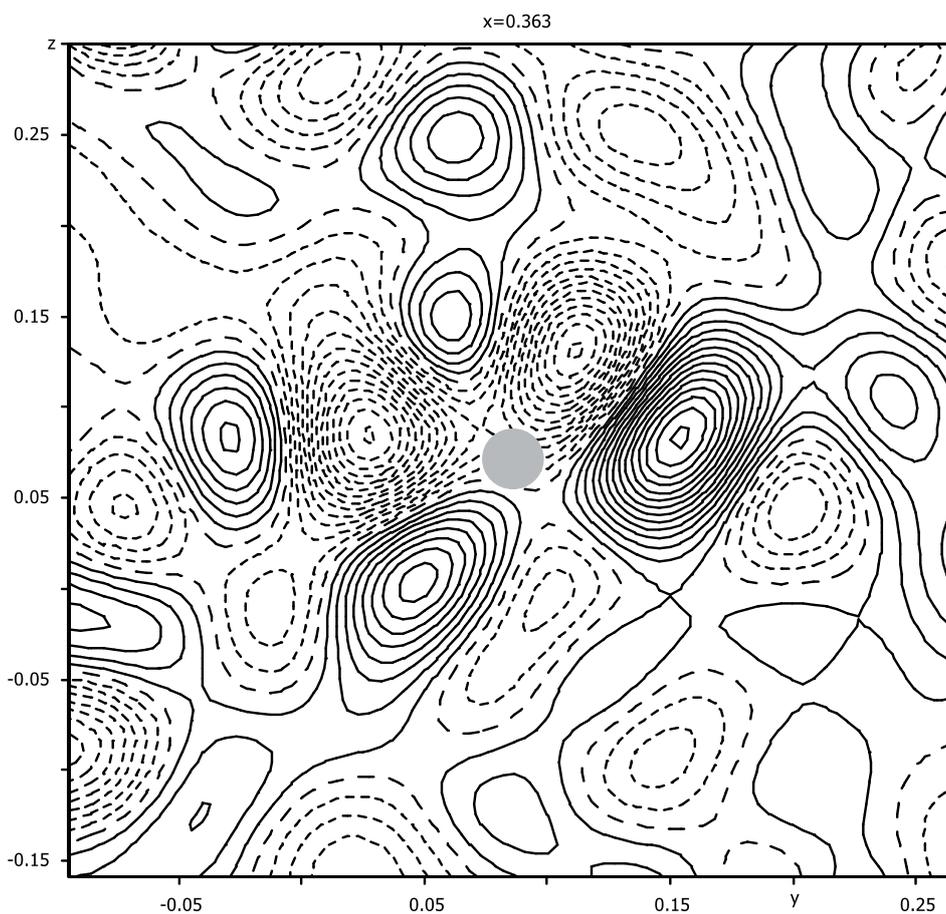


[On the screen: contour plot of the first section]

In "Contours" define both positive and negative contours to  $0.1 \text{ e}^-/\text{\AA}^3$ ;

In "Atoms edit" add Ag1;

Examine the sections using "M+" and "M-"



*We can see residua of positive density in the vicinity of the Ag atom.*

### Quit Contour

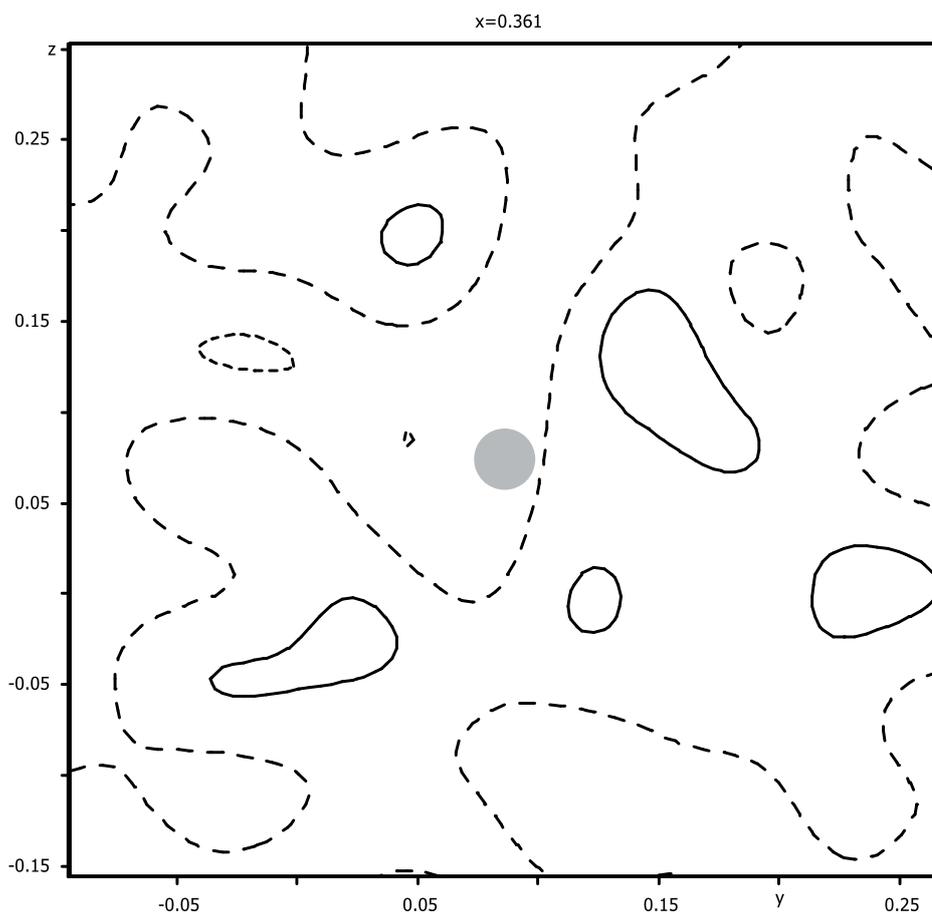
Run "Edit atoms" and select Ag1.

"Action → Edit/define atoms": check "Anharmonic ADP", third order;

Run Refine

*Refinement converges with R factor 1.14 %.*

In Contour draw the same difference Fourier section as previous (calculate new maps). Use the same limits for contours.



*The residua have significantly decreased.*

### **11. Density modeling using the joint probability density function**

Run Contour, start "New plot" – select j.p.d.f.

[On the screen: Select atoms and basic parameters for j.p.d.f]

Select Ag1 and S1; Next

[On the screen: Plane/Volume]

For 1<sup>st</sup> atom use Ag1; for the 2<sup>nd</sup> and 3<sup>rd</sup> atom use difference to 1<sup>st</sup> 1 0 0 and 0 1 0, respectively;

Define scope of the section: 6 6 6 and "1st point to" 3 4 2.5;

Use cutoff distance for atoms 4 Å; NEXT

Define new  Use old

	Atom	Coordinates	Difference to 1st
1st	Ag1	361445 0.086636 0.073546	
2nd		361445 0.086636 0.073546	1 0 0
3rd		361445 1.086636 0.073546	0 1 0

**Scope**

Interpolation step	Scope of section	1st point put to
0.05	6 6 6	3 4 2.5 [Ang]

Cutoff distance for atoms  [Ang]

[On the screen: Select individual atoms for j.p.d.f]

Select Ag1, and all symmetry related sulphur atoms close to Ag1 and note their symmetry codes (i.g. S1#s5c3t0,-1,-1); NEXT

**Select individual atoms for j.p.d.f.**

Atom	Distance	Symmetry code
Ag1	1.118	x,y,z
S1	2.019	-x+y,-x,z#s3
S1	2.552	-x+y+1/3,y-1/3,z+1/6#s5c3t0,-1,-1
Ag1	2.596	-x+y+2/3,-x+1/3,z+1/3#s3c2
Ag1	2.822	-x+y+1/3,y-1/3,z+1/6#s5c3t0,-1,-1
S1	2.931	-y+2/3,x-y+1/3,z+1/3#s2c2
S1	3.096	-y+2/3,-x+1/3,z-1/6#s4c2t0,0,-1
Ag1	3.460	-y+1/3,x-y-1/3,z-1/3#s2c3t0,-1,-1
Ag1	3.621	-y+2/3,-x+1/3,z-1/6#s4c2t0,0,-1
Ag1	4.073	-y+1/3,-x+2/3,z+1/6#s4c3t0,0,-1
S1	4.156	x,x-y,z+1/2#s6
Ag1	4.206	x-1/3,x-y-2/3,z-1/6#s6c2t-1,-1,-1
S1	4.299	x+1/3,y-1/3,z-1/3#c3t0,-1,-1

In "Atoms Edit" of Contour define the Ag1 atom and all four S1 atoms using their symmetry codes.

Press "Run 3d maps"

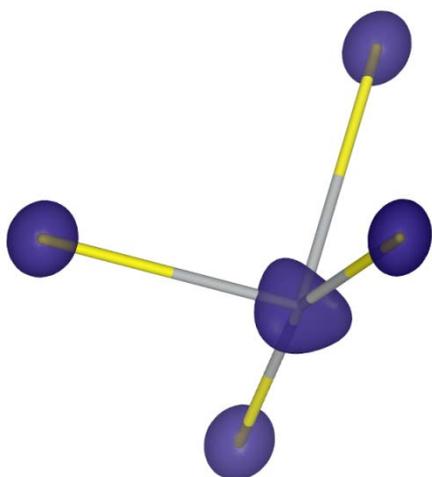
Jana2006 will call an external program for drawing isosurfaces, previously defined in "Tools → Programs", in our case VESTA

Setting drawing options:

In "Edit → Bonds" define bond between Ag and S; maximal distance 3.15 Å,

In "Objects → Structural model" select "Stick",

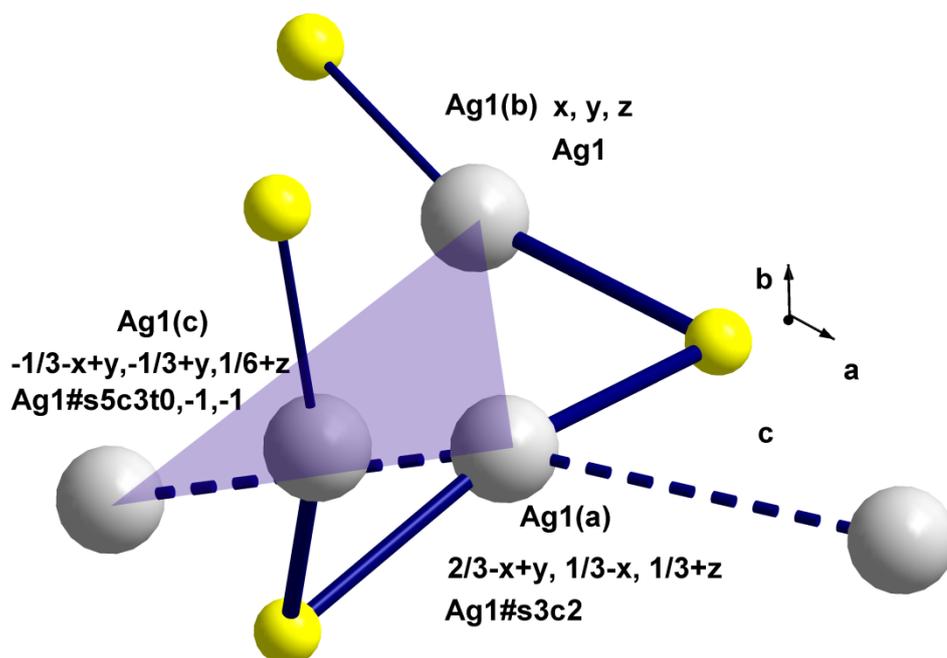
In "Properties" check "Do not show unit cell".



The application of non-harmonic parameters led to the triangular shape of the electron density centered in Ag1 position. The electron density is extended in directions between of Ag-S bonds.

## 12. Drawing one particle potential curve

Sulphur and Silver form spirals defined by short Ag-S bonds. The possible exchange paths for silver atoms within and between the spirals can be tested with help of one particle potential along a proposed path. One of proposed paths is shown in the following figure where it goes along sides of the indicated triangle:



Run Contour, start "New plot" – select j.p.d.f.

[On the screen: Select atoms and basic parameters for j.p.d.f]

Select Ag1; Next

[On the screen: Plane/Volume]

Define the displayed volume according to the following screenshot; OK

	Atom	Coordinates	Difference to 1st
1st	Ag1#s3c2	.391859 -0.028111 0.40688	
2nd	Ag1	361444 0.086636 0.073547	30415 0.114747 -0.333333
3rd	Ag1#s5c3t0,-1,-1	58525 -0.246697 0.240214	33333 -0.218587 -0.166667

Scope		
Interpolation step	Scope of section	1st point put to
0.05	7 7 2	2 2 1 [Ang]
<input type="button" value="Adjust"/>		

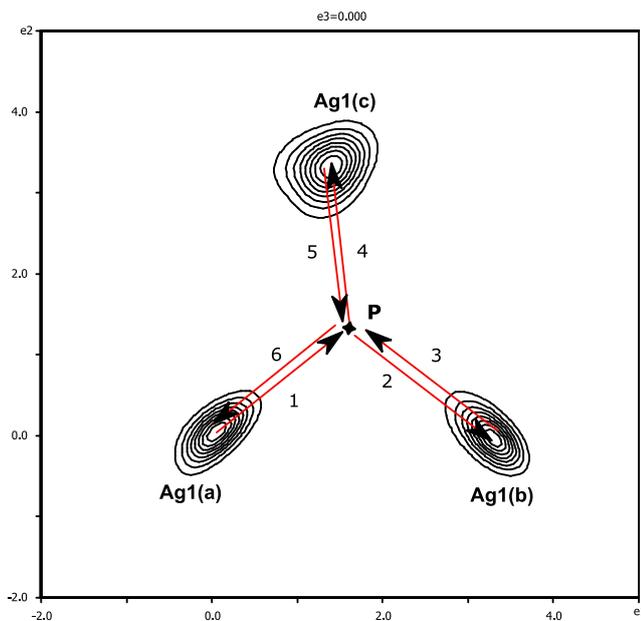
  

Cutoff distance for atoms	4	[Ang]
---------------------------	---	-------

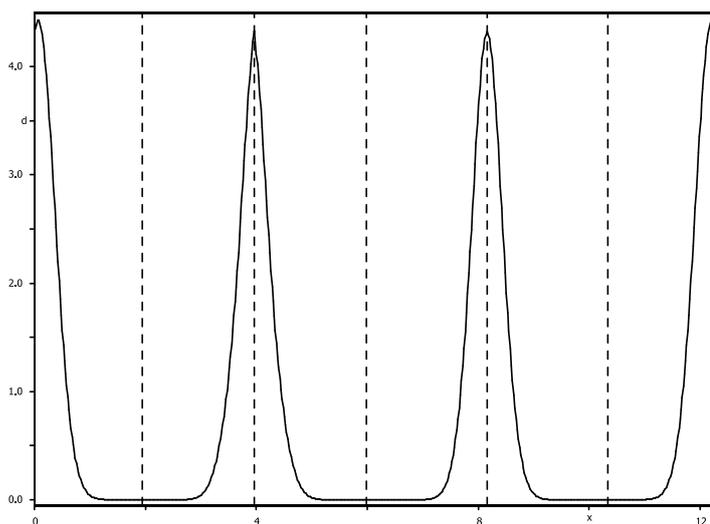
Select Ag1#s3c2, Ag1#s5c3t0,-1,0 and Ag1; NEXT

Select individual atoms for j.p.d.f.		
Atom	Distance	Symmetry code
Ag1	1.800	-x+y+1/3,y-1/3,z+1/6#s5c3t0,-1,-1
Ag1	2.121	-x+y+2/3,-x+1/3,z+1/3#s3c2
Ag1	2.308	x,y,z
Ag1	4.097	x-1/3,x-y-2/3,z-1/6#s6c2t-1,-1,-1
Ag1	4.353	-y+1/3,-x+2/3,z+1/6#s4c3t0,0,-1
Ag1	4.367	-y+1/3,x-y-1/3,z-1/3#s2c3t0,-1,-1
Ag1	4.374	-y,-x,z+1/2#s4

In "Curves" "Use mouse to define polyline" and draw the line Ag1(a)—P—Ag1(b)—P—Ag1(c)—P—Ag1(a) by mouse (2<sup>nd</sup> mouse button quits the selection). You can also fill in these points directly in the textboxes of the "Curves" dialogue. Fractional coordinates of the point P are approximately 0.267 -0.63 0.235. Ag atoms should be written with corresponding symmetry codes, i.e. Ag1#s3c2.



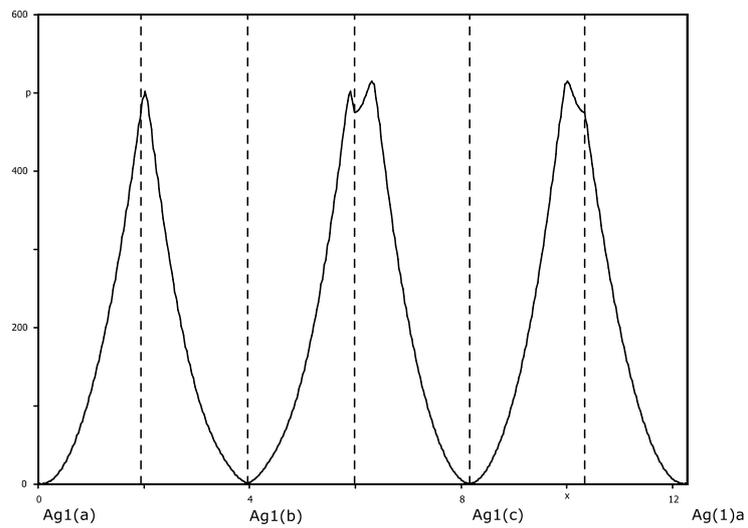
In the first plot we can see an electron density curve. The maximal electron density is located in Ag1 atoms.



Press "Continue"

Adjust "y-Scale": Min and Max in meV: 0 600;

*The resulting curve is one particle potential path. The peaks represent the potential barrier between Ag1 atoms when the exchange path runs through the point P. These values suggest that the silver transfer within and between neighboring Ag-S-Ag spirals is possible.*





# Example 10.2: Oxa

## multipole refinement

X-ray data from an oxalic acid sample measured at 110K to a high resolution limit. The crystal contains also crystal water:  $C_2O_4H_2 \cdot 2H_2O$

Input files: oxa.m40, oxa.m50, oxa.m90 and oxa.m95 – Jana files from a conventional refinement

### 14. Drawing density map based on the regular refinement

*[On the screen: Basic Jana window]*

Start Jana2006

“File → Structure → Open”: open structure “oxa”

*This is result of conventional structure refinement*

Run refinement

*Refinement converges in 1 cycle to  $R(obs)=2.74\%$*

*[On the screen: Basic Jana window]*

Double-click the icon Contour; Press the button “New plot”

Select “Draw a general section”; OK;

*[On the screen: Fourier commands]*

In “Basic” page for “Map type” select “F(obs) – Fourier”

clear “Omit non-matching reflections”

select “Use weighting of reflections”

clear “Apply  $\sin(\theta)/\lambda$  limit”

In “Scope” page select “automatically”, “Independent parallelepiped” and “Use default map orientation”

Change the step to 0.05 Å

OK

*[On the screen: Plane/Volume]*

This form defines the general section to be drawn from the calculated map.

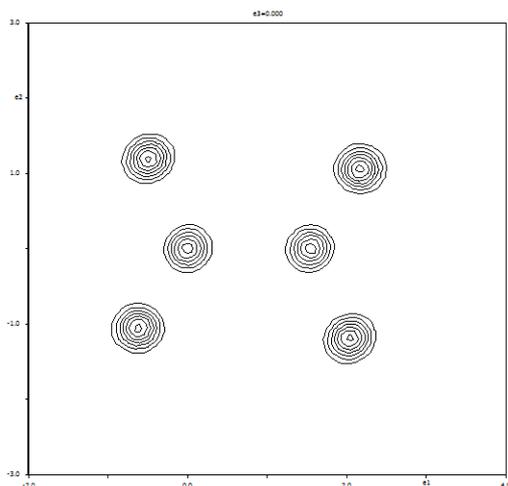
Define: 1<sup>st</sup> atom C1; 2<sup>nd</sup> atom C1#s3; 3<sup>rd</sup> atom O1

#s3 encodes symmetry operation (the third one in the list in EditM50)

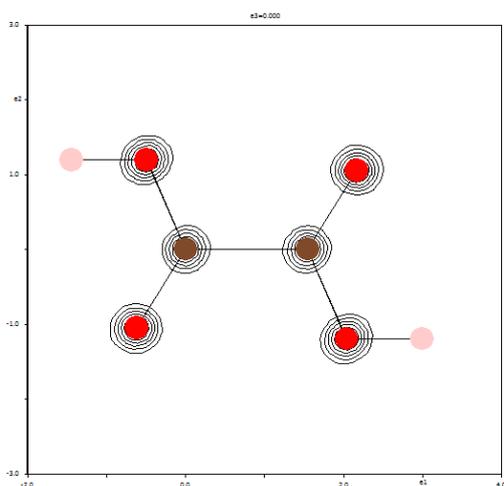
Set the “Interpolation step” to 0.05 Å, “Scope of section” 6 6 0; 1<sup>st</sup> point to 2 3 0

OK;

*After calculation the density section through oxalic acid molecule will appear:*



Atomic positions can be included into the map by clicking the pointer at different locations and selecting atoms close to the given location. The following atomic position should be selected: C1, O1, H1, O2, C1#s3, O1#s3, H1#s3; O2#s3.



Quit; Save it as Plane#1; OK

[On the screen: Basic Jana window]

Now we shall visualize the difference map.

Double-click the icon Contour; Press the button: "New plot"

Select "Calculate new ones" and "Draw a general section"; OK;

[On the screen: Fourier commands]

In "Basic" page for "Map type" select "F(obs)-F(calc) – difference Fourier"

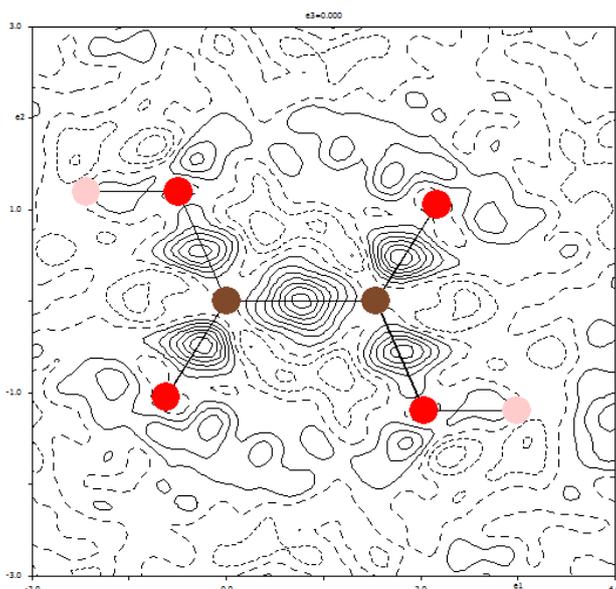
Keep all remaining settings unchanged; OK;

[On the screen: Plane/Volume]

Select "Use old"; OK

[On the screen: Difference Fourier map through the oxalic acid]

Press the button "Atoms ON"



Press the button “Contours” to see contour interval. The value should be about  $0.05 \text{ e}^-/\text{\AA}^3$ .  
 The positive density clouds are in vicinities of possible bonds. This indicates that the multipole model can reflect real charge densities in this crystal.

Quit Contour

### 15. Kappa refinement

[On the screen: Basic Jana window]

We shall keep backup copy of the conventional refinement. Refinement will now continue with new job name.

Start “File → Structure → Save As”

Save structure as “Oxa-Kappa”

Continue with the new structure

[On the screen: Basic Jana window]

Double-click the icon EditM50

In page “Composition” define multipoles “MOLLY”;

In page “Multipole parameters” define orbital populations; for O and C atoms keep the default values; for H atom select “Slater form factor” with the default values for H-N and H-Dzeta;

OK; YES to rewrite M50

[On the screen: Basic Jana window]

Double click the icon “Edit atoms”;

Select all atoms; Choose “Action → Edit/define” or double click on the selected atoms;

[On the screen: Atom edit]

In the column “Multipole parameters” select “kappa”; OK; OK;

Yes to rewrite the changed files

[On the screen: Basic Jana window]

Right click on the icon “Refine”;

In the “Various” page press “Equations” and define the following equations:

$\text{pv}[\text{H3}] = \text{pv}[\text{H2}]$

$\text{kappa}[\text{H2}] = \text{kappa}[\text{H1}]$

$\text{kappa}[\text{H3}] = \text{kappa}[\text{H1}]$

OK; OK; Yes+start

Refinement converges to  $R(\text{obs})=2.69\%$

The kappa refinement made only small improvement. This is in accordance with the difference Fourier map in which strong asphericity has been visible.

### 16. Distance and angular restraints for H atom

Way how hydrogen atoms are described is a delicate point for charge density refinement. Generally hydrogen electron can be related to any reference point. In order to have reasonable deformation maps it is worthwhile to fix the reference positions of hydrogen atoms close to its ideal values. For the oxalic acid we can use the distance and angular restraints to values refined against neutron diffraction data. For distance H1-O1 this value is 1.07 Å with angle H1-O1-C1 113° and for O3-H2 and O3-H3 0.97 Å with angle H2-O3-H3 about 106°.

[On the screen: Basic Jana window]

Right click on the icon "Refine";

In the page "Various" define the following "Distance restraints":

O1 H1; Value 1.07; s.u. 0.001;

O3 H2; Value 0.97; s.u. 0.001;

O3 H3; Value 0.97; s.u. 0.001;

OK;

In the page "Various" define the following "Angle restraints":

H1 O1 C1; Value 113; s.u. 0.01;

H2 O3 H3; Value 106; s.u. 0.01;

OK

In the page "Various" define the following "Keep commands":

ADP; Riding; Central O1; Extension 1.2; One hydrogen: H1;

ADP; Riding; Central O3; Extension 1.2; Two hydrogens: H2, H3;

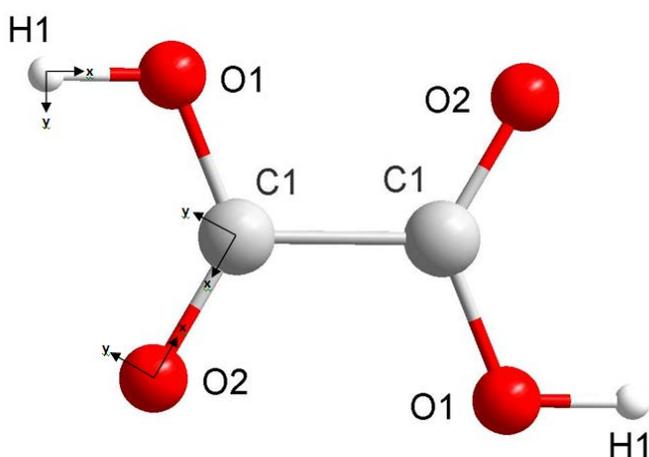
OK; Yes+start;

Use all to "significant discrepancies";

Refinement converges to  $R(\text{obs})=2.74\%$

### 17. Multipole refinement

For defining of multipole parameters it is convenient to select a local coordinate systems for each atom. The following figure shows a recommended choice for atoms C1, O1, O2 and H1:



The axis **x** is oriented along the bond from the central atom to one of non-hydrogen atoms (here called "first atom"). Our choice of "first atom" for central atoms C1, O1, O2 and H1 is O2, C1, C1 and O1, respectively. According to the definition in Jana2006, the second axis (here **y**) is perpendicular to the axis **x** and it lies in the plane defined by the central, first and second atom in such a way that the angle between the axis **y** and vector from the central atom to the second one is smaller than 90°. Our choice of "second atom" for central atoms C1, O1, O2 and H1 is O1, O2, C1 and C1, respectively. Note that second atoms need not make bonds with the central atom.

The similar choice can also be used for the molecule of crystal water.

[On the screen: Basic Jana window]

In order to save the result of the kappa refinement a new structure will be opened:

Start "File → Structure → Save As"

[On the screen: File manager for saving structure]

In File manager focus the right-bottom textbox and define a new name for testing of the kappa refinement i.e. "Oxa-Multipole"; OK

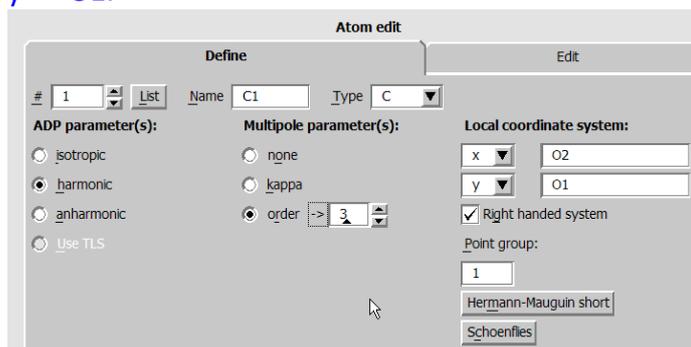
Yes to continue with the new structure

[On the screen: Basic Jana window]

Run "Edit atoms";

Double click the first atom – C1; switch from "kappa" to "order"

Change multipole parameters to order 3 and define the coordinate system **x** → O2 and **y** → O1.



Using the list box on the top left corner go to the next atom – O1.

Change multipole parameters to order 3 and define the coordinate system **x** → C1 and **y** → O2. Go to the next atom – O2.

Change multipole parameters to order 3 and define the coordinate system **x** → C1 and **y** → O1. Go to the next atom – O3.

Change multipole parameters to order 3 and define the coordinate system **x** → H2 and **y** → H3. Go to the next atom – H1.

Change multipole parameters to order 1 and define the coordinate system **x** → O1 and **y** → C1. Go to the next atom – H2.

Change multipole parameters to order 1 and define the coordinate system **x** → O3 and **y** → H3. Go to the next atom – H3.

Change multipole parameters to order 1 and define the coordinate system **x** → O3 and **y** → H2.

OK; OK; Yes to the question "Do you want rewrite changed files?"

[On the screen: Basic Jana window]

Right click on the icon "Refine";

In the page "Basic" select the number of cycles 100 and damping factor 0.1;

In the page "Various" press "Fixed commands" and fix the following parameters:

“Set individual”, P00[\*], “Set to” 0;

“Individual”, kappa'[\*];

[\*] stands for all atoms. P000 will be zero for all atoms while kappa' will be fixed to the current value.

OK; OK; YES+Start

Refinement converges to  $R(\text{obs})=1.75\%$ .

### 18. Multipole refinement including kappa' parameters

[On the screen: Basic Jana window]

Right click on the icon “Refine”;

In the “Various” fix the following parameters:

Delete or disable “Individual”, kappa'[\*];

In the “Equation” define two equations for H atoms;

kappa'[H2]=kappa'[H1]

kappa'[H3]=kappa'[H1]

OK; OK; Yes+start;

Refinement converges to  $R(\text{obs})=1.69\%$ .

It may happen that at this point R value is higher, around 1.75%. That means water molecule is in a false minimum. In such case: change number of multipoles for O3, H2 and H3 to zero; fix kappa'; repeat refinement; change number of multipoles back to 3,1,1 (for O3, H2, H3); repeat refinement; release kappa', repeat refinement

### 19. Fourier maps

[On the screen: Basic Jana window]

Double-click the icon Contour; Press the button “New plot”

Select “Calculate new map” and “Draw a general section”;OK;

[On the screen: Fourier commands]

In “Basic” use default setting i.e. Map type  $F(\text{obs})-F(\text{calc})$  – difference Fourier;

Keep all remaining parameters unchanged; OK;

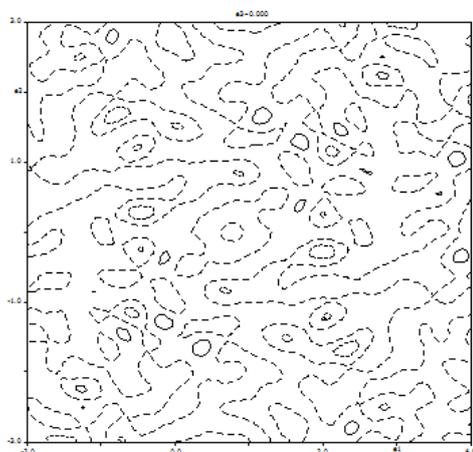
[On the screen: Plane/Volume]

Select “Use old”;OK

[On the screen: Difference Fourier map through the oxalic acid]

Press the button “Atoms ON”.

Press the button “Contours” and modify the positive and negative contours to  $0.05 \text{ e}^-/\text{\AA}^3$



The map does not show any clear positive or negative maxima which means that the model explain the experimental density adequately.

## 20. Interpretation of multiple parameters – map visualization

[On the screen: Basic Jana window]

Double-click the icon Contour; Instead of “Fourier maps” select “Charge density maps”;OK

[On the screen: Define atoms and basic parameters for charge density maps]

Select all atoms; Calculate “deformation density”;NEXT;

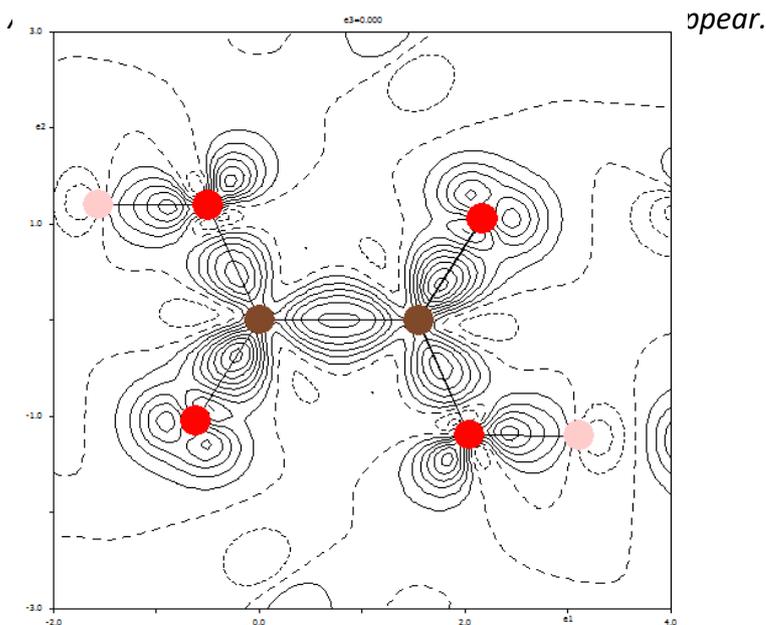
[On the screen: Plane/Volume]

Select “Use old”; NEXT

[On the screen: Select individual atoms for charge density]

Select all atoms; NEXT

Press the button “Atoms ON”;



## 21. Topological analysis – critical points

[On the screen: Basic Jana window]

Run “Tools → Topological analysis → Find critical points”

[On the screen: Define parametrs for CP search]

Select “Type of search” “between all bonds within interval”;

For all other parameters keep in default values;

OK;

[On the screen: Select atoms for distance check]

Select all; OK

[On the screen: Basic Jana window]

Run “Edit/View → View of CP report”;

[On the screen: Viewer for critical points]

The listing contain information about critical point along all important bonds in the molecule.

Bond	Fractional coordinates			$\rho$	Laplacian	Hess eigenvalues	Ellipsity
	x	y	z				

C1-C1[-x,-y,-z]	0.0000	0.0000	0.0000	1.77	-13.55	-	-	11.08	0.23
C1-O1	0.0011	0.0187	0.0875	2.50	-31.96	-	-	11.41	0.13
C1-O2	-	0.1228	0.0465	2.97	-36.60	-	-	19.71	0.17
O1-H1	0.0331	-	0.2065	1.62	-22.14	-	-	22.66	0.01
O3...H1	0.0041	0.0592	0.2493	0.54	5.16	-3.86	-3.36	12.38	0.15
O3-H2	0.0499	0.1790	0.3755	2.21	-49.22	-	-	23.40	0.02
O3-H3	-	-	0.3421	2.30	-61.79	-	-	24.39	0.03

## 22. Topological analysis – Basin integration

[On the screen: Basic Jana window]

Run “Tools → Topological analysis → Basin integration”

[On the screen: Select atoms for basic integration]

Select all; OK

[On the screen: Define parameters for integration]

Use default values; OK

Calculation can take some time ...

Run “Edit/View → View of Inb report”;

The integrated values for individual atoms should be:

Atom	Number of electrons	Charge
C1	5.147	0.853
O1	9.124	-1.124
O2	8.773	-0.773
O3	9.378	-1.378
H1	0.396	0.604
H2	0.407	0.593
H3	0.419	0.581

# Example 11.1: bezcox

## Composite structure

**Sr<sub>1.272</sub>CoO<sub>3</sub>**

**Revised: 28 April 2014**

Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: bezcox.hkl, bezcox.cif\_od

Frame scaling, absorption correction: done by diffractometer software

### 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click bezcox

### 2. *Import Wizard*

Select “Known diffractometer formats”; NEXT

Select “Oxford Diffraction – CCD”; NEXT

[On the screen: “Define basic input file:”]

Select “Input from cif\_od file”; file name “bezcox.cif\_od”; OK

[On the screen: “Complete/Correct experimental parameters”]

Leave all settings unchanged; NEXT

[On the screen: “Define the reference cell/split by twinning”]

Leave all settings unchanged; NEXT

For absorption correction select “None or done before importing”; NEXT

FINISH

### 3. *Data Repository*

OK; YES to accept the data set

[On the screen: “Information about starting symmetry wizard”]

NEXT

### 4. *Symmetry Wizard*

[On the screen: “Tolerances for crystal system recognition”.]

Symmetry wizard can be started separately by “File → Reflection file → Make space group test”.

Leave all settings default; NEXT

[On the screen: Select Laue symmetry]

Select Trigonal -3m1 Laue symmetry; NEXT

[On the screen: Select cell centering]

In the list we can see that R-reverse centering is almost fulfilled.

Click on “Details” and examine strongest reflections contradicting R-reverse centering

The most of printed reflections follow the rule  $-h+k+l=3n$ . Similarly, reflections contradicting R-obverse centering follow the rule  $h-k+l=3n$ . This can be a sign of obverse/reverse twinning.

Return back to the page with tolerances and check there “Introduce twin laws in case of subgroup”

Follow steps of the symmetry wizard, select -3m1 Laue symmetry, NEXT  
Now, only 128 reflections contradicts the R (obverse or reverse) centering  
Select R-reverse; NEXT

Before introducing the twinning, R-reverse centering was better fulfilled. This indicates that the major twin domain has R-reverse centering.

Select R-3m; NEXT

[On the screen: Select superspace group]

R-3m(00g)0s

[On the screen: Final step of the superspace test]

Accept the superspace group in the standard setting: R-3m(00g)0s;

Accept twinning matrices induced by the space group test; FINISH; OK

Continue with creation of reflection file with default options;

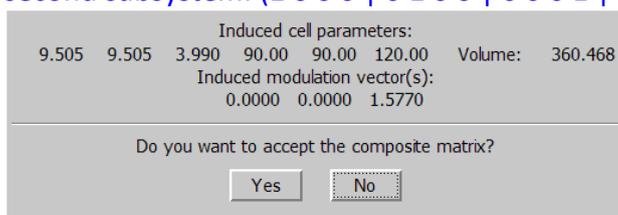
[On the screen: Structure solution]

Press "Quit";

## 5. Define W-matrix

Using Tools → Reciprocal space viewer we can clearly distinguish the composite subsystems. This compound has the simplest W matrix, which only exchanges the "l" and "m" index. That means that "h k l m" are reflections of the first subsystem while "h k m l" are reflections of the second subsystem.

Open "Edit M50", change number of composite parts to 2 and define W-matrix for the second subsystem: (1 0 0 0 | 0 1 0 0 | 0 0 0 1 | 0 0 1 0)



"Induced cell parameters" are parameters of the second subsystem, as follow from the W matrix

## 6. Structure Solution

Double-click the icon "Structure solution".

[On the screen: window of Structure solution]

In "Formula" textbox type list of chemical elements for Sr<sub>1.272</sub>CoO<sub>3</sub>: Sr Co O

Select "use Superflip"; "Peaks from Jana2006 but first run Fourier"

Select "Use a specific random seed" and type value "111"

Press "Run solution";

The option "Peak from Jana2006 but first run Fourier" is necessary for proper interpretation of Fourier map for composite structure because we need to look for both subsystems. Superflip converges (after noise suppression) with R value 20%. It confirms the symmetry R-3m(00g)0s.

Fixing the random seed to 111 guarantees for most processors that the Superflip returns exactly the same results like described in this cookbook. For this example finding proper solution would require many attempts with Superflip.

Press "Quit" to leave the structure solution wizard

## 7. Verification of the structure solution

Double click on the icon "Edit atoms";

Select oxygen atoms if present and delete them;

At this stage found oxygen positions are not reliable;

Double click on the Co1 atom and check its coordinates;

Co1        0.333333 0.666667 0.166667 - in the first subsystem

Move to the Co2 atom;

Co2        0.000000 0.333333 0.250000 – in the second subsystem

The solution program cannot distinguish at this stage between chemical types of heavy atoms because both atoms are placed in different subsystem and we cannot compare their electron densities directly.

OK;OK; Yes to save the changes;

Double click on the icon “Contour”;

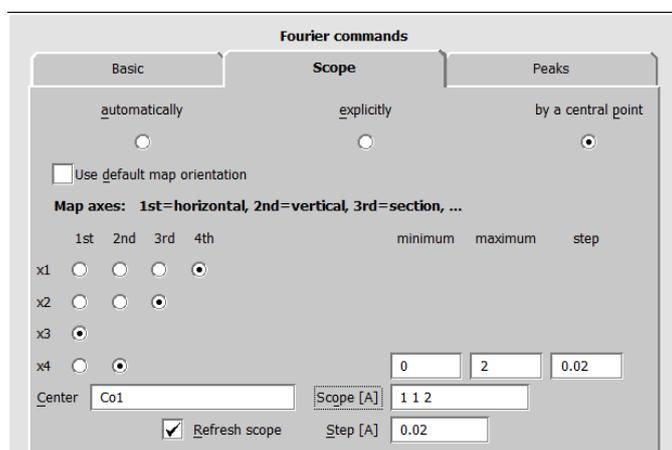
Press “New plot”; Select “Calculate new ones” and “Draw maps as calculated”; OK;

[On the screen: window of Fourier commands]

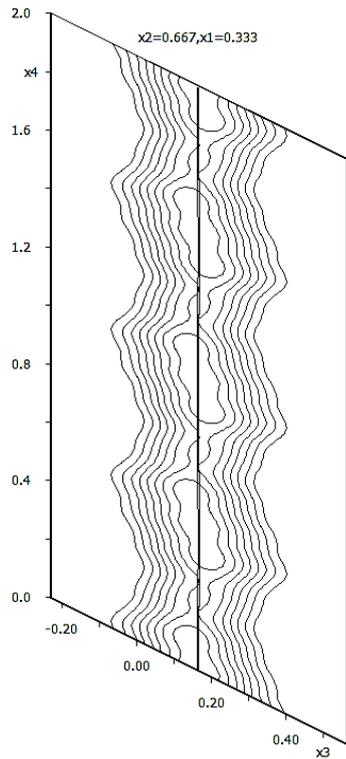
On the page “Basic” define Composite part no. 1;

Map type “F(obs) – Fourier”;

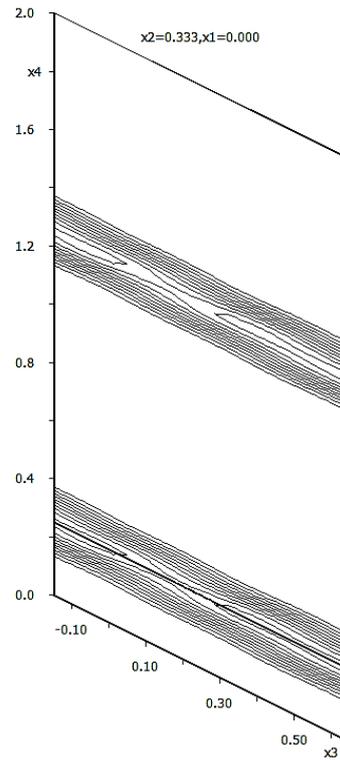
On the page “Scope” select the central point Co1; select the x3-x4 section; scope 1 1 2; OK



Repeat the procedure for Co2;



*x3-x4 section for Co1*



*x3-x4 section for Co2*

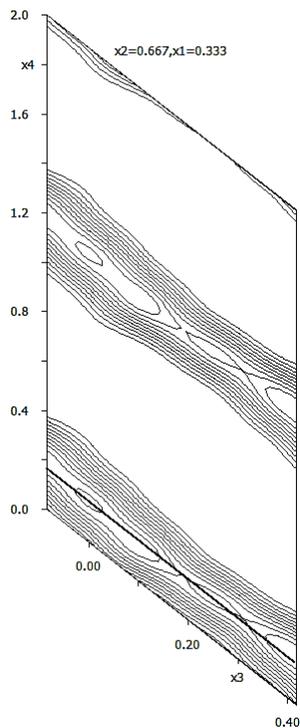
*Note: Both maps are summed over x1 and x2.*

Press "New plot"; Select "Calculate new ones" and "Draw maps as calculated"; OK;

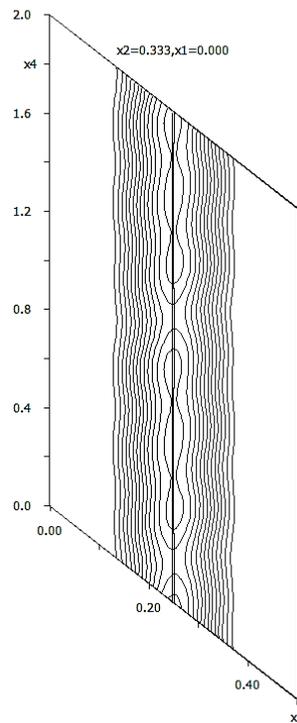
[On the screen: window of Fourier commands]

On the page "Basic" define Composite part no. 2;

Repeat map calculations for both atoms.



*x3-x4 section for Co1*



*x3-x4 section for Co2*

Start "Parameters → Twin fractions" and change the twin fraction to 0.5

Activate refinement of twin fraction

In Refinement options change number of cycles to 100

Run refinement

*Refinement converges with R values 34%, 24%, 41%, 58%, 67% and 97%*

Start "Edit/View → View of Refine" and read information following the header "Composite part #2".

*Here we can see unit cell and symmetry of the second composite subsystem. Note that the second subsystem has also different centering because centering vectors are also transformed by W matrix.*

```

Composite part #2

      | 1.000 0.000 0.000 0.000|
W(2) = | 0.000 1.000 0.000 0.000|
      | 0.000 0.000 0.000 1.000|
      | 0.000 0.000 1.000 0.000|

Cell parameters      :      9.5050   9.5050   3.9899   90.000   90.000   120.000   Volume :      312.2
Reciprocal parameters : 0.121483 0.121483 0.250632 90.000   90.000   60.000   Volume : 0.003203

Modulation vector q(1): 0.000000 0.000000 1.577038

Centrosymmetric super-space group: X-3c1(00g)000

List of centring vectors:

0.000000 0.000000 0.000000 0.000000
0.666667 0.333333 0.000000 0.333333
0.333333 0.666667 0.000000 0.666667

Symmetry operators:

  x1   x2   x3   x4
-x2  x1-x2  x3   x4
-x1+x2 -x1  x3   x4
  x2   x1  -x3+1/2 -x4
x1-x2 -x2  -x3+1/2 -x4
-x1  -x1+x2 -x3+1/2 -x4
-x1  -x2  -x3   -x4

Refinement program
structure :

  x2  -x1+x2  -x3  -x4
x1-x2  x1  -x3  -x4
-x2  -x1  x3+1/2  x4
-x1+x2  x2  x3+1/2  x4
  x1  x1-x2  x3+1/2  x4

```

page= 3  
19:21:28 17-01-11

Double click on the icon “Edit atoms”; Double click on the atom Co2;

The “Edit” page shows that the parameter *Uiso* is negative. It indicates that atom type is Sr.

Go the “Define” page and change the atom type to Sr and rename it to Sr1;

Run refinement

Refinement converges with R values 32%,21%, 40%, 58%, 70% and 97% and the isotropic ADP parameters become positive.

## 8. Making results compatible with Acta Cryst. (1999), B55, 841-848

Start “Tools → Transformation → Origin shift” and move origin to the position of Co1.

Position of Sr1 changes to -1/3, -1/3, 1/4.

Start Edit atoms, select Sr1, Action: Transform selected atoms

Select symmetry operator  $-x2 \ x1-x2 \ x3 \ x4$

Run Refinement

R factors of the previous refinement are exactly repeated

Now we are compatible with published positions of Co1 and Sr1.

## 9. Oxygen

Run refinement to obtain input for Fourier

Run difference Fourier for composite part No 1, with Scope=“automatically”, default map orientation, independent parallelepiped

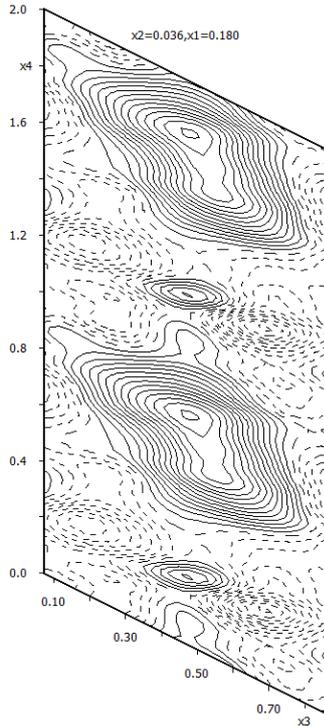
We use composite part 1, because we expect oxygen belonging to Co coordination

YES to start procedure for including atoms

Locate the strongest maximum with reasonable distance to Co (probably Max2)

Include this maximum as O1 in position about 0.17, 0.04, 0.5

Start Contour and plot section x3-x4 through O1, scope 1 1 2, difference Fourier, using summation of x1, x2 over 1 Å;



section x3-x4 of O1

The section reveals O1 should be described with crenel function,  $x40=0.75$ ,  $\delta=0.5$

Plot section x1-x2, difference Fourier, x4 from 0 to 1, scope 5 5 0, step 0.5A, center 0 0 0.5  
 The section x1-x2 with center at (0,0,1/2) with scope about 5 Å as a function x4 shows the character of the modulation

Fourier commands

Basic Scope Peaks

automatically explicitly by a central point

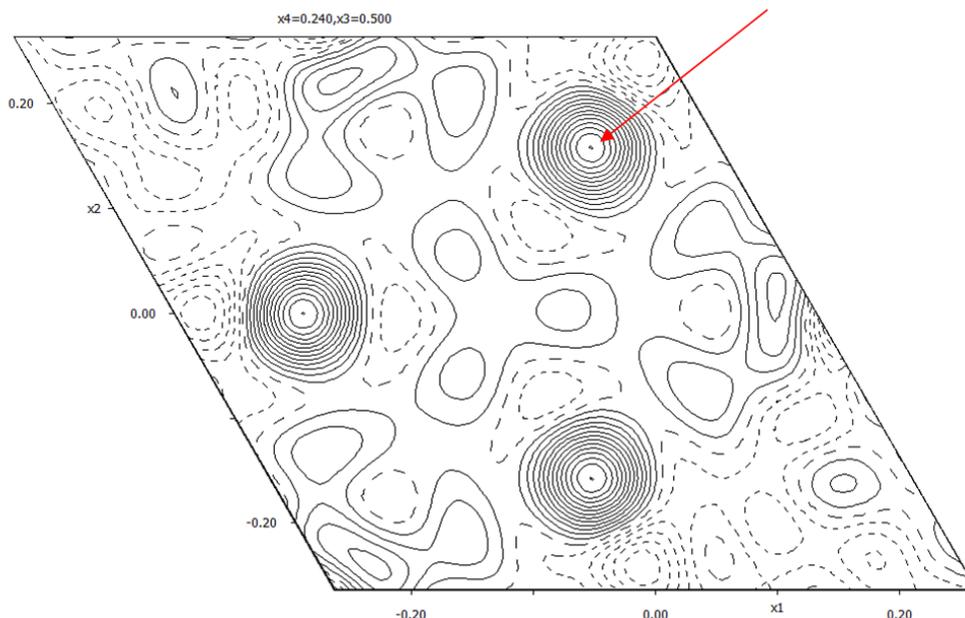
Use default map orientation

Map axes: 1st=horizontal, 2nd=vertical, 3rd=section, ...

	1st	2nd	3rd	4th	minimum	maximum	step
x1	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>			
x2	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>			
x3	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>			
x4	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>			

Center:  Scope [Å]:  Step [Å]:

:



Run "Movie" to see the discontinuous character of the modulation.

The three oxygen positions are generated by the three fold axis. From the above figure on possibility for oxygen position is about (0.157,0.157,0.5) (as indicated by the arrow) with crenel of length 0.5 with  $x_4$  center 0.25.

Start Edit atoms and double-click O1

Define the crenel function for O1 and delete its position modulation wave

In page Edit press Occupancy and set  $x_{40}=0.25$  and  $\delta=0.5$  (page "Edit").

In page Edit modify the atomic position of O1 to the one found in the difference Fourier and reset size occupancy (it should be 0.5).

Finally in the page "Define" define type of modulation functions – Legendre polynomials.

Run refinement

Refinement converges with R values 26%,13%, 36%, 58%, 66% and 88%

Set harmonic ADP for all atoms

Repeat refinement

R values are almost unchanged

## 10. More modulation waves

Add one by one more position and ADP modulation waves.

Co: 4 for position, 4 for ADP

O1: 4 for position, 2 for ADP

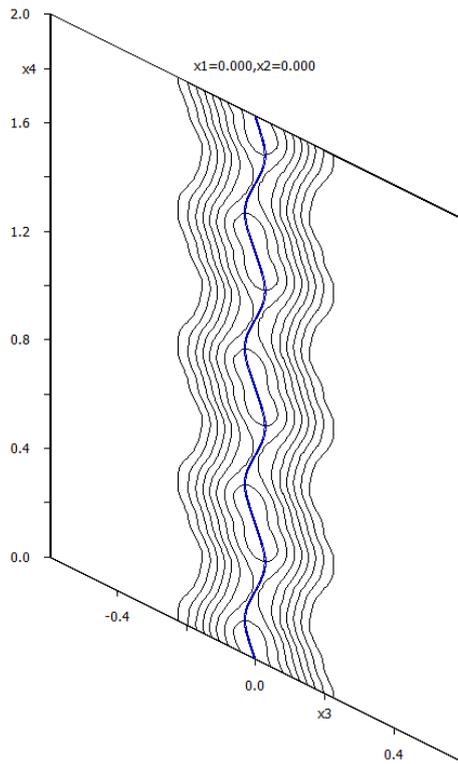
Sr1: 4 for position, 4 for ADP

The last refinement will converge with R values 4.3%,2.5%, 4.2%, 9.2%, 21.5% and 59%

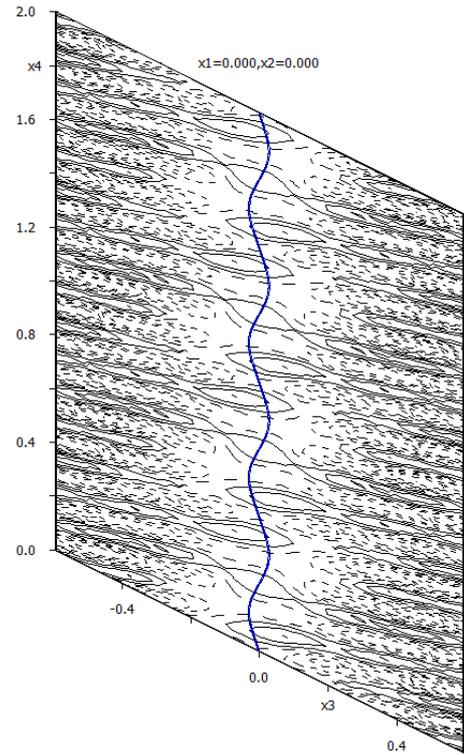
With fourth order satellites it is doubtful if we could achieve better results because they are almost completely unobserved. However, the fit for 2<sup>nd</sup> and 3<sup>rd</sup> order satellites is not yet satisfactory

## 11. Sawtooth for Sr1

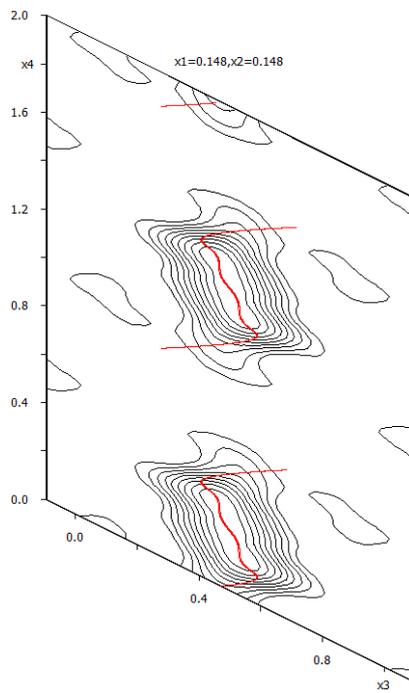
Start Contour and plot  $x_3$ - $x_4$  section (observed and difference Fourier) for Co1, O1 and  $x_2$ - $x_4$  section for Sr1. Use 1 Å summation. Do not forget to switch composite subsystem in the Basic page of Fourier commands.



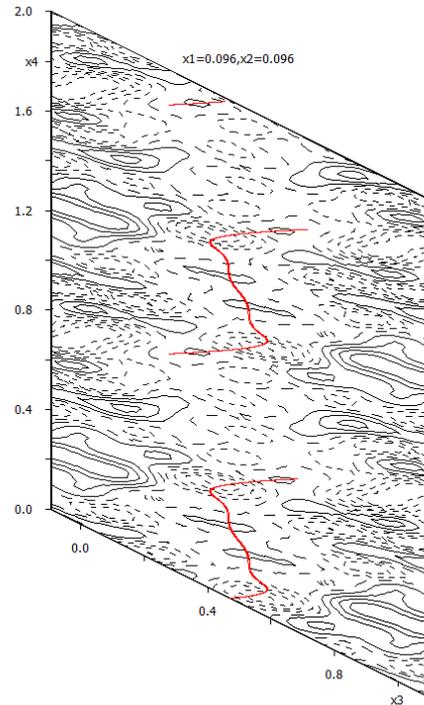
x3-x4 section for Co1



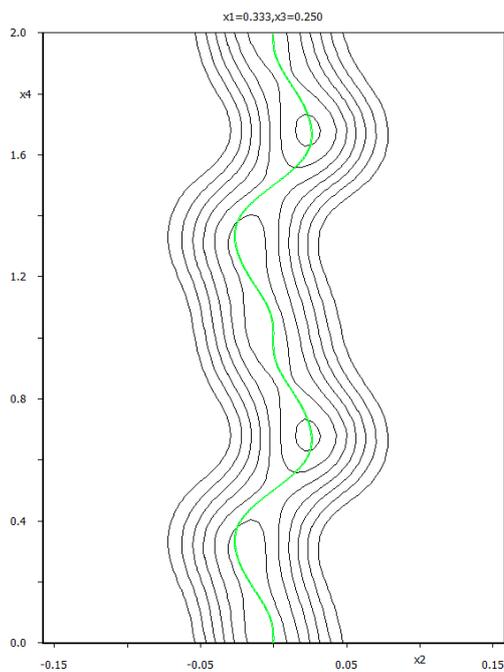
difference section, contour step 0.2



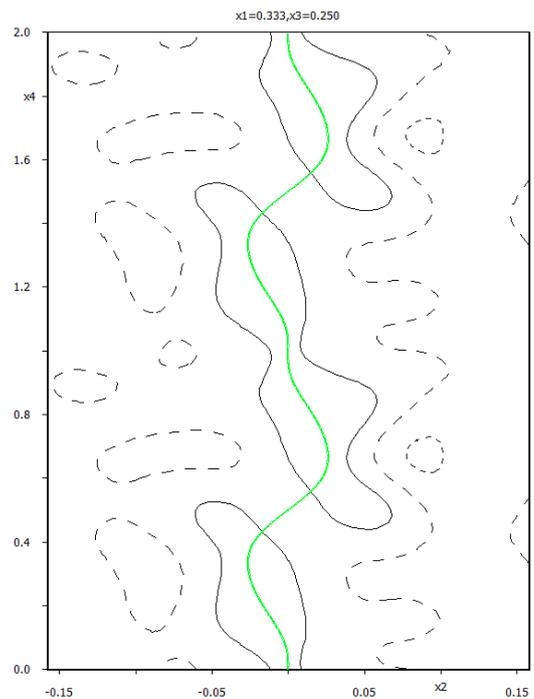
x3-x4 section for O1



difference section, contour step 0.2



x2-x4 section for Sr1



difference section, contour step 0.2

*The largest different peaks are around Sr1 position. Now we shall attempt to describe modulation function of Sr1 with Lagrange polynomials, with crenel defined at  $x_{40}=0$  with  $\delta=1$*

Make backup copy (File → Structure → Save As)

Start Edit atoms

Remove all ADP and position modulation waves of Sr1 except the first position modulation wave;

Activate in the Crenel for Sr1 and the the edit page set  $x_{40}=0$  and  $\delta=1$ . Keep  $x_{40}$  and  $\delta$  fixed

In the page “Define” Parameters activate Legendre polynomials

In refinement commands set Damping factor 0.1

Run refinement

During the refinement change Damping factor to 0.5

*Refinement converges with R values 10.3%, 4.0%, 9.3%, 37.7%, 46% and 53%*

Add one by one position and ADP modulation waves for Sr1 up to three position waves and three ADP waves.

*The last refinement will converge with R values 3.7%, 1.9%, 3.6%, 8.2%, 18.7% and 55%. This is significant improvement comparing with the structure model without sawtooth function.*

### **Anharmonic ADP for Co1**

“Start Contour → New plot → Calculate new ones”

In Basic page select Difference Fourier and Composite part no. 1

In Scope select central point Co1, section x1-x2, scope 6 6 1

OK

In Contour make summation only along x3 (not x4)

**Fourier commands**

Basic      Scope      Peaks

automatically      explicitly      by a central point

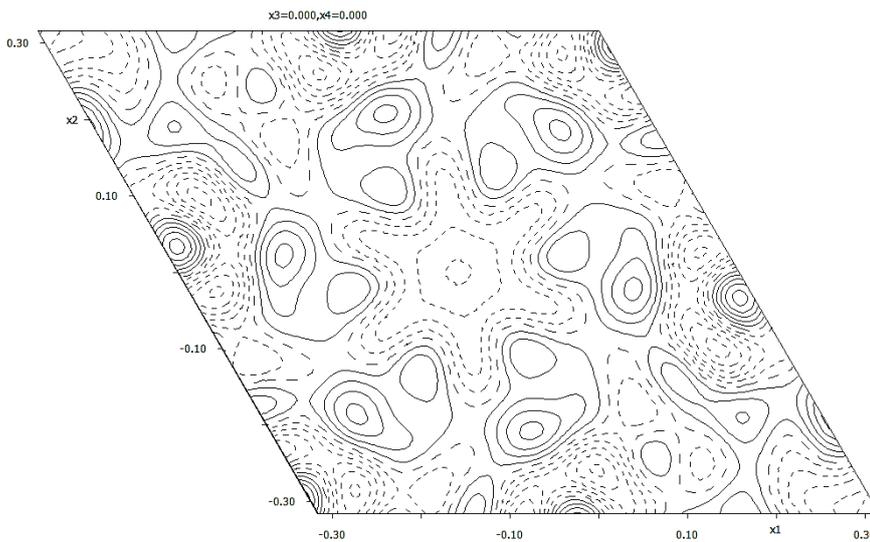
Use default map orientation

**Map axes: 1st=horizontal, 2nd=vertical, 3rd=section, ...**

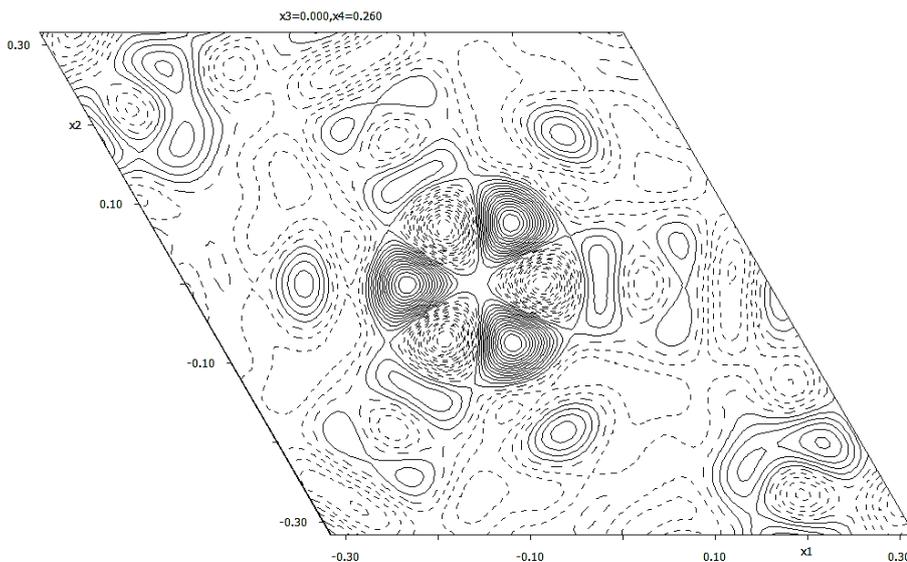
	1st	2nd	3rd	4th	minimum	maximum	step
x1	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>			
x2	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>			
x3	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>			
x4	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>			

Center       Scope [A]              

Step [A]



*x1-x2 section through Co1, contour step 0.05, x4=0*



*x1-x2 section through Co1, contour step 0.05, x4=0.26*

*The neighborhood of Co1 is changing from octahedron to trigonal prisma (check it with drawing program). The trigonal coordination induces a slightly triangular shape of ADP.*

*However, the region in x4 in which the effect is detectable is very narrow and the number of modulation waves for ADP's of the order 3 would be very large to describe such abrupt change.*

*The atom Co1 should therefore be split into two positions by crenel – the first one Co1 (x40=0, delta=0.45) and the second one Co1' (x40=0.25, delta 0.05). After adjusting of occupancies to  $a_i=1/6$  for both atoms the two Legendre waves for position and harmonic ADP Co1 should be used.*

*For the Co1' only average parameters for position and ADP up to the third order.*

*Final R values : 3.2%, 1.8%, 3.0%, 7.3%, 13.9% and 55%*

# Example 12.1: Ba<sub>5</sub>Co<sub>5</sub>

Simple antiferromagnetic magnetic structure ( $k = 0$ )

Revised: 6 May 2019

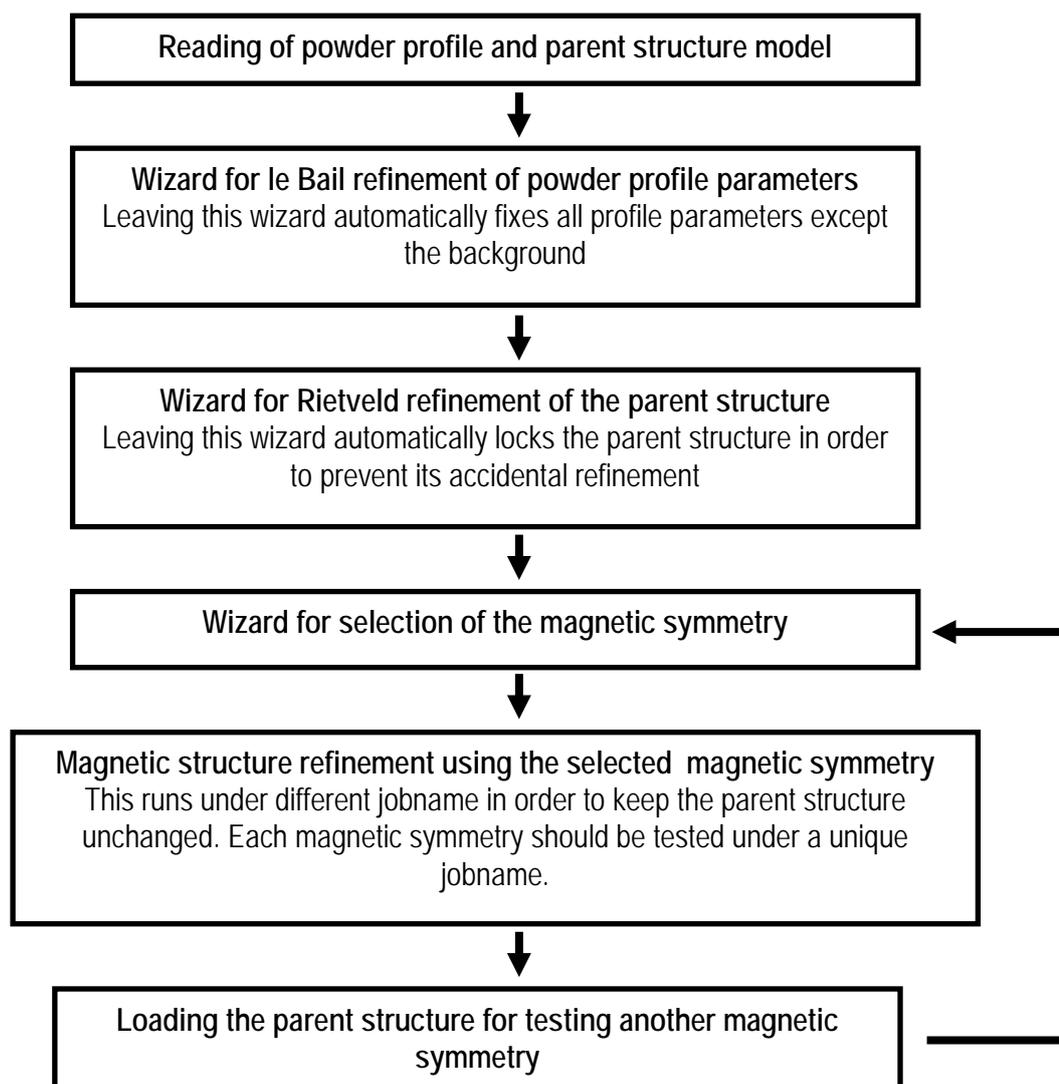
Ba<sub>5</sub>Co<sub>5</sub>ClO<sub>13</sub>

Powder data measured with the ILL neutron source at 1.4 K

For more details: Mentré, O., Kauffmann, M., Ehora, G., Daviero-Minaud, S., Abraham F. & Roussel, P. (2008). *Solid State Sciences* **10**, 471-475.

Input files: Ba5Co5.dat (powder profile data)  
Ba5Co5\_nuclear.cif (nuclear structure)

In order to facilitate the work with magnetic structures, Jana2006 offers special wizards and protects the basic file - the parent structure. However, for experienced users of Jana, all operations offered by wizards can be also done manually by starting the tools directly from the basic user interface. The standard work with magnetic structures based on powder data follows this scheme:



### 23. Creating new jobname

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click Ba5Co5

[On the screen: Specify type of the file to be imported]

Select "Magnetic parent structure: nuclear model from CIF"; NEXT

[On the screen: Select input CIF file]

Right pane: select (by the button with arrow) the input file Ba5Co5\_nuclear.cif; OK

### 24. Define magnetic propagation vector and form factors

[On the screen: Define magnetic propagation vector and form factors]

For Number of non-zero magnetic propagation vectors select 0

For "Atom type" select "Co"; check "Use as a magnetic atom"

For "Magnetic formfactor <j0>" select Co4+; NEXT; Finish

The parent structure has been created

### 25. Import the reflection file

[On the screen: Specify type of the file to be imported]

Select "Powder data - Various CW formats"; NEXT

Check that the name of the input file is "Ba5Co5.dat" and the format is "Free format of 2th, I, [sig(I)"; NEXT

[On the screen: Complete/correct experimental parameters];

For "Wave length" type 2.52; NEXT; Finish

[On the screen: Data repository]

OK; YES to "Do you want to accept made changes?"

### Refining of profile parameters by le Bail technique.

[On the screen: Information]

NEXT;

[On the screen: Refinement of the powder profile by the le Bail algorithm]

"Show powder profile"

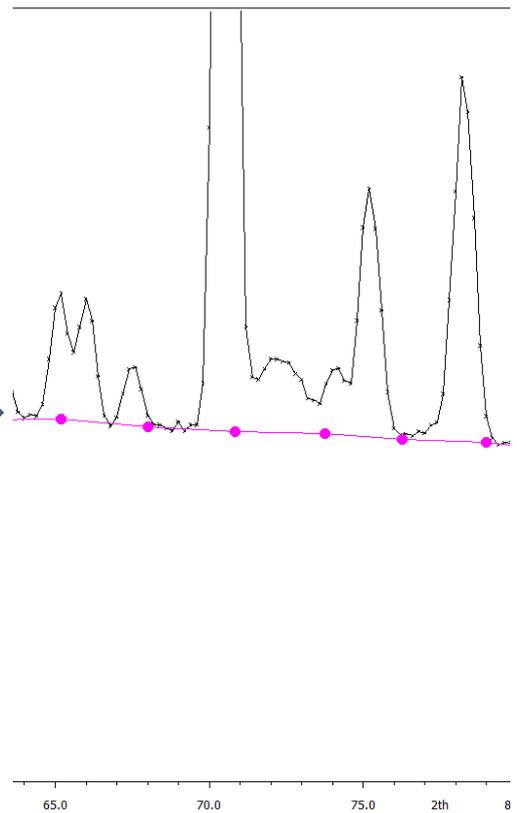
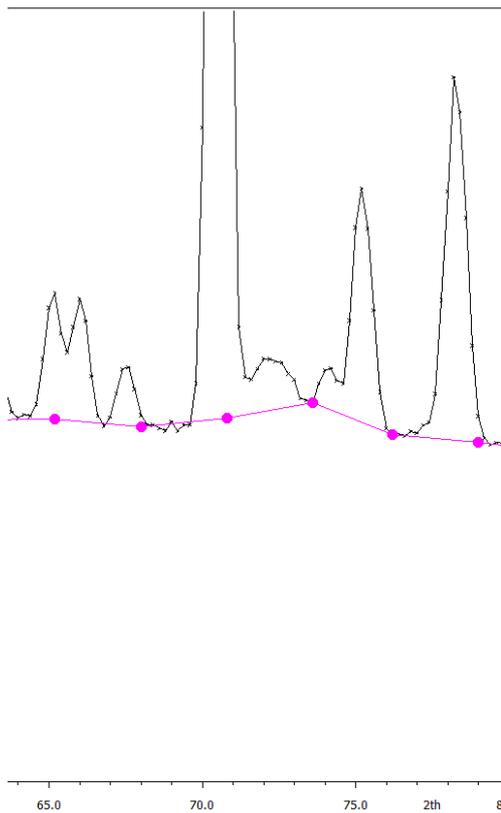
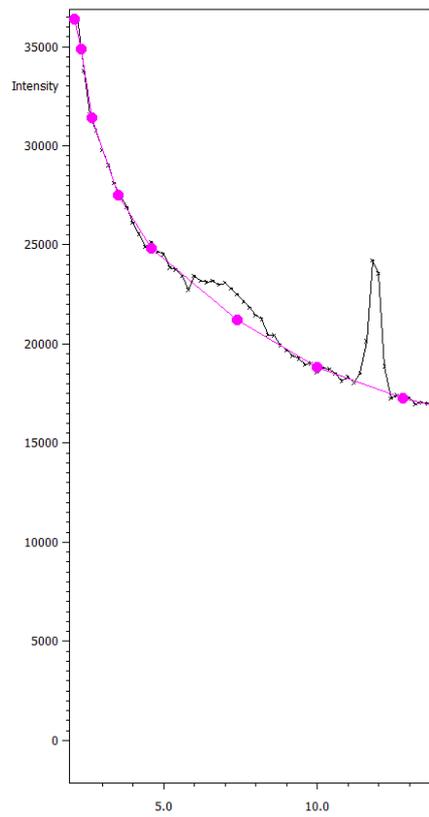
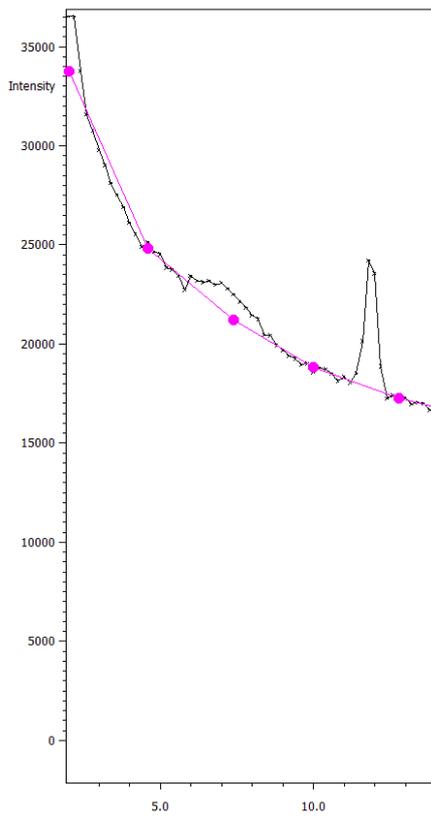
As common for powder neutron data the background is strongly varying with the diffraction angle. It is recommended to estimate it manually and use just a few additional parameters.

Manual background: "Create new"; Use default parameters; OK

The automatic procedure has created a first estimation of the manual background, which can be modified manually: the points can be dragged by the left mouse button; dragging a point to the position of neighboring point deletes the point; clicking between two points creates a new point.

Using "X+", "Y+", enlarge the profile plot

Modify background point at high and low angles as indicated in the next figures:



“QUIT”; Select “Accept the new manual background” and “Reset polynomial coefficients to zeros”; OK

*This means that the polynomial background will be refined and combined with the manual background*

"Edit profile parameters";

[On the screen: Powder options]

In the page "Cell" activate refinement of a and c parameters;

In the page "Profile" check if starting value of GW is 50 and activate its refinement;

In the page "Corrections" activate refinement of "shift" parameter; OK; YES to save changes  
"Run Refine";

*The refinement should converge to  $R_p \sim 2.7\%$ .*

"Edit profile parameters";

[On the screen: Powder options]

In the page "Profile" change activate refinement of GU and GV; OK; YES to save changes  
"Run Refine";

*The refinement should converge to  $R_p \sim 2.1\%$ .*

"Show powder profile" to see the fit of the calculated profile; QUIT

NEXT;

YES to "Do you really want to leave the form for le Bail refinement?"

*Now we will refine the scale parameter for the nuclear structure*

[On the screen: Refinement of the nuclear structure by the Rietveld method]

"Edit refinement commands"; On the page "Various" select "Fixed commands";

Check that the fixed commands "fixed all \*" is present if not select "All parameters" and fill into the editing window "Atoms/parameters" by the wild character "\*" which means all atoms

Press "Add";

*The command will appear in the panel as "fixed all \*"*

OK; OK;

"Run Refine";

*The refinement should converge to  $R_p \sim 3.4\%$ .*

NEXT;

YES to "Do you really want to leave the form for Rietveld refinement?"

NEXT to accept the Information

## **26. Testing different irreps to get the best single irrep model**

[On the screen: Representation analysis]

*This window has an informative character. You can see here all irreps leading to magnetic ordering. The "details" buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.*

Press "Display representations" and look at the representation "mGM5-".

Individual 2x2 representation matrices of each of 24 operations:

representation: mGM5- Dimension: 2

-----

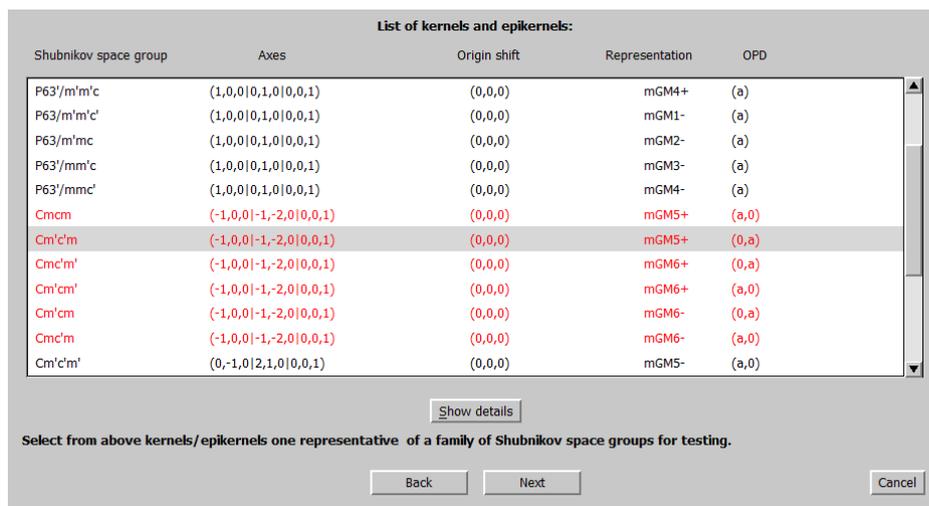
Symmetry operator	Symbol	Matrix	Character
(x, y, z, m)	1	1.000 0.000     0.000 1.000	2.000 2.000
(-y, x-y, z, m)	3	-0.500 0.866     -0.866 -0.500	-1.000 -1.000
(-x+y, -x, z, m)	3	-0.500 -0.866     0.866 -0.500	-1.000 -1.000
(-x, -y, z+1/2, m)	21	1.000 0.000     0.000 1.000	2.000 2.000
(y, -x+y, z+1/2, m)	63	-0.500 0.866     -0.866 -0.500	-1.000 -1.000
(x-y, x, z+1/2, m)	63	-0.500 -0.866     0.866 -0.500	-1.000 -1.000
(y, x, -z, m)	2	-0.500 0.866     0.866 0.500	0.000 0.000

List of irreducible representations  
structure :

(x-y, -y, -z, m)	2	-0.500 -0.866     -0.866 0.500	0.000 0.000
(-x, -x+y, -z, m)	2	1.000 0.000     0.000 -1.000	0.000 0.000
(-y, -x, -z+1/2, m)	2	-0.500 0.866     0.866 0.500	0.000 0.000
(-x+y, y, -z+1/2, m)	2	-0.500 -0.866     -0.866 0.500	0.000 0.000
(x, x-y, -z+1/2, m)	2	1.000 0.000     0.000 -1.000	0.000 0.000
(-x, -y, -z, m)	-1	-1.000 0.000     0.000 -1.000	-2.000 -2.000
(y, -x+y, -z, m)	-3	0.500 -0.866     0.866 0.500	1.000 1.000
(x-y, x, -z, m)	-3	0.500 0.866     -0.866 0.500	1.000 1.000
(x, y, -z+1/2, m)	m	-1.000 0.000	-2.000

Close the window; NEXT;

[On the screen: List of kernels and epikernels]



Select e.g. magnetic group Cmcm' and press "Show details".

```

*****
Epikernel magnetic space group for the representation mGM5- *
*****

Order parameter direction: (0,a)

 centrosymmetric space group: Cmcm'

List of centring vectors:

0.000000 0.000000 0.000000
0.500000 0.500000 0.000000

Symmetry operators:

  x   y   z   m
-x  -y  z+1/2 m
-x   y   z   m
  x  -y  z+1/2 m
  x  -y  -z   -m
-x   y  -z+1/2 -m
-x  -y  -z   -m
  x   y  -z+1/2 -m

Symmetry operations are related to the original axes. The following transformation brings it to the standard setting:

a' = -b
b' = 2a +b
c' = c

```

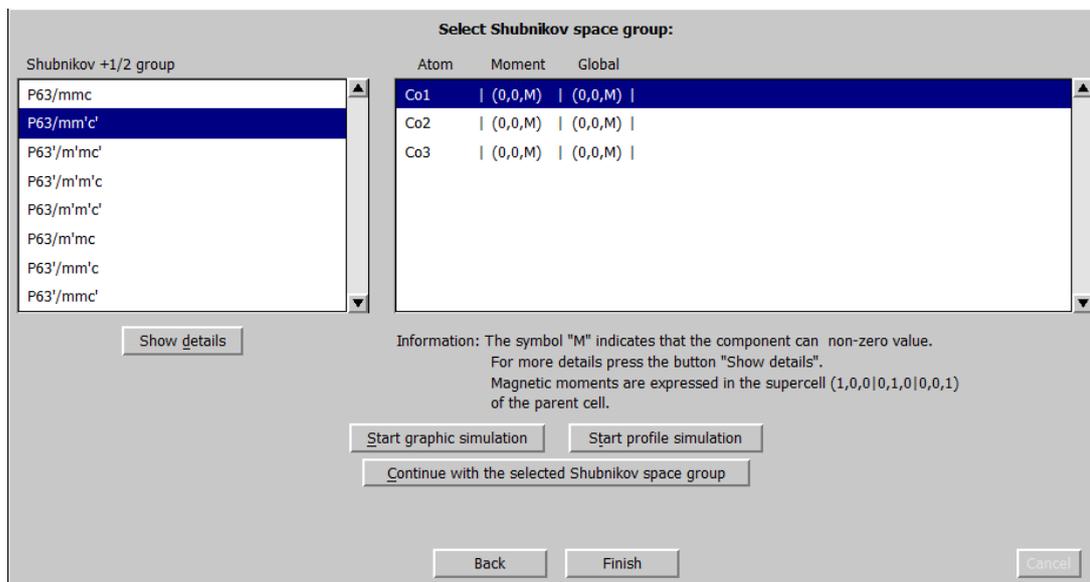
*It shows symmetry operators of the selected magnetic group, transformation to the standard setting and the relevant order parameter.*

Close;

Select one of the hexagonal magnetic space groups; NEXT

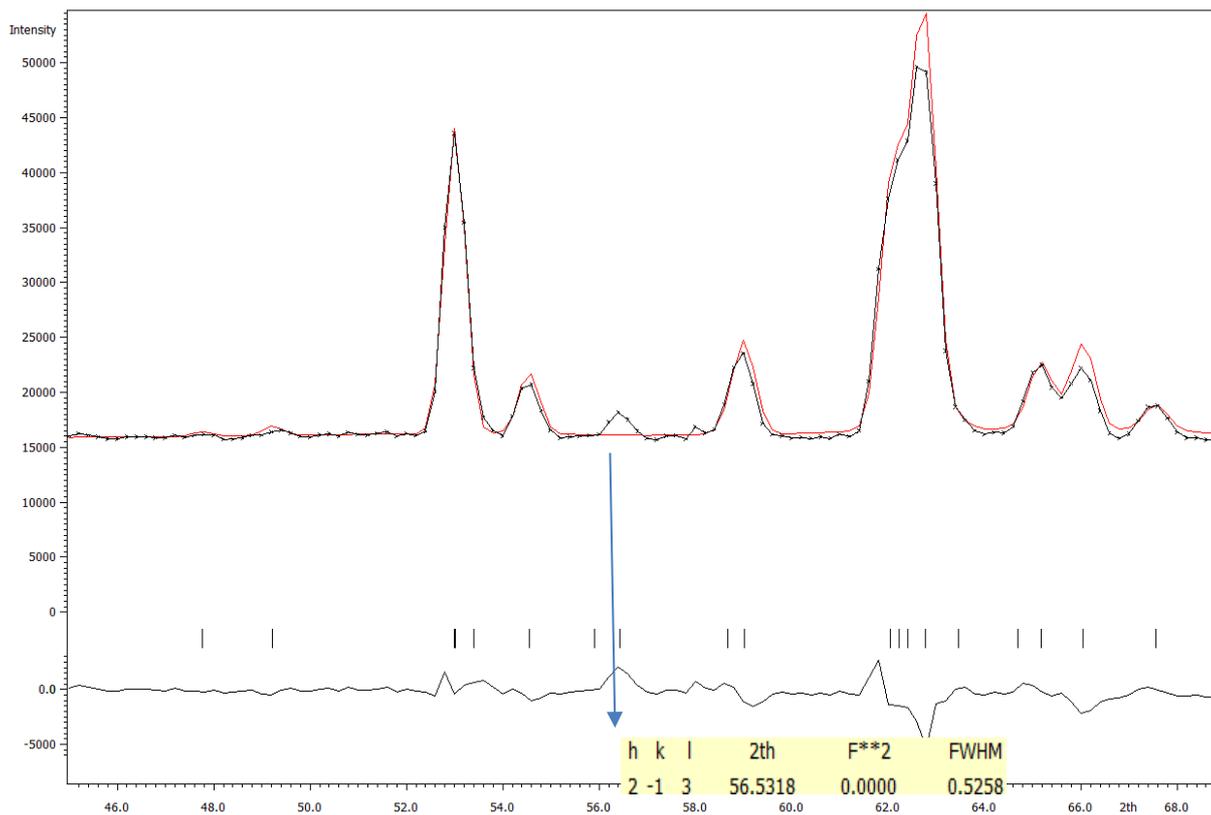
*This will pass all present hexagonal magnetic space groups to further testing.*

*[On the screen: Select Shubnikov space group]*



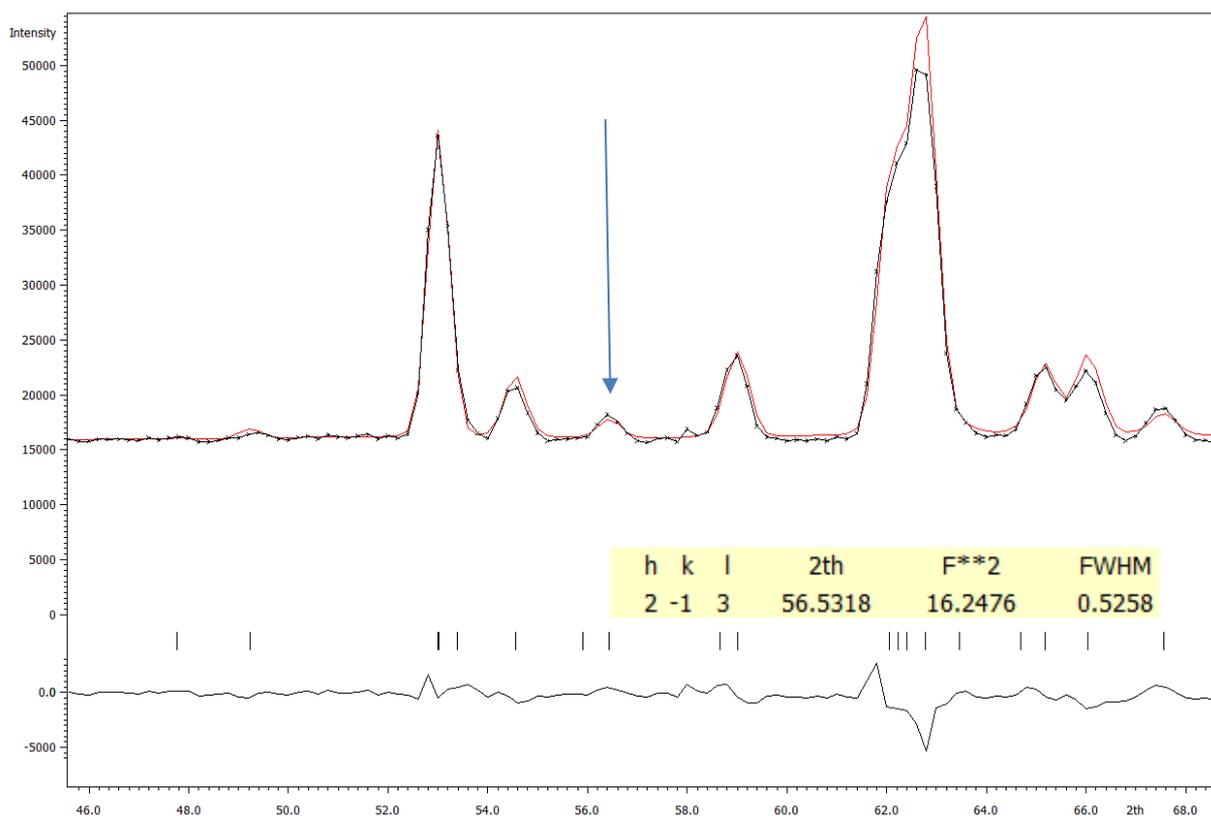
*For an individual Shubnikov space group the tool shows components of the magnetic vector of all magnetic atoms in the structure. The button "Show details" gives a more detailed analysis. In our case only two Shubnikov space groups –  $P6_3/mm'c'$  and  $P6_3'/m'm'c'$  – allow magnetic ordering for all Co atoms. Note that for the first of them the global magnetic moment for is generally non-zero, which means that this arrangement allows a ferromagnetic ordering. As ferromagnetism has not been detected for this compound, the first model can be excluded from the analysis. However, we shall test both models to check if such a decision can also be based on the diffraction experiment.*

Select the Shubnikov space group  $P6_3/mm'c'$  and press "Start profile simulation". Use "Go to 2th/hkl" textbox and find position of the reflection 2 -1 3 . Click on the tick corresponding to the reflection 2 -1 3:



*Although the peak is clearly visible, the calculated structure factor is zero.*

ESC; Press “Quit” and then select Shubnikov space groups  $P6_3'/m'm'c$  and investigate again



However, in making such conclusion we have to take into account that the simulation procedure uses randomly generated magnetic moments and that the result can be affected by an actual random choice. This is why we recommend repeating the simulation when some doubt exists.

For this Shubnikov space group the intensity of  $(2,-1,3)$  is non-zero in accordance with the diffraction pattern. As this reflection is systematically absent for the nuclear structure ( $c$  glide plane), it is clear that it originates from magnetic scattering. As apparent from the Shubnikov space group test, all magnetic moments are directed along the  $z$ -axis. This leads to the systematic extinctions  $l = 2n + 1$  for reflections  $(2h, -h, -h, l)$  but only in the case that the glide plane “ $c$ ” is combined with the time inversion operation. The fact that the peak  $(2,-1,3)$  is clearly detectable gives us another support for the Shubnikov space group  $P6_3'/m'm'c$ .

Select again the Shubnikov space group  $P6_3/mm'c'$  and press “Start graphic simulation”;  
Select “Use Vesta to draw the magnetic structure”;

Press “Draw+return” or “Draw+continue”;

In the case that bond between atoms are created go to “Edit→Bonds...” and delete all automatically generated bond limits

If necessary, you can modify the length of the displayed vectors by “Edit→Vectors...”

Vectors - Ba5Co5\_test\_mag\_tmp\_tmp.cif

Phase: 1 Ba5 Cl1 Co5 O13

Crystallographic Sites		Individual Atom			Vector
No.	Label	x	y	z	
1	Ba1	0.66667	-0.66667	0.45959	
2	Ba2	1.33333	-0.33333	0.36991	
3	Ba3	1.00000	0.00000	0.25000	
4	Co1	1.00000	0.00000	0.50000	1
5	Co2	1.00000	0.00000	0.39525	2
6	Co3	0.66667	-0.66667	0.32182	3
7	Cl1	0.33333	0.66667	0.25000	
8	O1	0.83937	-0.83937	0.35074	
9	O2	1.14584	-0.14584	0.45052	
10	O3	0.66667	-0.66667	0.25000	

Preview

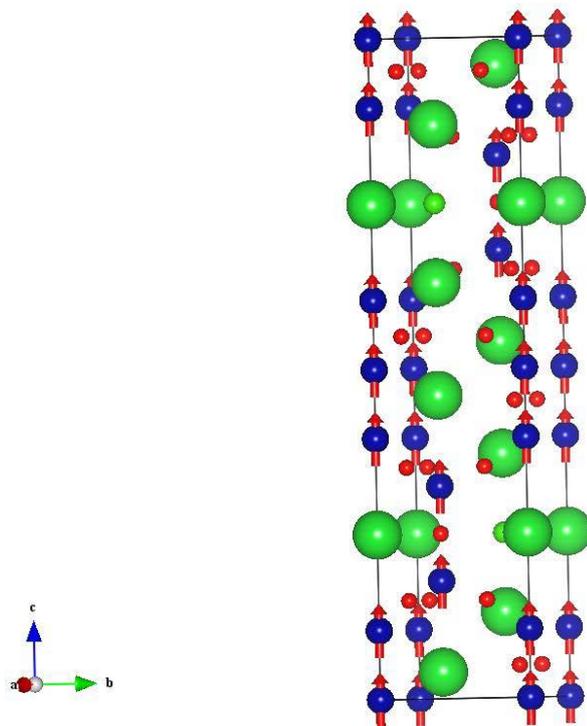
<< Set >> Remove

Vectors

No.	[u v w]	Modulus	r (Å)
1	[0.00000 0.00000 0.08275]	2.00	0.50
2	[0.00000 0.00000 0.08275]	2.00	0.50
3	[0.00000 0.00000 0.08275]	2.00	0.50

Scale factor for modulus: 0.6

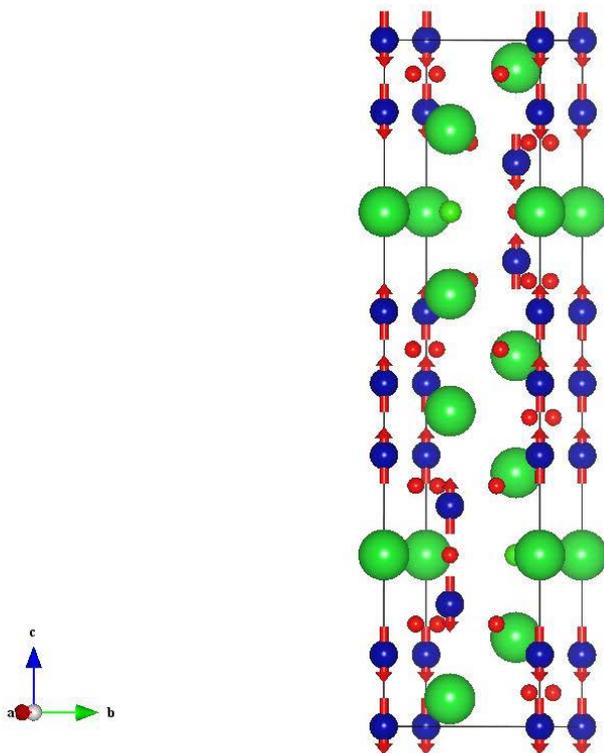
OK Cancel



You can see that in this case the magnetic moments, which are in the simulation chosen

identical for the independent magnetic atoms, are not compensated in the unit cell.

Repeat this procedure for  $P6_3/m'm'c$



## 27. Refinement of the magnetic structure in $P6_3/m'm'c$ (GM2+)

[On the screen: Select Shubnikov space group]

Select the Shubnikov space group  $P6_3/m'm'c$  and press the button "Continue with the selected Shubnikov space group";

Finish; YES to the question "Do you want to continue with the last kernel/epikernel?";

[On the screen: Select structure name]

Use the default name "Ba5Co5\_01"; OK

The test will be done under the new job name in order to keep the parent structure unchanged. The program will open another Jana window, which can be used to refine the selected model. The Jana window with the parent structure remains active.

[On the screen: Basic window]

Right-click the icon of Refine and select the page "Various".

Click "Fixed commands" and make sure the coordinates of all atoms are fixed:

fixed xyz \*

Click "Restrictions" and make sure ADP parameters all atoms are restricted to be the same:

restric \* 12

The "Fixed commands" and "Restrictions" are created automatically by the program when preparing the testing structure.

OK; select the page "Basic"

Check if the "Number of cycles" is 100 and the "Damping factor" is 0.1;

"Use Marquart technique" check that the Fudge factor is 0.001;

OK; Start refinement;

*Refinement converges with  $R_p \sim 3.3\%$ ,  $R(\text{obs}) \sim 8.5\%$ .*

## 28. Refinement of the magnetic structure in $P6_3/m'm'c$ (GM4+)

Return the Jana window with the parent structure.

[On the screen: Select Shubnikov space group]

Select  $P6_3/m'm'c$  and press the button "Continue with the selected Shubnikov space group";

[On the screen: Select structure name]

Use the default name; OK

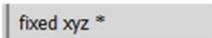
*The program will open another Jana window which can be used to refine the selected model.*

*The Jana window with the parent structure remains active.*

[On the screen: Basic window]

Right-click the icon of Refine and select the page "Various".

Click "Fixed commands" and make sure the coordinates of all atoms are fixed:



fixed xyz \*

Click "Restrictions" and make sure ADP parameters all atoms are restricted to be the same:



restric \* 12

OK; select the page "Basic"

Check that the "Number of cycles" is 100 and the "Damping factor" is 0.1;

"Use Marquart technique" check that the Fudge factor is 0.001;

OK; Start refinement;

*Refinement converges with  $R_p \sim 3.0\%$ ,  $R(\text{obs}) \sim 6.3, 6.5, 2.3\%$  for all, nuclear and magnetic reflections, respectively.*

## 29. Drawing of the magnetic structure

[On the screen: Basic window]

Double click on the icon "Plot structure";

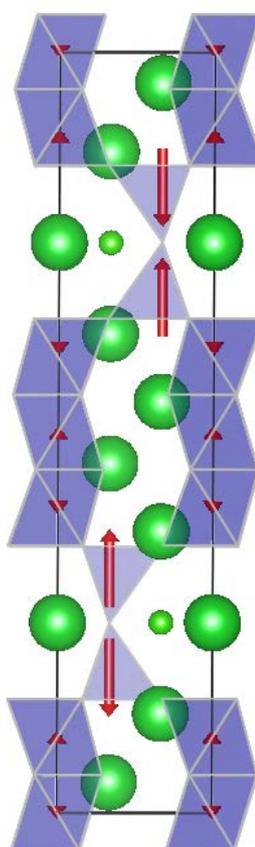
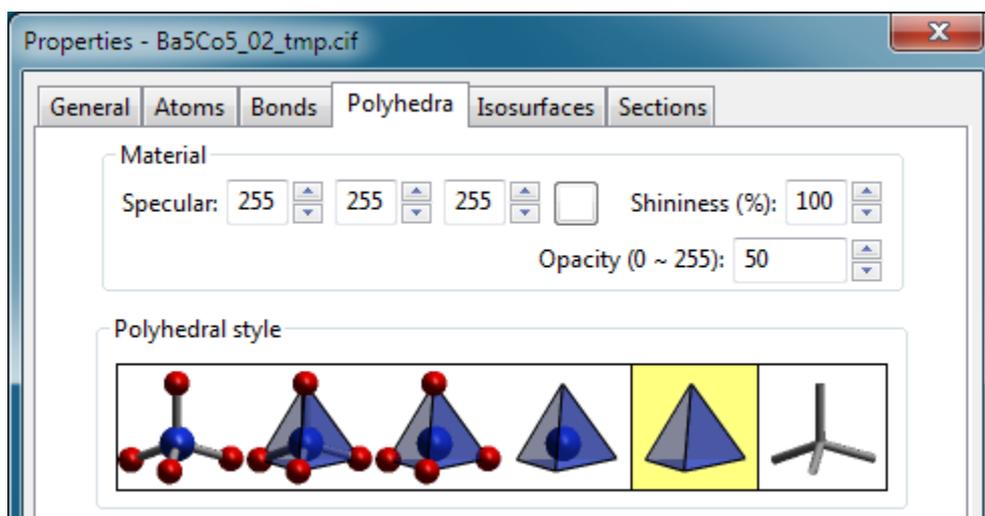
Press "Draw+return" or "Draw+continue";

Select "Objects→Structural models" and choose "Polyhedral"

Select "Edit→Bonds"; Delete bonds Ba O and Ba Cl; Apply; OK;

Select "Objects→Properties→Polyhedra";

Choose new polyhedral style and reduce the opacity to 50:



*The magnetic moments of atoms Co4 and Co5 are negligible. The atom Co6 is tetrahedrally coordinated by O atoms while the others have octahedral coordination.*



# Example 12.2: Ba6Co6

Commensurate magnetic structure – modulation (propagation) vector (0,0,1/2)

Revised: 5 May 2019

## Ba<sub>6</sub>Co<sub>6</sub>ClO<sub>16</sub>

Powder data measured with the ILL neutron source at 1.4 K

For more details: Mentré, O., Kauffmann, M., Ehora, G., Daviero-Minaud, S., Abraham F. & Roussel, P. (2008). *Solid State Sciences* **10**, 471-475.

Input files: Ba6Co6.dat (powder profile data)  
Ba6Co6\_nuclear.cif (nuclear structure)

### 30. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click Ba6Co6

### 31. Import Wizard

Select “Magnetic: nuclear model from CIF”; NEXT

Right pane: select the input file Ba6Co6\_nuclear.cif; OK

### 32. Define magnetic propagation vector and form factors

[On the screen: Define magnetic propagation vector and form factors]

Check “Use non-zero magnetic propagation vector” and fill its value: 0 0 1/2

Select atom type Co; check “Use as a magnetic atom”; select “Magnetic formfactor <j0>”  
Co4+; NEXT; FINISH

The parent structure is created

### 33. Import the reflection file

[On the screen: Specify type of the file to be imported]

Select “Various CW format”; NEXT;

Check that the name of the input file is “Ba6Co6.dat” and the data format is “Free format of  
2th, l, [sig(l)]; NEXT

[On the screen: Complete/correct experimental parameters];

Fill used wavelength 2.394; NEXT; FINISH

[On the screen: Data repository]

OK; YES to “Do you want to accept made changes?”

### 34. Refining of profile parameters by the le Bail technique.

[On the screen: Information]

NEXT

[On the screen: Refinement of the powder profile by the le Bail algorithm]

“Show powder profile”

Although the background is often strongly varying with the diffraction angle for powder

neutron data, in this case it is relatively smooth and it can be described without introducing a manual background.

“Quit”; “Edit profile parameters”;

[On the screen: Powder options]

In the page “Cell” activate refinement of a and c parameters;

In the page “Profile” change the starting value of GW to 50 and activate its refinement;

In the page “Corrections” activate refinement of “shift” parameter; for background enlarge the number of used Legendre polynomials to 10

OK; YES to save the changes

“Edit refinement commands”; In the page “Basic” change the number of cycles to 100; OK “Run Refine”;

The refinement should converge to  $R_p \sim 9.3\%$ .

“Edit profile parameters”;

[On the screen: Powder options]

In the page “Profile” change activate refinement of GU and GV

Change the peak-shape function to pseudo-Voigt and activate refinement LY

OK; YES to save the changes

“Run Refine”

The refinement should converge to  $R_p \sim 5.5\%$ .

NEXT; YES to leave the form for le Bail refinement

### 35. Refinement of the scale parameter for the nuclear structure

[On the screen: Refinement of the nuclear structure by the Rietveld method]

“Edit refinement commands”; On the page “Various” select “Fixed commands”;

Fix all parameters for all atoms (wild character \*); “Add”; OK; OK

“Run Refine”

The refinement should converge to  $R_p = 9.7\%$ ,  $R(\text{obs}) = 6.5\%$

NEXT; YES to leave the for for Rietveld refinement

### 36. Testing different irreps to get the best single irrep model

[On the screen: Information]

NEXT

[On the screen: Representation analysis]

Representation analysis:					
Representation	Dimension	Shubnikov space group	Axes	Origin shift	
mA1	1	P[c]-6m2	(1,0,0 0,1,0 0,0,2)	(0,0,0)	Details
mA2	1	P[c]-6c2	(1,0,0 0,1,0 0,0,2)	(0,0,1/4)	Details
mA3	1	P[c]-6m2	(1,0,0 0,1,0 0,0,2)	(0,0,1/4)	Details
mA4	1	P[c]-6c2	(1,0,0 0,1,0 0,0,2)	(0,0,0)	Details
mA5	2	P[b]m	(0,1,0 0,0,2 1,0,0)	(0,0,0)	Details
mA6	2	P[b]m	(0,1,0 0,0,2 1,0,0)	(0,1/4,0)	Details

Display representations

Back Next Cancel

This window has an informative character and shows all irreps leading to magnetic ordering. The "Details" buttons provides more information about an individual irrep. There are four highest symmetrical hexagonal Shubnikov space groups; two of them differ only in the origin position, but this may lead to different solutions in commensurate cases.

NEXT

[On screen: List of kernels and epikernels]

**List of kernels and epikernels:**

Shubnikov space group	Axes	Origin shift	Representation	OPD
P[c]-6m2	(1,0,0 0,1,0 0,0,2)	(0,0,0)	mA1	(a)
P[c]-6c2	(1,0,0 0,1,0 0,0,2)	(0,0,1/4)	mA2	(a)
P[c]-6m2	(1,0,0 0,1,0 0,0,2)	(0,0,1/4)	mA3	(a)
P[c]-6c2	(1,0,0 0,1,0 0,0,2)	(0,0,0)	mA4	(a)
A[a]mm2	(0,0,-2 -1,0,0 1,2,0)	(0,0,0)	mA5	(a,0)
A[a]ma2	(0,0,-2 -1,0,0 1,2,0)	(1/4,0,0)	mA5	(0,a)
A[a]mm2	(0,0,-2 -1,0,0 1,2,0)	(1/4,0,0)	mA6	(a,0)
A[a]ma2	(0,0,-2 -1,0,0 1,2,0)	(0,0,0)	mA6	(0,a)
P[b]m	(-1,0,0 0,0,-2 0,-1,0)	(0,0,0)	mA5	(a,b)
P[b]m	(-1,0,0 0,0,-2 0,-1,0)	(0,1/4,0)	mA6	(a,b)

Select from above kernels/epikernels one representative of a family of Shubnikov space groups for testing.

Select one of the hexagonal Shubnikov groups; NEXT

This will pass all present hexagonal Shubnikov groups to further testing.

[On the screen: Select Shubnikov space group]

**Select Shubnikov space group:**

Shubnikov group	Atom	Moment	Global
P[c]-6m2	Co1	(0,0,M)	(0,0,0)
P[c]-6c2+(0,0,1/4)	Co2	(0,0,M)	(0,0,0)
P[c]-6m2+(0,0,1/4)	Co3	(0,0,M)	(0,0,0)
P[c]-6c2			

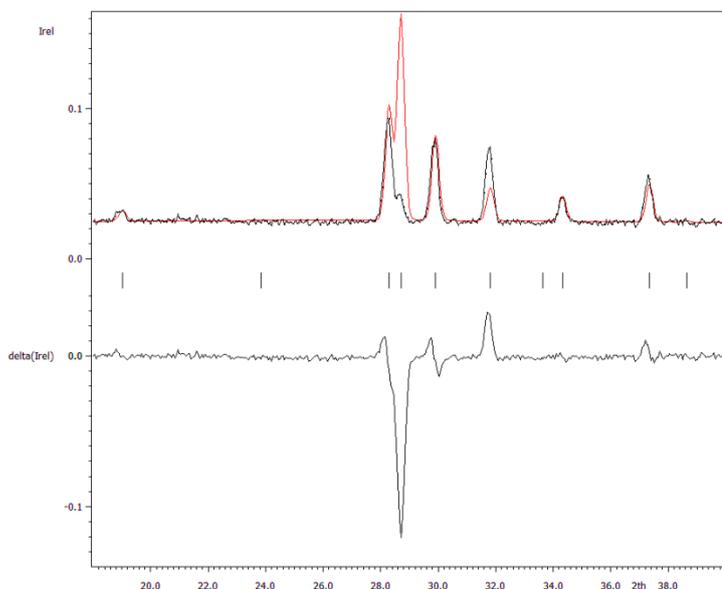
Information: The symbol "M" indicates that the component can have non-zero value. For more details press the button "Show details".  
Magnetic moments are expressed in the supercell (1,0,0|0,1,0|0,0,2) of the parent cell.

Only the second and the fourth Shubnikov group allows for non-zero magnetic moments for the Co atoms.

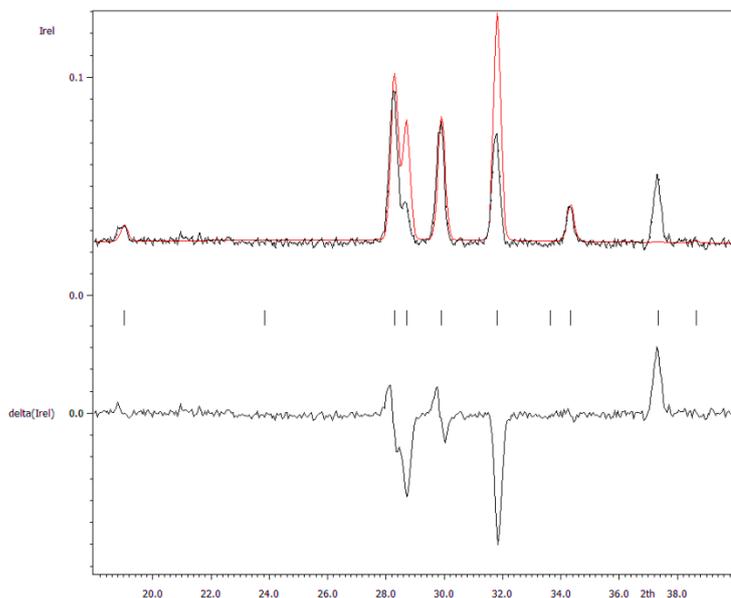
Select the Shubnikov group:  $P[c]-6c2$

Press "Start profile simulation";

Press "X exactly" and focus the region 18-40 degrees; Press "Fit Y":



Press "Quit" and repeat this procedure for the next magnetic Shubnikov group  $P[c]-6c2$  with origin shifted by  $(0,0,1/4)$ :



*At this stage none of them can be excluded.*

### **37. Refinement of the magnetic structure – $P[c]-6c2$**

[On the screen: Select Shubnikov space group]

Select the Shubnikov space group  $P[c]-6c2$  and press the button "Continue with the selected Shubnikov space group";

[On the screen: Select structure name]

Use the default name; OK

[On the screen: Basic window of Jana2006]

Right-click the icon of Refine and select the page "Various"

Use the button "Restrictions" and ensure that all atoms (i.e. \*) have been restricted to have identical ADP parameters.

The restriction "restric \* 12" has been set automatically when the program created the testing structure. To see the meaning of the restriction focus it by mouse and press "Load". "Load" opens the restriction for editing. Make sure that "Coordinates" and "Modulations" boxes are cleared and press "Rewrite" to close the editing mode.

OK

Select the page "Fixed commands" and (similarly like in the previous step) ensure that all atomic positions are fixed in their current values ("fixed xyz \*").

OK

Select the page "Basic" and check if the "Number of cycles" is 100 and the "Damping factor" is 0.1; OK; Start refinement

Refinement converges with  $R_p \sim 8.8\%$ ,  $R(\text{obs}) \sim 6.5\%$ ,  $6.5\%$ ,  $6.5\%$  for all, nuclear and magnetic reflections, respectively.

### 38. Drawing the resulting magnetic structure

[On the screen: Basic window]

Double click on the icon "Plot structure"

Select "Use Vesta to draw the magnetic structure"

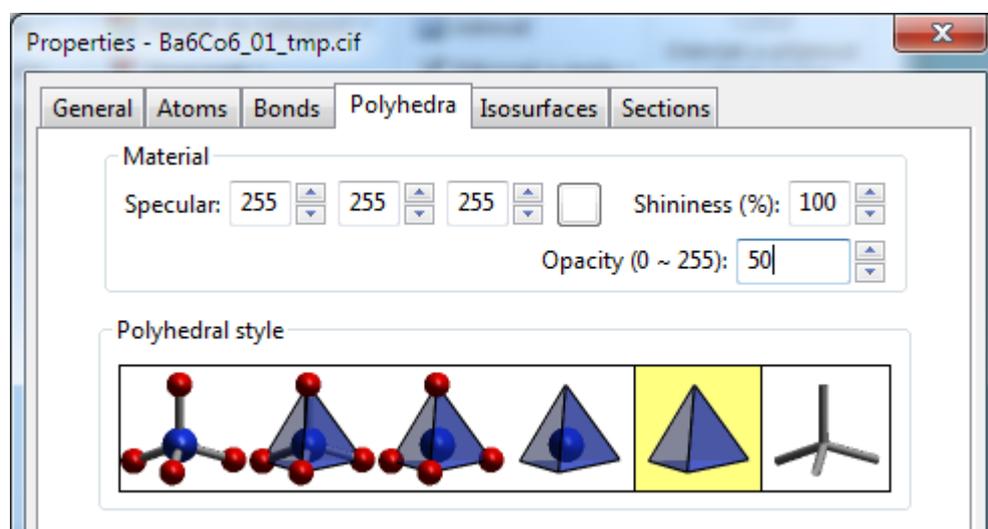
Press "Draw+return" or "Draw+continue"

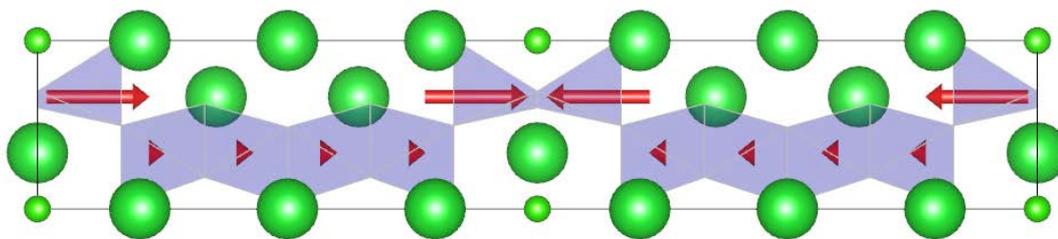
Select "Objects→Structural models" and choose "Polyhedral"

Select "Edit→Bonds"; Delete bonds Ba-O, Ba-Cl and O-O; Apply;OK;

Select "Objecs→Properties→Polyhedra";

Choose new polyhedral style and reduce the opacity to 50:





### 39. Refinement of the magnetic structure – $P[6c2]$ origin shifted by $(0,0,1/4)$

Return to the Jana window with the parent structure.

[On the screen: Select Shubnikov space group]

Select  $P[6c2+(0,0,1/4)]$  and press the button “Continue with the selected Shubnikov space group”;

YES to the question “Do you want to continue with the last kernel/epikernel?”;

[On the screen: Select structure name]

Use the default name; OK

[On the screen: The following transformation can bring the structure to the standard setting]

NO to refuse the suggested origin shift

[On the screen: Basic window]

Right-click the icon of Refine and select the page “Various”.

Similarly like in the previous test ensure (under “Restrictions”) that all atoms are restricted to have identical ADP and ensure (under “Fixed commands”) that coordinates of all atoms are fixed.

Select the page “Basic” and check that the “Number of cycles” is 100 and the “Damping factor” is 0.1; OK; Start refinement;

Refinement converges with  $R_p \sim 8.9\%$ ,  $R(\text{obs}) \sim 6.6\%$ ,  $6.5\%$ ,  $7.7\%$  for all, nuclear and magnetic reflections, respectively.

### 40. Comparing of two different results

[On screen: Basic window]

Double click on the icon “Plot structure”;

Select “Use Vesta to draw the magnetic structure”; OK

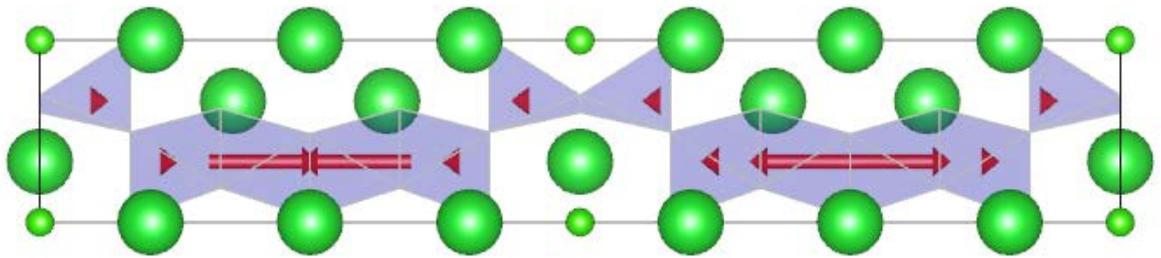
Press “Draw+return” or “Draw+continue”

In VESTA select “Objects→Structural models” and choose “Polyhedral”

Select “Edit→Bonds”; Delete bonds Ba-O, Ba-Cl and O-O; Apply; OK;

Select “Objecs→Properties→Polyhedra”;

Choose new polyhedral style and reduce the opacity to 50;



*The models are very different. In the first model the only significant magnetic moment was localized at the tetrahedrally coordinated Co atom, while in the second one the significantly non-zero magnetic moment was localized at the octahedrally coordinated site.*

*The first structure model has better R values. Moreover, the presence of magnetic moments at the tetrahedral site corresponds to the result in Example 12.1*



# Example 12.3: PrSrMnO

Commensurate magnetic structure – modulation (propagation) vector (1,0,0)

Revised: 28 November 2014

Powder data measured the ILL neutron source at 10 K

For more details: K. Knížek, J. Hejtmánek, and Z. Jiráček, C. Martin, M. Hervieu, and B. Raveau, G. André and F. Bourée, Chemistry of Materials, (2004), 1104-1110.

Input files: PrSrMnO.dat (powder profile data)  
PrSrMnO\_nuclear.cif (nuclear structure)

## 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click PrSrMnO

## 2. Import Wizard

Select “Magnetic: nuclear model from CIF”; NEXT

[On the screen: Select input CIF file]

Right pane: select the input file PrSrMnO\_basic.cif; OK

## 3. Define magnetic propagation vector and form factors

[On the screen: Define magnetic propagation vector and form factors]

Check “Use non-zero magnetic propagation vector” and fill its value: 1 0 0

For “Atom type” select “Mn”; check “Use as a magnetic atom”

For “Magnetic formfactor <j0>” select Mn<sup>3+</sup>; NEXT; FINISH

The parent structure is created

## 4. Import the reflection file

[On the screen: Specify type of the file to be imported]

Select “Various CW format”; NEXT

Check that the name of the input file is “PrSrMnO.dat” and the format is “ILL D1A/D2B (Rietveld-Hewat format)”; NEXT

[On the screen: Complete/correct experimental parameters];

For “Wave length” type 1.227; NEXT; FINISH

[On the screen: Data repository]

OK; YES to “Do you want to accept made changes?”

## 5. Refining of profile parameters by le Bail technique.

[On the screen: Information]

NEXT;

[On the screen: Refinement of the powder profile by the le Bail algorithm]

“Show powder profile”

The background is relatively smooth and it can be described without introducing manual background.

“Quit”;

“Edit profile parameters”;

[On the screen: Powder options]

In page “Cell” activate refinement of a, b and c parameters;

In the page “Profile” change the starting value of GW to 50 and activate its refinement;

In the page “Corrections” activate refinement of “shift” parameter and change the number of used Legendre polynomials to 10

OK; YES to rewrite the changes

“Edit refinement command”; In the page “Basic” change the number of cycles to 20

OK; “Run Refine”;

*The refinement should end with  $R_p \sim 7.8\%$ .*

“Edit profile parameters”;

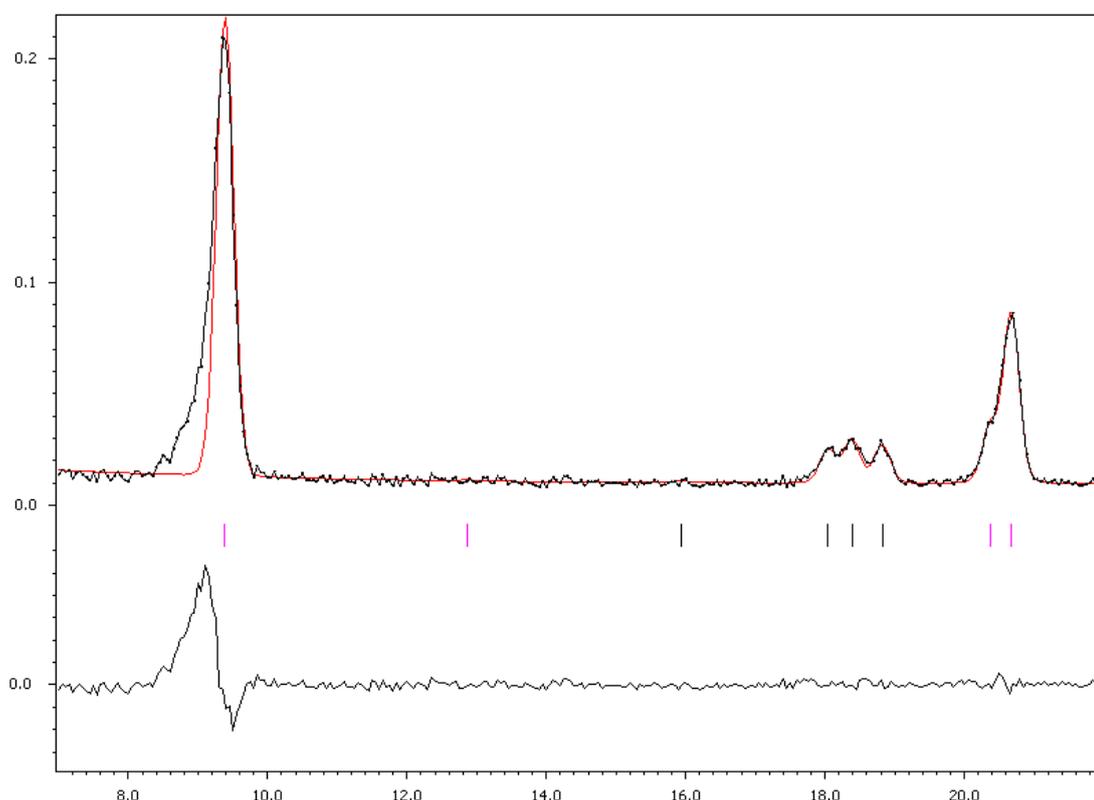
[On the screen: Powder options]

In the page “Profile” activate refinement of GU and GV; Change the peak-shape function to pseudo-Voigt and activate refinement of LY; OK; YES to the question about rewriting;

“Run Refine”

*The refinement should converge to  $R_p \sim 5.9\%$ .*

“Show powder profile”; Select the region  $2\theta$  from 7 to 22 degs – use the button “X exactly”.



*The first peak has a strong asymmetry. For neutron and synchrotron cases, such asymmetry can be described by the correction for divergence as introduced by Finger-Cox-Jephcoat, J. Appl. Cryst. (1994). 27, 892-900.*

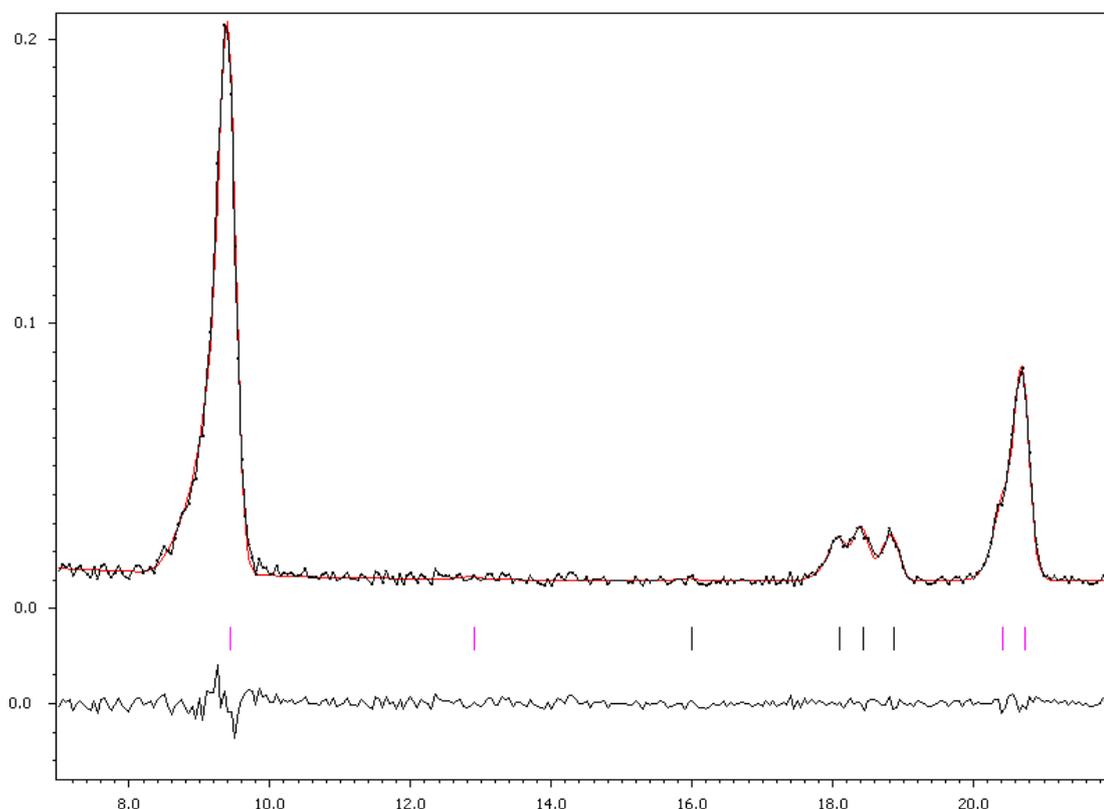
“Quit”

“Edit profile parameters”

[On the screen: Powder options]

In the page “Asymmetry” select “correction by divergence”

Activate refinement of HpS/L and HmS /L keeping their default values  
OK; YES to save changes  
"Run Refine";  
*The refinement should end with  $R_p \sim 4.7\%$ .*  
"Show powder profile"; Select the region  $2\theta$  from about 7 to 22 degs.



*The correction considerably improved the profile*  
"Quit"; NEXT; YES to leave the form for le Bail refinement

#### 6. Refinement of the scale parameter for the nuclear structure

[On the screen: Refinement of the nuclear structure by the Rietveld method]  
"Edit refinement commands"; On the page "Various" select "Fixed commands";  
Fix all parameters for all atoms ("\*" for "Atoms/Parameters" textbox); "Add"; OK; OK;  
*The command will appear in the panel as "fixed all \*"*  
"Run Refine"

*The refinement should converge to  $R_p \sim 11.6\%$ ,  $R(\text{obs}) \sim 3.6\%$ .*  
NEXT; YES to leave the form for Rietvel refinement

#### Testing different irreps to get the best single irrep model

[On the screen: Information]

NEXT

[On the screen: Representation analysis]

*This window has an information character. You can see here all irreps leading to non-paramagnetic ordering. The "details" buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.*

**Representation analysis:**

Representation	Dimension	Shubnikov space group	Axes	Origin shift	
Tau1	1	C[B]mmm	(0,1,0 0,0,1 1,0,0)	(0,0,0)	Details
Tau2	1	C[B]cce	(0,1,0 0,0,1 1,0,0)	(0,0,0)	Details
Tau3	1	C[B]mce	(0,0,1 0,1,0 -1,0,0)	(0,0,0)	Details
Tau4	1	C[B]mcm	(0,1,0 0,0,1 1,0,0)	(0,1/4,1/4)	Details
Tau5	1	C[B]mce	(0,1,0 0,0,1 1,0,0)	(0,0,0)	Details
Tau6	1	C[B]mcm	(0,0,1 0,1,0 -1,0,0)	(0,1/4,1/4)	Details
Tau7	1	C[B]ccm	(0,1,0 0,0,1 1,0,0)	(1/4,1/4,0)	Details
Tau8	1	C[B]mme	(0,1,0 0,0,1 1,0,0)	(0,1/4,1/4)	Details

Display representations

Back      Next      Cancel

**NEXT**

*[On the screen: List of kernels and epikernels]*

**List of kernels and epikernels:**

Shubnikov space group	Axes	Origin shift	Representation
C[B]mmm	(0,1,0 0,0,1 1,0,0)	(0,0,0)	Tau1
C[B]cce	(0,1,0 0,0,1 1,0,0)	(0,0,0)	Tau2
C[B]mce	(0,0,1 0,1,0 -1,0,0)	(0,0,0)	Tau3
C[B]mcm	(0,1,0 0,0,1 1,0,0)	(0,1/4,1/4)	Tau4
C[B]mce	(0,1,0 0,0,1 1,0,0)	(0,0,0)	Tau5
C[B]mcm	(0,0,1 0,1,0 -1,0,0)	(0,1/4,1/4)	Tau6
C[B]ccm	(0,1,0 0,0,1 1,0,0)	(1/4,1/4,0)	Tau7
C[B]mme	(0,1,0 0,0,1 1,0,0)	(0,1/4,1/4)	Tau8

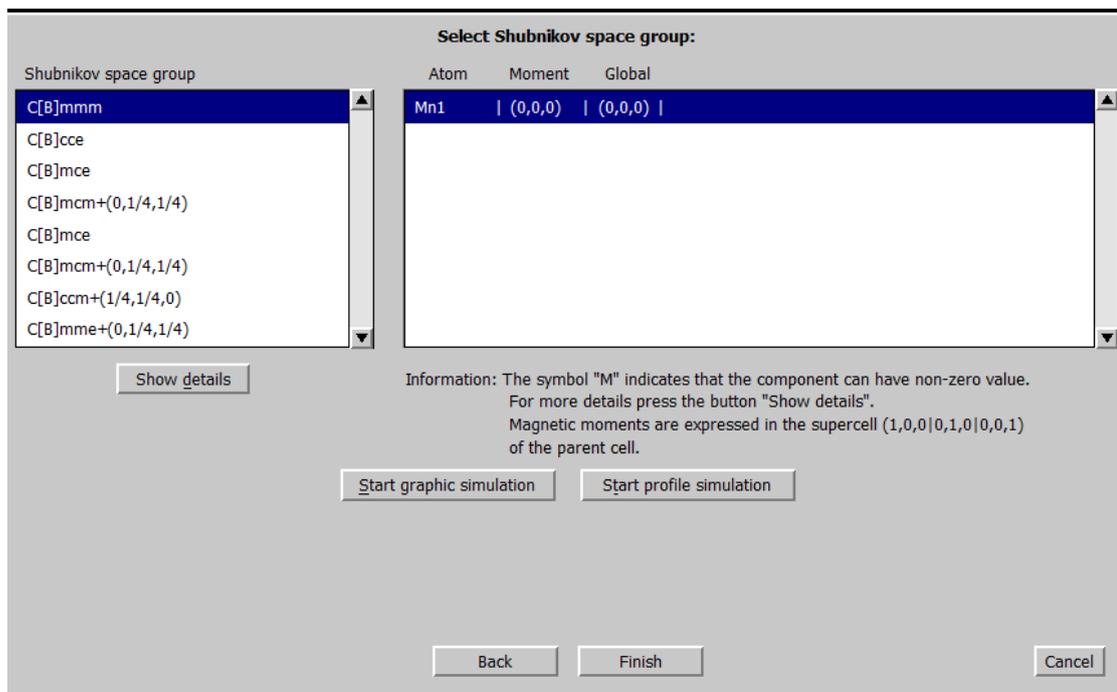
Show details

Select from above kernels/epikernels one representative of a family of Shubnikov space groups for testing.

Back      Next      Cancel

**NEXT**

*[On the screen: Select Shubnikov space group]*



This form shows that only for Shubnikov space group **No 2**, **No 4**, **No 6** and **No 8** allows non-zero magnetic moment for the Mn1 atom. In the following we shall test all four possibilities.  
Pr1 Sr1

### 7. Refinement in the Shubnikov space group C[B]cce (No 2 in the list)

[On the screen: Select Shubnikov space group]

Select the second line in the left panel; FINISH

YES to the question "Do you want to continue with the last kernel/epikernel";

[On screen: Select structure name]

Use the default name i.e. PrSrMnO\_01; OK

After selection of the actual Shubnikov group you can use either the cell and origin selection as follows from the setting of the parent structure or you can apply transformation to get a standard setting.

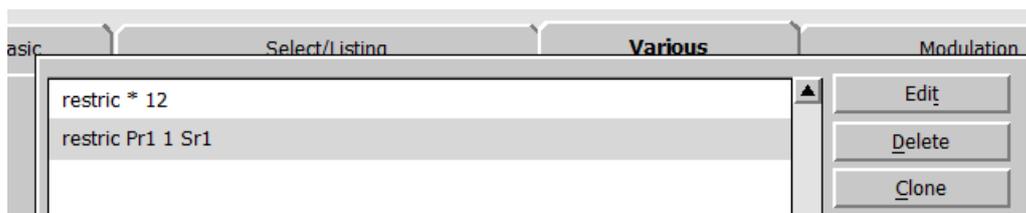
**NO** to the question "Do you want to apply this transformation?".

Right click on the icon "Refine"; Select the "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1;

Select the page "Various" and use the button "Restrictions"

Check that all atoms are restricted to have identical ADP parameters and not restricted occupancies;

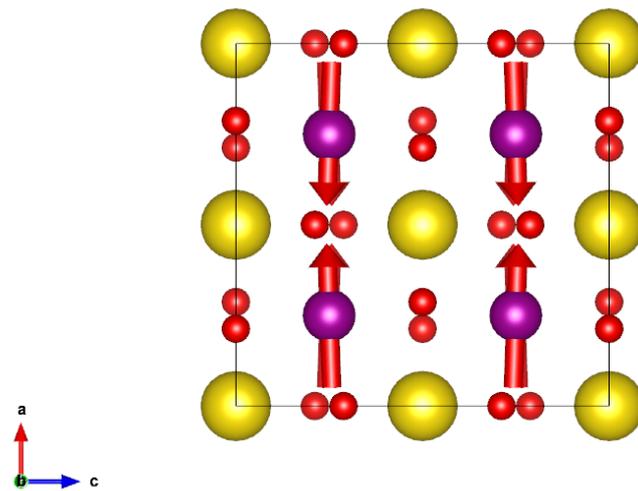
Restrict atoms Pr1 and Sr1, occupying the same position in the nuclear structure: identical Coordinates ADP parameters and "keep overall sum" for occupancies; Add;



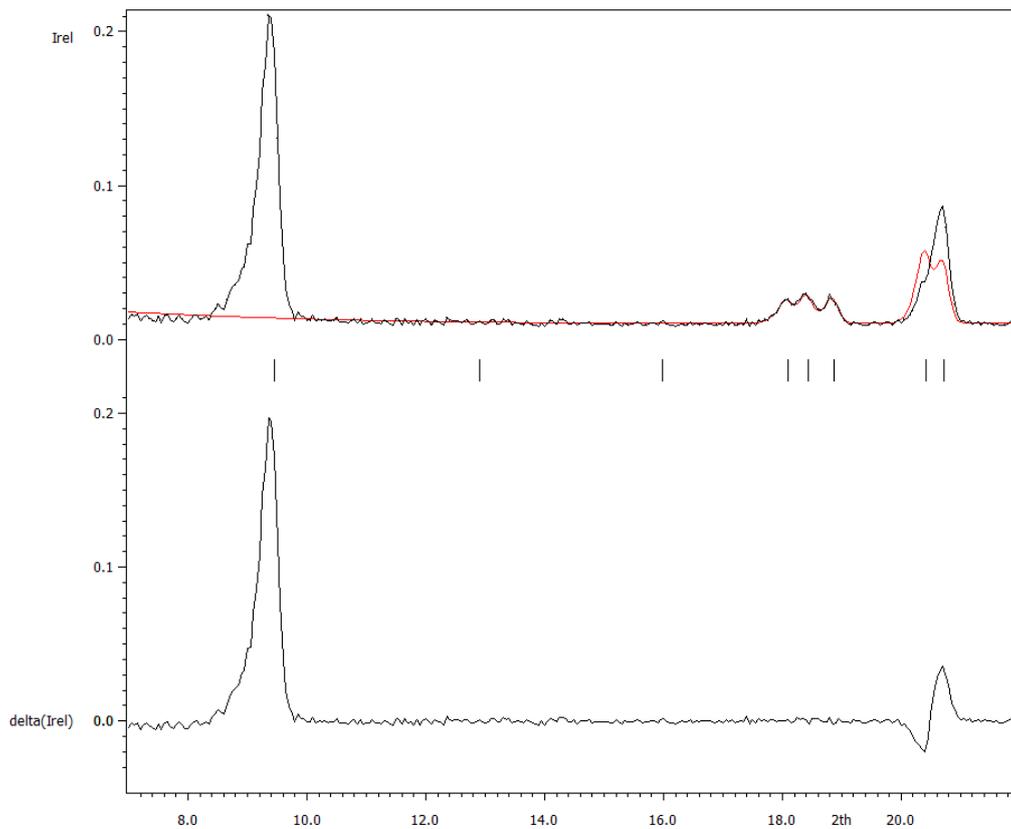
OK; "Yes+start";

Refinement converges with  $R_p \sim 10.1\%$ ,  $R(\text{obs}) \sim 3.7\%$ .  
This refinement is very unstable.

Double click on the icon "Plot structure" and select Vesta to draw the structure:



Use "Tools → Powder → Profile viewer" and check fit of the calculated powder profile:



The model cannot explain the peak at (1,0,0)  
"Quit"

1Sr1

**8. Refinement in the Shubnikov superspace group  $C[B]mcm$  with the origin shift  $(0,1/4,1/4)$  (№ 4 in the list)**

[On screen: Basic window]

"File → Structure → History" and select the parent structure PrSrMnO; OK;

[On screen: Basic window]

"Tools → Special tools → Representation analysis for magnetic structures";

[On screen: Representation analysis]

NEXT; NEXT; Select the fourth Shubnikov superspace group " $C[B]mcm+(0,1/4,1/4)$ "; FINISH

YES to the question "Do you want to continue with the last kernel/epikernel?";

[On screen: Select structure name]

Use the default name i.e. PrSrMnO\_02; OK

No to the question "Do you want to apply this transformation".

Right click on the icon "Refine"; Select the "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1;

Select the page "Various" and use the button "Restrictions"

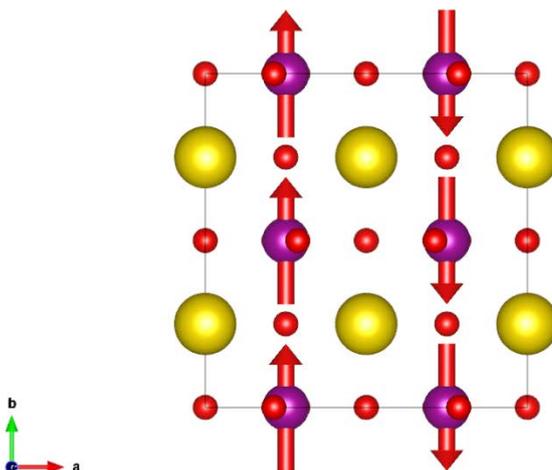
Check that all atoms are restricted to have identical ADP parameters and not restricted occupancies;

Restrict atoms Pr1 and Sr1, occupying the same position in the nuclear structure: identical Coordinates ADP parameters and "keep overall sum" for occupancies; Add;

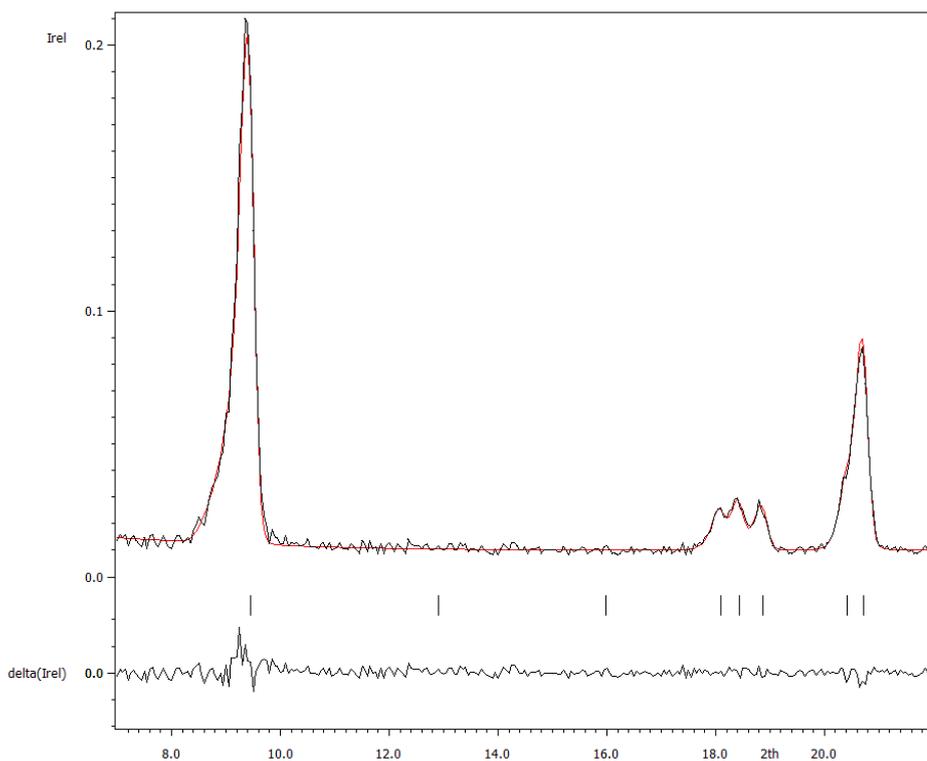
OK; OK; "Yes+start";

*Refinement converges with  $R_p \sim 6.0\%$ ,  $R(\text{obs}) \sim 3.2\%$ .*

Double click on the icon "Plot structure" and select Vesta to draw the structure::



Use "Tools → Powder → Profile" viewer and check fit of the calculated powder profile:



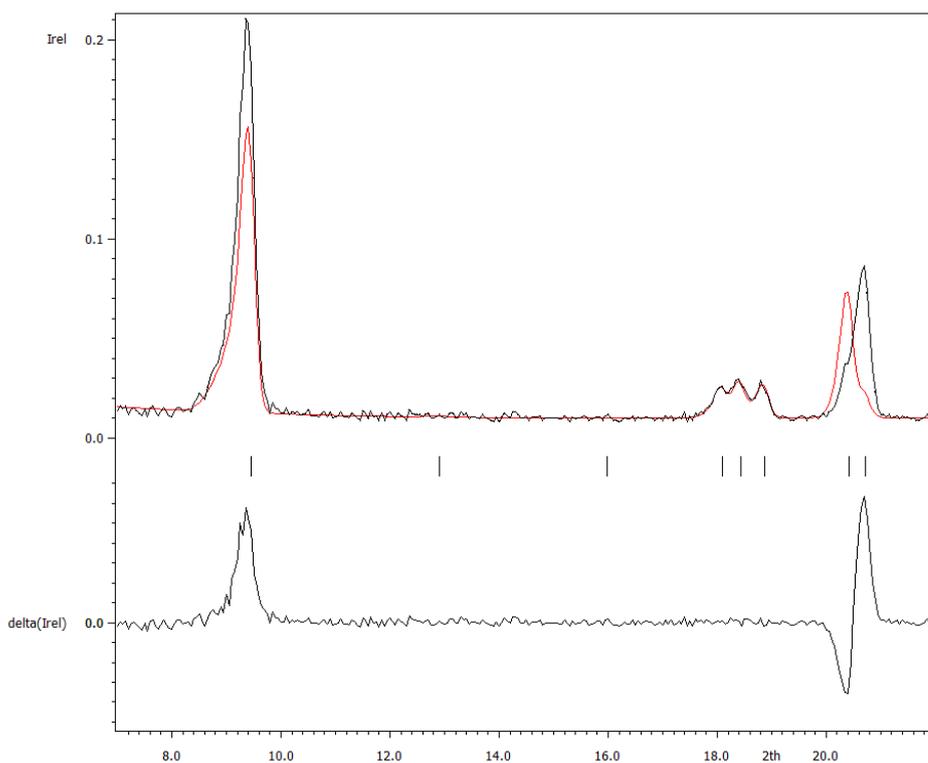
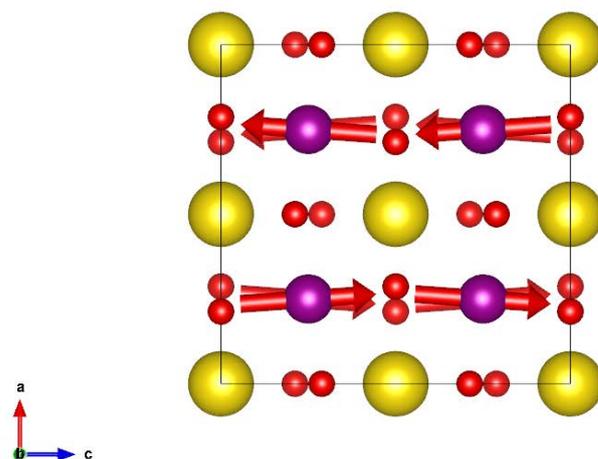
The profile fit is very good.

**9. Refinement in the Shubnikov superspace group  $C[B]mcm$  with the origin shift  $(0,1/4,1/4)$  (№ 6 in the list)**

The symbol in the table is the same as for the № 4 but both epikernels are generally different. Compare details for both. The first one has in the original setting the symbol  $A[C]mma$  and the second one  $A[C]mam$ . Both give the same symbol when transformed to the standard setting.

Make the same steps and calculation as in the previous test.

$R_p \sim 8.1\%$ ,  $R(\text{obs}) \sim 3.9\%$ .

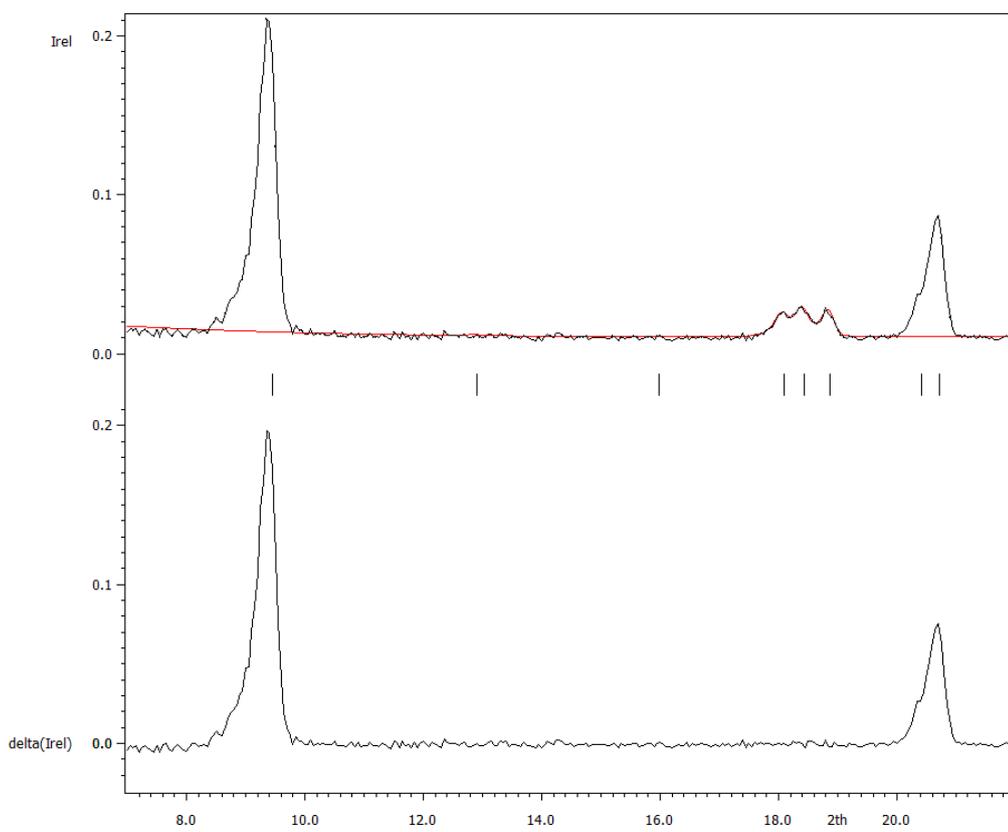
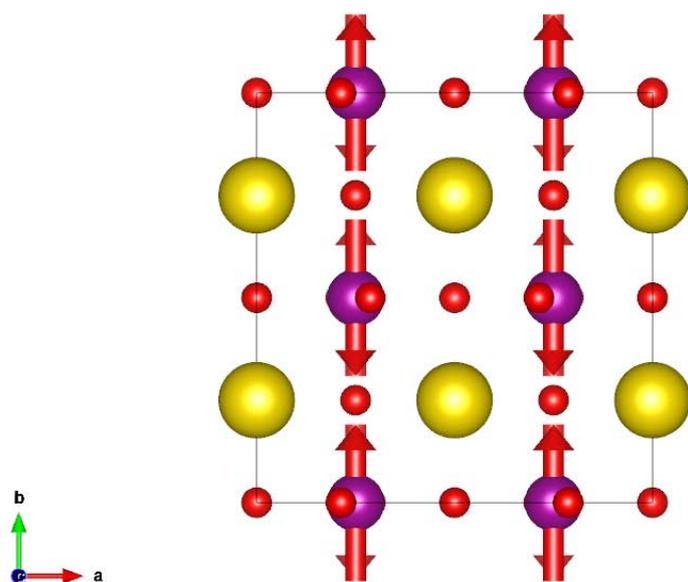


**10. Refinement in the Shubnikov superspace group  $C[B]mme+(0,1/4,1/4)$  (No 8 in the list)**

Make the same calculation for the last Shubnikov superspace group with sin wave (Line eight in "Select Shubnikov space group" dialogue).

$R_p \sim 11.5\%$ ,  $R(\text{obs}) \sim 3.1\%$ .

*This refinement is very unstable.*



# Example 12.4: MnWO<sub>4</sub>

## Incommensurate magnetic structure

Revised: 28 November 2014

Powder data measured the ILL neutron source at 10 K

For more details: L. Meddar, M. Josse, P. Deniard, C. La, G. Andre, F. Damay, V. Petříček, S. Jobic, M.H. Whangbo, M. Maglione & C. Payen: *Effect of Nonmagnetic Substituents Mg and Zn on the Phase Competition in the Multiferroic Antiferromagnet MnWO<sub>4</sub>* Chemistry of Materials, **21**, (2009), 5203-5214.

Input files: MnWO4.dat (powder profile data)  
MnWO4\_nuclear.cif (nuclear structure)

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click MnWO4

### 2. Import Wizard

Select “Magnetic: nuclear model from CIF”, NEXT

Right pane: select the input file MnWO4\_nuclear.cif

### 3. Define magnetic propagation vector and form factors

[On the screen: Define magnetic propagation vector and form factors]

Check “Use non-zero magnetic propagation vector” and fill its value: -0.209 0.5 0.453

Select atom type Mn; check “Use as a magnetic atom”; select “Magnetic form factor <j0>” Mn<sup>2+</sup>; NEXT; FINISH

The parent structure is created

### 4. Import the reflection file

[On the screen: Specify type of the file to be imported]

Select “Various CW format”; NEXT;

Check that the name of the input file is “MnWO4.dat” and the data format is “Free format of 2th, l, [sig(l)”]; NEXT

[On the screen: Complete/correct experimental parameters];

Fill used wavelength 2.4226; NEXT; FINISH

[On the screen: Data repository]

OK; YES to “Do you want to accept made changes?”

### 5. Refining of profile parameters by the le Bail technique.

[On the screen: Information]

NEXT

[On the screen: Refinement of the powder profile by the le Bail algorithm]

“Show powder profile”

The background is relatively smooth and it can be described without introducing manual

background.

“Quit”; “Edit profile parameters”;

[On the screen: Powder options]

In page “Cell” activate refinement of a, b, c parameters and beta angle;

Activate refinement of component q1 and q3 of the modulation vector. The q2 component is fixed for planar monoclinic superspace groups to 0.5;

Check that the maximal satellite index is set to 1;

In the page “Profile” change the starting value of GW to 50 and activate its refinement;

In the page “Corrections” activate refinement of “shift” parameter and enlarge the number of used Legendre polynomials to 20

OK; YES to save the changes

“Edit refinement commands”; In the page “Basic” change the number of cycles to 100 and the damping factor to 0.5; OK

“Run Refine”;

The refinement should converge to  $R_p \sim 5.2\%$ .

“Edit profile parameters”;

[On the screen: Powder options]

In the page “Profile” change activate refinement of GU and GV

Change the peak-shape function to pseudo-Voigt and activate refinement LY

OK; YES to save the changes

“Run Refine”

The refinement should converge to  $R_p \sim 3.4\%$ .

NEXT; YES to leave the form for le Bail refinement

## 6. Refinement of the scale parameter for the nuclear structure

[On the screen: Refinement of the nuclear structure by the Rietveld method]

“Edit refinement commands”; On the page “Various” select “Fixed commands”;

Fix all parameters for all atoms (wild character \*); “Add”; OK; OK

“Run Refine”

The refinement should converge to  $R_p = 12.8\%$ ,  $R(\text{obs}) = 5.5\%$ .

NEXT; YES to leave the form for Rietveld refinement

## 7. Testing different irreps to get the best single irrep model

[On the screen: Information]

NEXT

[On the screen: Representation analysis]

This window has an information character. You can see here all irreps leading to non-paramagnetic ordering. The “details” buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.

Representation analysis:				
Representation	Dimension	Shubnikov superspace group	Axes	Origin shift
mG1	2	P2/c.1'(a1/2g)00s	(1,0,0 0,1,0 0,0,1)	(0,0,0,0)
mG2	2	P2/c.1'(a1/2g)0ss	(1,0,0 0,1,0 0,0,1)	(0,0,0,0)

NEXT

[On the screen: List of kernels and epikernels]

List of kernels and epikernels:			
Shubnikov superspace group	Axes	Origin shift	Representation
P2/c.1'(a1/2g)00s	(1,0,0 0,1,0 0,0,1)	(0,0,0,0)	mG1
P2/c.1'(a1/2g)0ss	(1,0,0 0,1,0 0,0,1)	(0,0,0,0)	mG2

NEXT

[On the screen: Select Shubnikov superspace group]

Select Shubnikov superspace group:

Shubnikov superspace group	Atom	Moment	Global	sin#1	cos#1
P2/c.1'(a1/2g)00s	Mn1	(0,0,0)	(0,0,0)	(M,M,M)	(M,M,M)
P2/c.1'(a1/2g)0ss					

Information: The symbol "M" indicates that the component can have non-zero value.  
For more details press the button "Show details".  
Magnetic moments are expressed in the parent cell.

Start graphic simulation    Start profile simulation

Back    Finish    Cancel

Notice that for both SSG's there are non-zero amplitudes for sine and cosine waves. However only three amplitudes are independent as can be found from "Details":

```
*****
* List of relationships between magnetic moments of individual atoms *
*****

Atom: Mn1
=====
mx0=0          mxsin1 ... free          mxcos1=1.6787*mxsin1
my0=0          mysin1 ... free          mycos1=-0.59571*mysin1
mz0=0          mzsine ... free          mzcose=1.6787*mzsine
```

The cosine amplitudes have generally non-zero values but they are related with the sine amplitudes. However the coefficients are functions of y coordinate of the Mn1 atom, which means that these restrictions are non-linear. Later we shall see how these restrictions can be simplified.

In this case, both possibilities yield similar diffraction patterns and we cannot decide at this stage which solution makes a better fit.

Note: The presence of a rational non-zero modulation vector component  $q_y = 0.5$  leads to a specific problem of the origin selection. While for the space group  $P2/c$  the c glide planes

located at  $y=0$  and  $y=1/2$  are equivalent, in the SSG  $P2/c.1'(\alpha 1/2\gamma)00s$  they are not. In this SSG the first glide plane is connected with zero shift along the internal space while the second one with  $1/2$  shift. This means that the origin selection used for the starting structure model solved and refined from the main reflections, must be reconsidered for solution of modulated structure. Here two models shifted by  $1/2$  in  $y$  must be tested. Another possibility is to use non-standard SSG symbol  $P2/c.1'(\alpha 1/2\gamma)0_{SS}$ , which would generate reverse order of  $c$  glide planes. The second method is used in this example.

#### **8. Refinement in the first Shubnikov superspace group – $P2/c.1'(a1/2g)00s$**

[On the screen: Select Shubnikov space group]

Select the first line in the left panel; FINISH

YES to the question “Do you want to continue with the last kernel/epikernel”;

[On screen: Select structure name]

Use the default name i.e. MnWO4\_01; OK

Right click on the icon “Refine”; Select the page “Basic” and change the “Number of cycles” to 100 and the “Damping factor” to 0.1;

Select the page “Various”. Use the button “Restrictions”. All atoms are restricted to have identical ADP parameters;

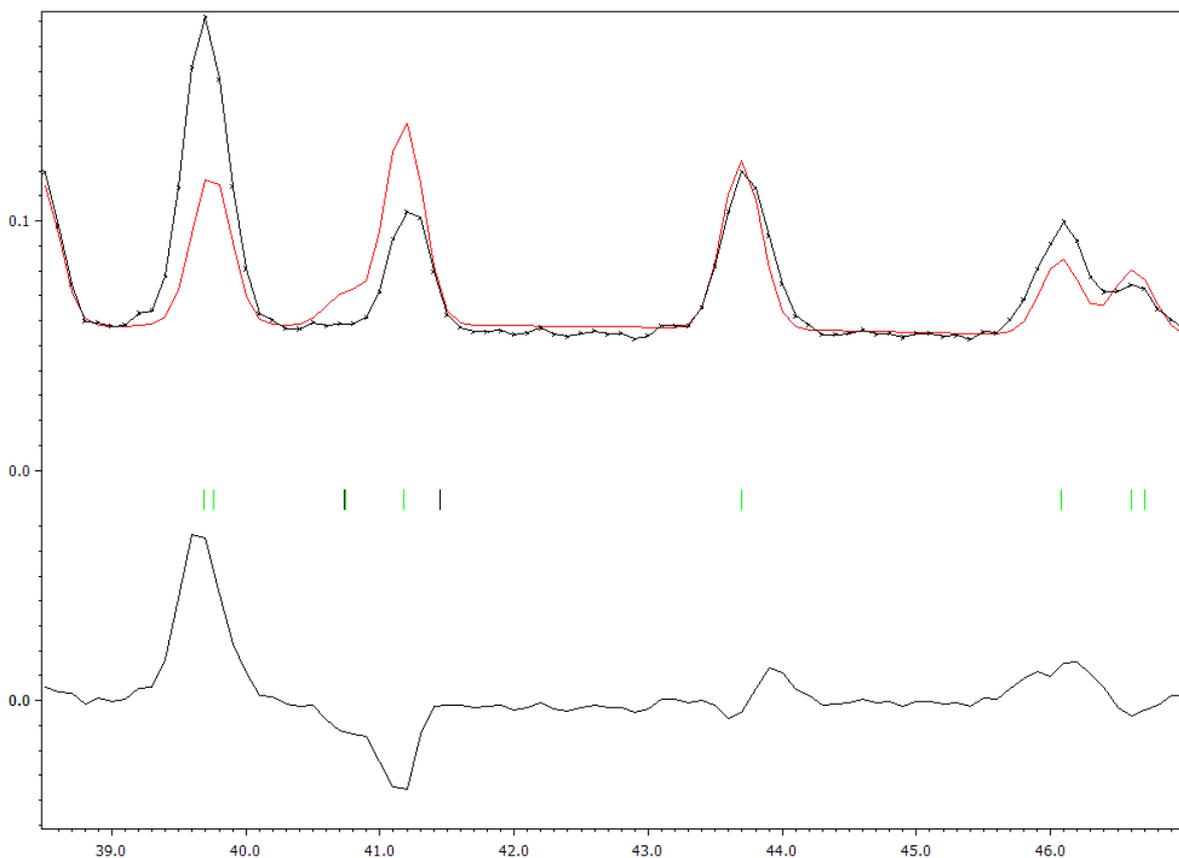
Restrict atoms Zn1 and Mn1, occupying the same position in the nuclear structure: identical Coordinates + Modulations + ADP parameters and “keep overall sum” for occupancies

Use button “Fixed commands” and fix all coordinates and delete or disable fixing of ADP’s (if present).

OK; OK; “Yes+start”;

The refinement should end with  $R_p \sim 4.9\%$  and Bragg  $R$  factors  $R(\text{obs}) = 5.3\%$ ,  $2.9\%$  and  $9.1\%$  for all, main and satellite reflections, respectively.

Use “Tools → Powder → Profile” viewer and check fit of the calculated powder profile and focus to the interval (38.5,47):



Quit

### 9. Refinement in the second Shubnikov superspace group – $P2/c.1'(a1/2g)0ss$

[On the screen: Basic window]

“File → Structure → History” and select the parent structure MnWO<sub>4</sub>; OK;

[On screen: Basic window]

“Tools → Special tools → Representation analysis for magnetic structures”;

Continue with representation analysis; OK;

[On the screen: Representation analysis]

NEXT; NEXT; Select  $P2/c.1'(a1/2g)0ss$ ; FINISH;

YES to the question “Do you want to continue with the last kernel/epikernel?”;

[On the screen: Select structure name]

Use the default name; OK

[On the screen: Basic window]

Right click on the icon “Refine”; Select the “Basic” and change the “Number of cycles” to 100 and the “Damping factor” to 0.1;

Select the page “Various”. Use the button “Restrictions”. All atoms are restricted to have identical ADP parameters;

Restrict atoms Zn1 and Mn1, occupying the same position in the nuclear structure: identical Coordinates + Modulations + ADP parameters and “keep overall sum” for occupancies

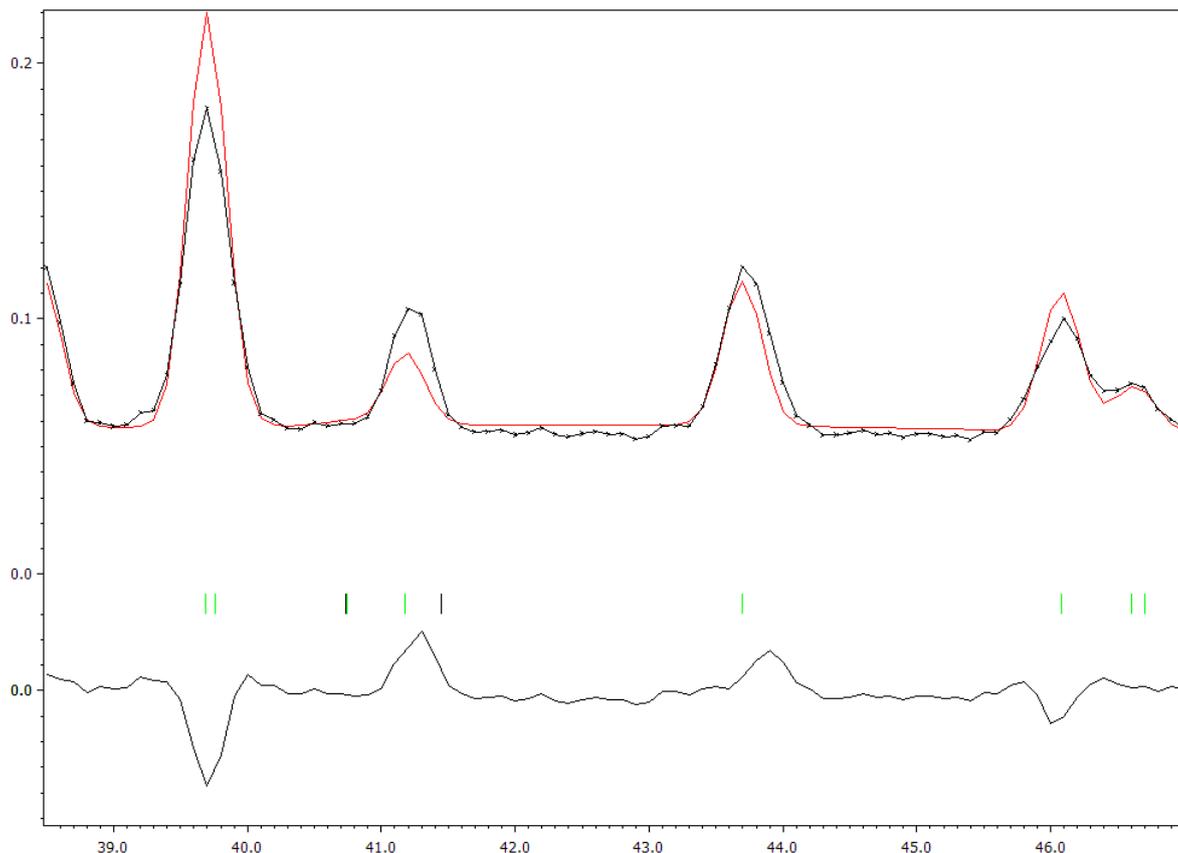
Use button “Fixed commands” and fix all coordinates and delete or disable fixing of ADP’s (if present).

OK; OK; “Yes+start”;

The refinement should end with  $R_p \sim 4.3\%$  and Bragg R factors  $R(obs) = 3.8\%$ ,  $2.3\%$  and  $5.5\%$

for all, main and satellite reflections, respectively.

Use “Tools → Powder → Profile” viewer and check fit of the calculated powder and focus to the interval (38.5,47):



The second solution gives significantly better profile fit and also better Bragg R values.  
Quit

#### 10. Transforming the final solution to the supercentered cell.

[On the screen: Basic window]

“Tools→Transformation→Transform to the X-centered cell”;

Create new structure e.g. “MnWO4\_02\_X”;

YES to the question “Do you want to continue with the new structure?”;

#### 11. Refinement in the supercentered setting

[On the screen: Basic window]

Run EditM50, go to “Symmetry”; Check the new SSG symbol; “X” stands for the supercentered setting. For more details about centering vectors expand the list of centering symbols at “cell centering” and re-select the symbol X

The generated supercell centering (0,1/2,0,1/2) is in accordance with the values from “findSSG” (except that the monoclinic axis is now “b”)

ESC; ESC;

Right click on the icon “Refine”; Select the “Basic” and change the “Number of cycles” to 100 and the “Damping factor” to 0.1;

Select the page “Various”; Use the button “Restrictions” and restrict all atoms to have identical ADP parameters and not restricted occupancies; Add;

Restrict atoms Zn1 and Mn1, occupying the same position in the nuclear structure: identical

Coordinates + Modulation + ADP parameters and “keep overall sum” for occupancies;  
Add; OK

Use button “Fixed commands” and fix coordinates for all atoms, i.e. \*.

OK; OK; “Yes+start”;

*The refinement should finish with  $R_p \sim 5.0\%$  and Bragg R factors  $R(\text{obs}) = 4.3\%$ ,  $3.0\%$  and  $6.4\%$  for all, main and satellite reflections, respectively.*

YES to the question “Open the listing”; Check the symmetry restrictions:



```
Equations induced by symmetry :
x[Zn1]=0.5
z[Zn1]=0.25
x[Mn1]=0.5
z[Mn1]=0.25
mx0[Mn1]=0
my0[Mn1]=0
mz0[Mn1]=0
mysini[Mn1]=0
Refinement program
structure :
mxcos1[Mn1]=0
mzcos1[Mn1]=0
x[W1]=0
z[W1]=0.25
alpha=90
gamma=90
```

*Now the y component of the sine wave and x and z components of the cos wave are fixed to zero values. This setting makes a full separation of internal and external space (before the transformation some wave components depended on the y coordinate).*



# Example 12.5: HoNi

Magnetic structure refined from single crystal data –  $k=(0,0,1)$

Revised: 23 October 2017

Single crystal data

For more details: not yet published

Input files: HoNi.hkl (powder profile data)  
HoNi\_nuclear.cif (nuclear structure)

## 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click HoNi

## 2. *Import Wizard*

Select “Magnetic: nuclear model from CIF”, NEXT

Right pane: select the input file HoNi\_nuclear.cif

## 3. *Define magnetic propagation vector and form factors*

[On the screen: Define magnetic propagation vector and form factors]

Check “Use non-zero magnetic propagation vector” and fill its value: 0 0 1

Select atom type Ho; check “Use as a magnetic atom”; select “Magnetic form factor

<j0>+c<j2>” Ho3+; NEXT; FINISH

The parent structure is created

## 4. *Import the reflection file*

[On the screen: Specify type of the file to be imported]

Select “reflection file corrected for LP and absorption”; NEXT;

Check that the name of the input file is “HoNi.hkl” and the data format is “General file on I”;

Type in the “Input format:” (3i5,2f10.2); NEXT

[On the screen: Complete/correct experimental parameters];

Fill used wavelength 0.794 Å ; NEXT; NEXT; FINISH

[On the screen: Data repository]

OK; YES to “Do you want to accept made changes?”

## 5. *Testing different irreps to get the best single irrep model*

[On the screen: Information]

NEXT

[On the screen: Representation analysis]

This window has an information character. You can see here all irreps leading to non-paramagnetic ordering. The “details” buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.

**Representation analysis:**

Representation	Dimension	Shubnikov space group	Axes	Origin shift	
Tau1	1	P[1]4mm	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
Tau2	1	P[1]4nc	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
Tau3	1	P[1]42mc	(1,0,0 0,1,0 0,0,1)	(0,1/2,0)	Details
Tau4	1	P[1]42nm	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
Tau5	2	P[1]21	(0,1,0 0,0,1 1,0,0)	(1/4,0,1/4)	Details

**NEXT**

*[On the screen: List of kernels and epikernels]*

**List of kernels and epikernels:**

Shubnikov space group	Axes	Origin shift	Representation
P[1]4mm	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Tau1
P[1]4nc	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Tau2
P[1]42mc	(1,0,0 0,1,0 0,0,1)	(0,1/2,0)	Tau3
P[1]42nm	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Tau4
C[B]mc21	(1,1,0 -1,1,0 0,0,1)	(0,1/4,0)	Tau5
P[1]mn21	(0,1,0 1,0,0 0,0,-1)	(0,1/4,0)	Tau5
P[1]21	(0,1,0 0,0,1 1,0,0)	(1/4,0,1/4)	Tau5

Select from above kernels/epikernels one representative of a family of Shubnikov space groups for testing.

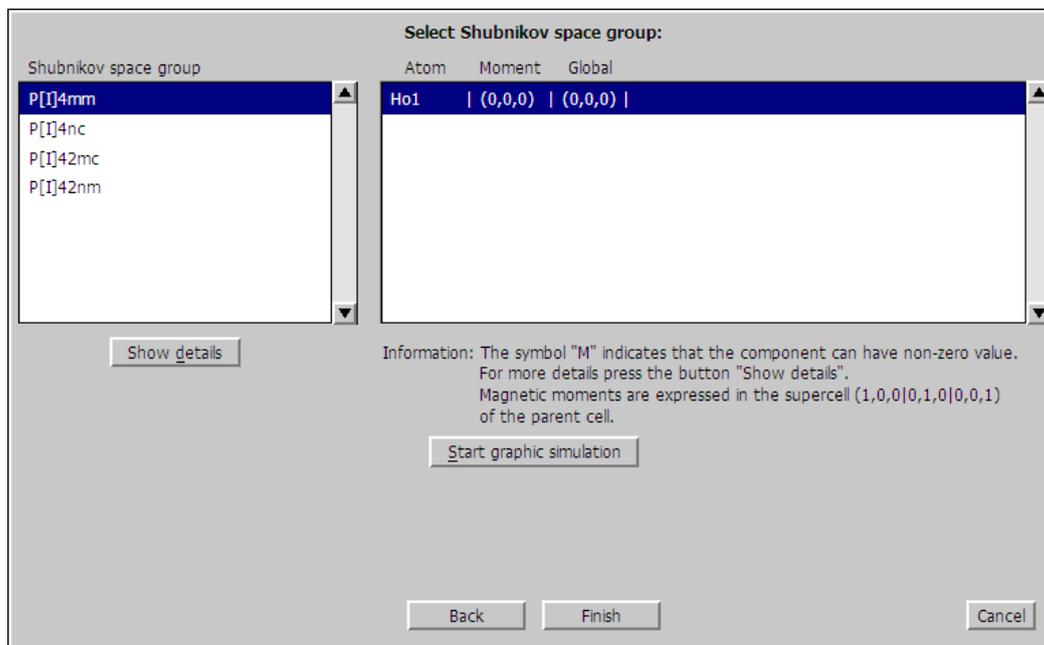
Select one of the tetragonal Shubnikov space groups; **NEXT**

*This will pass all present tetragonal Shubnikov space groups to further testing.*

**NEXT**

## 6. Testing tetragonal Shubnikov space groups

*[On the screen: Select Shubnikov superspace group]*



Note that only the second ShSG P[1]4nc allows for a non-zero magnetic moment.

Select it and press 'Continue with the selected Shubnikov space group';

[On the screen: Select structure name]

Use the default name "HoNi\_01"; OK

[On the screen: Basic window of Jana2006]

Right-click the icon of Refine and select the page "Various"

Use the button "Restrictions" and ensure that all atoms (i.e. \*) have been restricted to have identical ADP parameters.

OK

Select the page "Fixed commands" and (similarly like in the previous step) ensure that all atomic positions are fixed in their current values ("fixed xyz \*").

OK

Select the page "Basic" and check if the "Number of cycles" is 100 and the "Damping factor" is 0.1; OK;

## 7. Refinement in the tetragonal Shubnikov space group – P[1]4nc

[On the screen: Basic window]

Start refinement;

Refinement converges with  $R(\text{obs}) \sim 20.8\%$ ,  $12.8\%$ ,  $40.8\%$  for all, nuclear and magnetic reflections, respectively.

[On the screen: Basic window]

"Parameters → Extinction"

[On the screen: Extinction model]

Start "Parameters → Extinction"

Select Isotropic, Type1, Gaussian; OK; Yes to rewrite changes

Run refinement

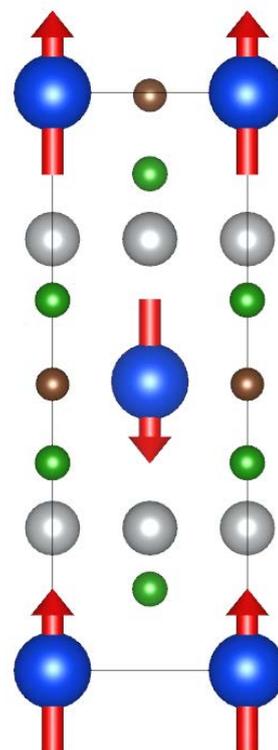
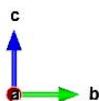
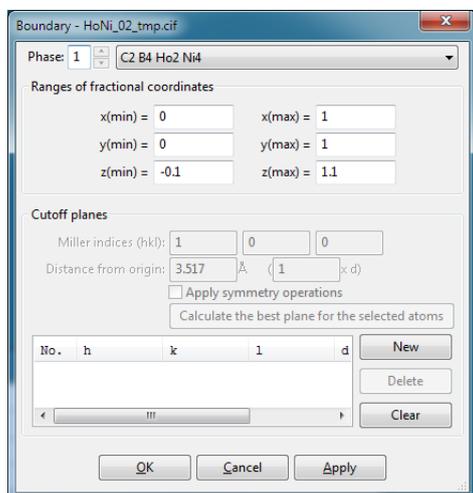
Refinement converges with  $R(\text{obs}) \sim 17.4\%$ ,  $8.2\%$ ,  $40.8\%$  for all, nuclear and magnetic reflections, respectively.

Right click on the icon "Refine";

Select the page "Various" and use the button "Restrictions";  
 Disable the command "restrict \* 12" which keeps ADP's of all atoms identical. OK;  
 Use the button "Fixed commands" and disable the command "fixed xyz \*" which fixes coordinates of all atoms. OK; OK; Yes+start;  
*Refinement converges with  $R(\text{obs}) \sim 16.7\%$ ,  $7.7\%$ ,  $39.4\%$  for all, nuclear and magnetic reflections, respectively.*

[On the screen: Basic window]

Double click on the icon "Plot structure"; Use the Vesta program to draw the structure;  
 Press "Draw+return" or "Draw+continue";  
 In Vesta enlarge the boundaries in z direction:



## 8. Testing orthorhombic Shubnikov space group $C[B]mc21$

[On the screen: Basic window of the parent structure, with the representation analysis]

"Back → Select the space group  $C[B]mc21$  → Next;

Select the only space group and press 'Continue with the selected Shubnikov space group';

[On the screen: Select structure name]

Use the default name "HoNi\_02"; OK

NO to the question "Do you want to apply this transformation?";

[On the screen: Basic window]

Start refinement;

Refinement converges with  $R(\text{obs}) \sim 12.8\%$ ,  $12.3\%$ ,  $14.3\%$  for all, nuclear and magnetic reflections, respectively.

[On the screen: Basic window]

"Parameters → Extinction"

[On the screen: Extinction model]

Start "Parameters → Extinction"

Select Isotropic, Type1, Gaussian; OK; Yes to rewrite changes

[On the screen: Basic window]

Run refinement

Refinement converges with  $R(\text{obs}) \sim 9.6\%$ ,  $7.8\%$ ,  $14.6\%$  for all, nuclear and magnetic reflections, respectively.

Right click on the icon "Refine";

Select the page "Various" and use the button "Restrictions";

Disable the command "restrict \* 12" which keeps ADP's of all atoms identical. OK;

Use the button "Fixed" and disable the command "fixed xyz \*" which fixes coordinates of all atoms. OK; OK; Yes+start;

Refinement converges with  $R(\text{obs}) \sim 8.4\%$ ,  $6.7\%$ ,  $13.0\%$  for all, nuclear and magnetic reflections, respectively.

Start "Parameters → Twin fractions";

[On the screen: Edit twin fraction]

Selection of the orthorhombic Shubnikov space group represents a lowering symmetry from the original one (parent symmetry). This can create different magnetic domains related by the lost symmetry operations. The lost symmetry operation has been automatically created by the program as a twinning operation. The default value of the relative fraction was 0.5 which means 1:1 ratio. In the final stage this value can be refined.

Press the button "Show twinning matrix".

[On the screen: Twinning matrix #2]

As expected the twinning operation is the four-fold axis, which was present in the tetragonal description but it is missing in the orthorhombic description.

OK;

[On the screen: Edit twin fraction]

Change the volume fraction to zero and activate the refinement key for the volume fraction.

OK; Yes to the question "Do you want to rewrite changed files?".

[On the screen: Basic window]

Run refinement

Refinement converges with  $R(\text{obs}) \sim 8.3\%$ ,  $6.7\%$ ,  $12.6\%$  for all, nuclear and magnetic reflections, respectively.

[On the screen: Basic window]

Start "Parameters → Twin fractions";

[On the screen: Edit twin fraction]

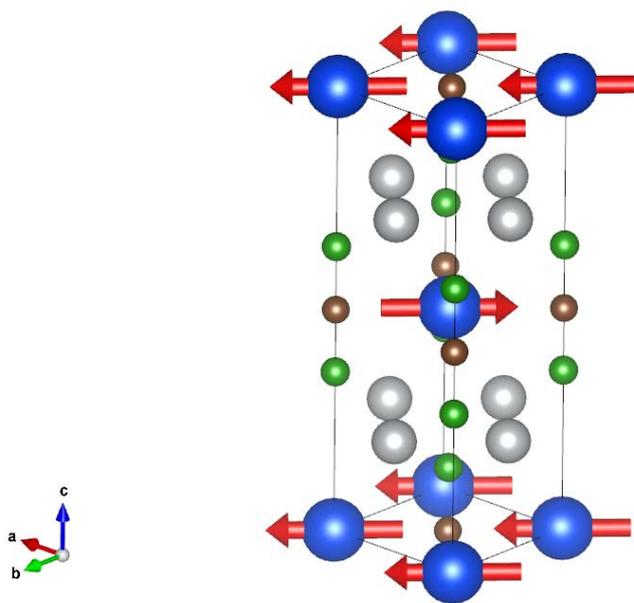
Check that the volume fraction return to the value close to 0.41.

[On the screen: Basic window]

Double click on the icon "Plot structure"; Use the Vesta program to draw the structure;

Press "Draw+return" or "Draw+continue";

In Vesta enlarge the boundaries in z direction (like in the previous plot):

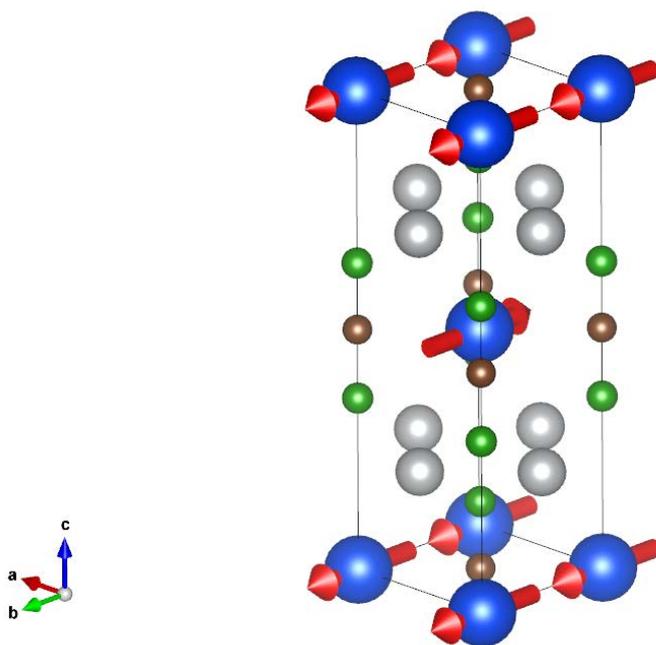


**9. Testing orthorhombic Shubnikov space group  $P[1]mn21$**

[On the screen: Basic window]

Repeat the procedure from the previous point but now for the Shubnikov space group  $P[1]mn21$ .

Refinement converges with  $R(\text{obs}) \sim 8.8\%$ ,  $7.4\%$ ,  $12.4\%$  for all, nuclear and magnetic reflections, respectively.



# Example 12.6: ISODISTORT

## Practical introduction to Jana2006-ISODISTORT communication

Revised: 05 May 2019

Input files: Ba5Co5.m40, Ba5Co5.m41, Ba5Co5.m50, Ba5Co5.m90, Ba5Co5.m95

### 10. Creating CIF file from the parent structure

[On the screen: Basic window]

Start Jana2006

Start "File → Structure → Open" and open the structure Ba5Co5;

"Tools for magnetic structures → Run ISODISTORT wizard";

### 11. Start ISODISTORT home page

[On the screen: ISODISTORT=>Jana2006]

Press "Run ISODISTORT";

Your Internet default browser will open the page:

<http://stokes.byu.edu/iso/isodistort.php>

## ISODISTORT

Version 6.5.0, April 2018

Harold T. Stokes, Branton J. Campbell, and Dorian M. Hatch, Department of Physics and Astronomy, Brigham Young University, Provo, Utah, 84602, USA, stokes@byu.edu

**Description:** ISODISTORT is a tool for exploring the structural distortion modes of crystalline materials. It provides a user-friendly interface to many of the algorithms used by the [Isotropy Software Suite](#), allowing one to generate and explore distortion modes induced by irreducible representations of the parent space-group symmetry. It also provides a Java applet for visualizing and interactively manipulating the free parameters associated with these modes.

[Help](#), [Tutorials](#), [Version History](#)

[Legacy copy of ISODISTORT version 5.6.1, August 2013](#)

Begin by entering the structure of parent phase: ?

[Get started quickly with a cubic perovskite parent.](#)

Import parent structure from a CIF structure file:   No file selected.

If you don't have a parent CIF, create one using [ISOCIF](#).

Alternatively, you can begin with a previously-saved distortion: ?

[Get started quickly with a distorted perovskite example.](#) (Select this link and click "OK" on the next page to test your Java installation.)

Import an ISODISTORT distortion file:   No file selected.

How to cite ISODISTORT: ISOTROPY Software Suite, iso.byu.edu.

Also B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, "ISODISPLACE: An Internet Tool for Exploring Structural Distortions." *J. Appl. Cryst.* **39**, 607-614 (2006).

Browse for the CIF file "Ba5Co5.cif"; OK

[On the screen: ISODISTORT search]

## ISODISTORT: search

Reading CIF file...

Done.

Space Group: 194 P6<sub>3</sub>/mmc D6h-4, Lattice parameters: a=5.63760, b=5.63760, c=24.15760, alpha=90.00000, beta=90.00000, gamma=120.00000

Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting

Ba1 4f (1/3,2/3,z), z=-0.04041, Ba2 4f (1/3,2/3,z), z=0.36991, Ba3 2b (0,0,1/4), Co4 2a (0,0,0), Co5 4e (0,0,z), z=0.39525, Co6 4f (1/3,2/3,z), z=-0.17818, Cl1 2c (1/3,2/3,1/4), O2 12k (x,2x,z), x=0.16063, z=-0.14926, O3 12k (x,2x,z), x=-0.14584, z=-0.04948, O4 2d (1/3,2/3,3/4)

### Graphical display of parent

Atomic radius (Angstroms):  Maximum bond length (Angstroms):  Applet width (pixels):

### Types of distortions to be considered

Strain:

Displacive: all  none  Ba  Co  Cl  O

Occupational: all  none  Ba  Co  Cl  O

Magnetic: all  none  Ba  Co  Cl  O

Rotational: all  none  Ba  Co  Cl  O

Important: You must click on Change to implement any changes in the above type of distortions to be considered.

### Method 1: Search over all special k points

Crystal system(s): triclinic  monoclinic  orthorhombic  tetragonal  trigonal  hexagonal  cubic

Space-group symmetry:  Conventional lattice:  Primitive lattice:  Maximal subgroups only

### Method 2: General method - search over specific k points

Specify k point:  a=  b=  g=  # of independent incommensurate modulations=

Change number of superposed IRs:

Important: You must click on Change to implement any changes in the number of superposed IRs.

### Method 3: Search over arbitrary k points for specified space group and lattice

Select either space group symmetry:  or point group (crystal class):

Specify a real-space sublattice of the parent lattice with Default  P  A  B  C  I  F  O centering.

Specify a primitive reciprocal-space superlattice

Choose a representative basis:

a' =  a +  b +  c

b' =  a +  b +  c

c' =  a +  b +  c

### Method 4: Mode decomposition of a distorted structure

Upload distorted structure from CIF file:  No file selected.

Read old mCIF format

### Space-Group Preferences

These preferences apply to subsequent distortions but do not affect your parent structure:

Monoclinic axes: a(b)c  c(-b)a  ab(c)  ba(-c)  (a)bc  (-a)cb

Monoclinic cell choice: 1  2  3

Orthorhombic axes: abc  ba-c  cab  -cba  bca  a-cb

Trigonal axes: hexagonal  rhombohedral

Origin choice: 1  2

Superspace group setting: standard (IT-C)  basic (IT-A)

Important: You must click on Change to implement any changes in the above preferences.

Define distortions to be considered:

In our case we are interested just in magnetic ordering;

Press Change;

In the box for "Method 2" select GM k16(0,0,0), which means  $k=(0,0,0)$ :

Press OK;

Select irreducible representation

[On the screen: ISODISTORT irreducible representation ]

*Comparing with the "Representation analysis" list of Jana2006, only irreducible representations allowing non-zero magnetic moments are listed. In the next step we will demonstrate two dimensional irreducible representation mGM5+.*

Select the representation mGM5+ and press OK;

*Representation analysis of Jana2006 (for comparison):*

Representation analysis:				
Representation	Dimension	Shubnikov space group	Axes	Origin shift
mGM1+	1	P63/mmc	(1,0,0 0,1,0 0,0,1)	(0,0,0)
mGM1-	1	P63/m'm'c'	(1,0,0 0,1,0 0,0,1)	(0,0,0)
mGM2+	1	P63/mm'c'	(1,0,0 0,1,0 0,0,1)	(0,0,0)
mGM2-	1	P63/m'mc	(1,0,0 0,1,0 0,0,1)	(0,0,0)
mGM3+	1	P63'/m'mc'	(1,0,0 0,1,0 0,0,1)	(0,0,0)
mGM3-	1	P63'/mm'c	(1,0,0 0,1,0 0,0,1)	(0,0,0)
mGM4+	1	P63'/m'm'c	(1,0,0 0,1,0 0,0,1)	(0,0,0)
mGM4-	1	P63'/mmc'	(1,0,0 0,1,0 0,0,1)	(0,0,0)
mGM5+	2	P21/m	(0,1,0 0,0,1 1,0,0)	(0,0,0)
mGM5-	2	P21/m'	(0,1,0 0,0,1 1,0,0)	(0,0,0)
mGM6+	2	P21'/m	(0,1,0 0,0,1 1,0,0)	(0,0,0)
mGM6-	2	P21'/m'	(0,1,0 0,0,1 1,0,0)	(0,0,0)

*[On the screen: ISODISTORT: order parameter direction]*

*Here we can see the kernel and the set of epikernels (isotropy subgroups) associated with mGM5+.*

List of kernels and epikernels in Jana2006 (for comparison). The order parameters may differ depending on the setting of the basis.

List of kernels and epikernels:			
Shubnikov space group	Axes	Origin shift	Representation
P63'/mmc'	(1,0,0 0,1,0 0,0,1)	(0,0,0)	mGM4-
Cm'c'm	(1,0,0 1,2,0 0,0,1)	(0,0,0)	mGM5+ ←
Cmcm	(1,0,0 1,2,0 0,0,1)	(0,0,0)	mGM5+ ←
Cmcm'	(1,0,0 1,2,0 0,0,1)	(0,0,0)	mGM5-
Cm'c'm'	(1,0,0 1,2,0 0,0,1)	(0,0,0)	mGM5-
Cmc'm	(1,0,0 1,2,0 0,0,1)	(0,0,0)	mGM6+
Cm'cm	(1,0,0 1,2,0 0,0,1)	(0,0,0)	mGM6+
Cmc'm'	(1,0,0 1,2,0 0,0,1)	(0,0,0)	mGM6-
Cm'cm'	(1,0,0 1,2,0 0,0,1)	(0,0,0)	mGM6-
P21/m	(0,1,0 0,0,1 1,0,0)	(0,0,0)	mGM5+ ←
P21/m'	(0,1,0 0,0,1 1,0,0)	(0,0,0)	mGM5-
P21'/m	(0,1,0 0,0,1 1,0,0)	(0,0,0)	mGM6+

[Show details](#)

Return one step back in your Internet browser and select the representation mGM2+; OK;  
 [On the screen: ISODISTORT: order parameter direction]

Select the listed ODP and press OK

[On the screen: ISODISTORT: distortion]

Select a small starting values (0.1) for magnetic moments of Co4, Co4 and Co6;

Select "CIF file" and press OK;

Save it as a Text Document with name GM2+ into the working directory.

## ISODISTORT: distortion

Space Group: 194 P6<sub>3</sub>/mmc D6h-4, Lattice parameters: a=5.63760, b=5.63760, c=24.15760, alpha=90.00000, beta=90.00000, gamma=120.00000

Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting

Ba1 4f (1/3,2/3,z), z=-0.04041, Ba2 4f (1/3,2/3,z), z=0.36991, Ba3 2b (0,0,1/4), Co4 2a (0,0,0), Co5 4e (0,0,z), z=0.39525, Co6 4f (1/3,2/3,z), z=-0.17818, C11 2c (1/3,2/3,1/4), O2 12k (x,2x,z), x=0.16063, z=-0.14926, O3 12k (x,2x,z), x=0.16063, z=-0.14926

Include magnetic Co distortions

k point: GM, k16 (0,0,0)

IR: mGM2+, mk16t3

P1 (a) 194.270 P6<sub>3</sub>/mm'c', basis={(0,-1,0),(1,1,0),(0,0,1)}, origin=(0,0,0), s=1, i=2, k-active=(0,0,0)

Lattice parameters of undistorted supercell: a=5.63760, b=5.63760, c=24.15760, alpha=90.00000, beta=90.00000, gamma=120.00000

View distortion  View diffraction  ISOVIS distortion  ISOVIS diffraction

CIF file  Distortion file  Domains  Primary order parameters  Modes details  Complete modes details  TOPAS.STR  FULLPROF.pcr  IR matrices  Subgroup tree

Enter mode and strain amplitudes:

P6<sub>3</sub>/mmd[0,0,0]mGM2+ (a) 194.270 P6<sub>3</sub>/mm'c', basis={(0,-1,0),(1,1,0),(0,0,1)}, origin=(0,0,0), s=1 i=2, ferromagnetic, k-active=(0,0,0)

[Co4:a:mag]A2g(a)

[Co5:e:mag]A2g(a)

[Co6:f:mag]A2g(a)

P6<sub>3</sub>/mmd[0,0,0]GM1+ (a) 194.264 P6<sub>3</sub>/mmcs=1 i=1

Parameters:

"View distortion":

Atomic radius:  Angstroms

Maximum bond length:  Angstroms

Length of magnetic moment vectors:  Angstroms/magneton

Applet width:  pixels

Viewing range: xmin  xmax  ymin  ymax  zmin  zmax  "View distortion" and "View diffraction":

Maximum magnetic moment per mode:  magnetons

Generate TOPAS.STR output for subgroup tree

Number of decimal places in CIF file:

Use alternate (possibly nonstandard) setting

Basis vectors of subgroup lattice relative to parent:

a' =  a +  b +  c

b' =  a +  b +  c

c' =  a +  b +  c

Origin of subgroup relative to parent:  a +  b +  c

Make CIF movie

minimum master amplitude:

maximum master amplitude:

number of frames:

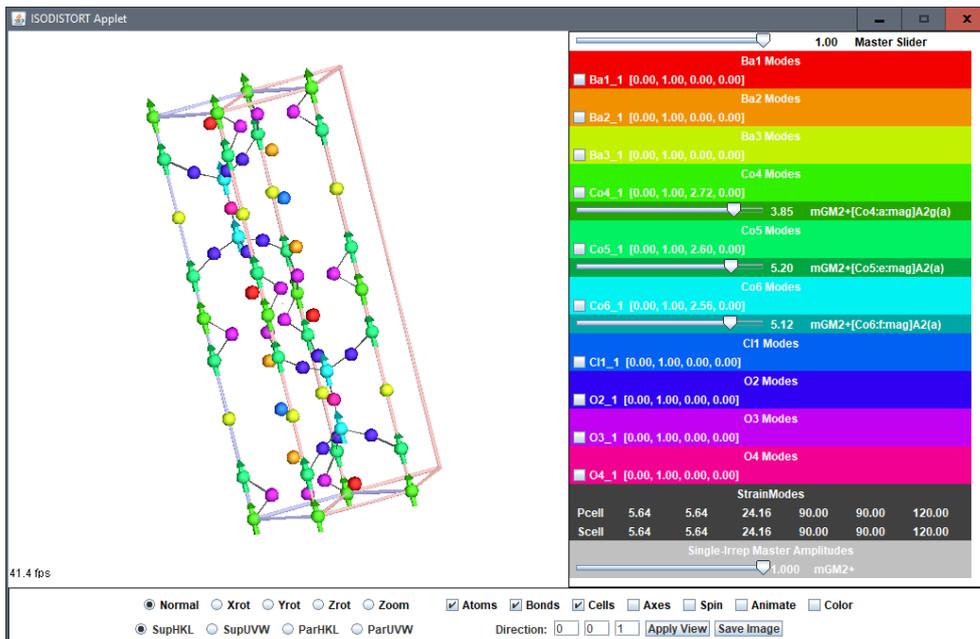
variation of the master amplitude:  linear  sine-wave

fractional number of complete periods:

Select "View distortion" and press OK;

Make the steps related with usage of Java.

*If Java offers an update please do it, otherwise the applet may be blocked. In some cases the Java security level needs to be adjusted in Java Control Panel (and the browser restarted and the work repeated ...).*



Using the sliders, magnetic moments of Co atoms can be changed to see mutual arrangement of magnetic moments of symmetry related atoms.

Return back to the page ISODISTORT irreducible representation and select now mGM4+

Repeat the work as for GM2+ and save the CIF file as a Text Document with name GM4+ into the working directory.

Return to Jana2006

## 12. Refining the model mGM2+

[On the screen: ISODISTORT => Jana2006]

Press button "Refresh the list"

Select the magnetic space group P63/mm'c' irrep: mGM2+

Press button "Continue with the selected isotropic subgroup";

Select structure name e.g. Ba5Co5\_01;

[On the screen: Basic window]

Run Refine;

Refinement converges with  $R_p \sim 2.9\%$ ,  $R(\text{obs}) \sim 8.1\%$ .

## 13. Refining the model mGM4+

[On the screen: Basic window]

[On the screen: ISODISTORT => Jana2006]

Select the magnetic space group P63'/m'm'c irrep: mGM4+

Press button "Continue with the selected isotropic subgroup";

Select structure name e.g. Ba5Co5\_02;

[On the screen: Basic window]

Run Refine;

*Refinement converges with  $R_p \sim 2.6\%$ ,  $R(\text{obs}) \sim 5.4\%$ .*

The results are identical with those from example 12.1.

# Example 12.7: DyMn<sub>6</sub>Ge<sub>6</sub>

Incommensurate magnetic structure –  $k=(0,0,0.1651)$ ;  $k=(0,0,0)$

Revised: 6 May 2019

## DyMn<sub>6</sub>Ge<sub>6</sub>

Neutron powder data measured at 11K on DMC at PSI (Switzerland)

Available at the Bilbao crystallographic server, database magndata, #1.1.10

References:

J. Rodríguez-Carvajal & F. Bourée, EPJ Web of Conferences **22**, 00010 (2012)

P. Schobinger-Papamantellos et al, Journal of Alloys and Compounds, 203 (1994) 243

Input files: **dymn6ge6.dat** (powder profile data)  
**dymn6ge6\_nuclear.cif** (nuclear structure)

### 14. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click dymn6ge6

### 15. Import Wizard

Select “Magnetic parent structure: nuclear model from CIF”; NEXT

Right pane: select the input file dymn6ge6\_nuclear.cif; OK

### 16. Define magnetic propagation vector and form factors

[On the screen: Define magnetic propagation vector and form factors]

Choose the “Number of non-zero magnetic propagation vectors” to ‘1’ and fill its value: 0 0.1651

Select atom type Dy; check “Use as a magnetic atom”; select “Magnetic formfactor <j0>”  
Dy3+;

Select atom type Mn; check “Use as a magnetic atom”; select “Magnetic formfactor <j0>”  
Mn3+;

NEXT; FINISH

*The parent structure is created*

### 17. Import the reflection file

[On the screen: Specify type of the file to be imported]

Select “Various CW format”; NEXT;

Check that the name of the input file is “dymn6Ge6.dat” and the format is “PSI format”;

Select “Debye-Scherrer method”

NEXT

[On the screen: Complete/correct experimental parameters];

Fill used wavelength 1.7037; Temperature 11; NEXT; FINISH

[On the screen: Data repository]

OK; YES to “Do you want to accept made changes?”

## 18. Refining of profile parameters by the le Bail technique.

[On the screen: Information]

NEXT

[On the screen: Refinement of the powder profile by the le Bail algorithm]

“Show powder profile”

The background is relatively smooth and it can be described without introducing manual background.

“Quit”;

“Edit profile parameters”;

[On the screen: Powder options]

In page “Cell” activate refinement of a and c parameters and the third component of the modulation vector – q3;

In the page “Profile” keep the starting value of GW to 50 and activate its refinement;

In the page “Corrections” activate refinement of “shift” parameter and change the number of used Legendre polynomials to 10

OK; YES to save the changes

“Edit refinement commands”; In the page “Basic” change the number of cycles to 20; OK

“Run Refine”;

The refinement should converge to  $R_p \sim 4.95\%$ .

“Edit profile parameters”;

[On the screen: Powder options]

In the page “Profile” activate refinement of GU and GV

Change the peak-shape function to pseudo-Voigt and activate refinement LX

OK; YES to save the changes

“Run Refine”

The refinement should converge to  $R_p \sim 2.98\%$ .

“Show powder profile”

Select the region  $2\theta$  from 30 to 45 degs – use the button “X exactly”. A couple of observed peaks may correspond to some impurity. Also at about  $2\theta = 5$ , an anomaly in the background is observed. No peaks are possible there.

“Quit”;

“Edit profile parameters”;

[On the screen: Powder options]

In page “Corrections”, press button “Define excluded regions” : from 0 to 7; “Add”, “OK”, “OK”;

“Run Refine”;

The refinement should end with  $R_p \sim 2.90\%$ .

NEXT; YES to leave the form for le Bail refinement

## 19. Refinement of the scale parameter for the nuclear structure

[On the screen: Refinement of the nuclear structure by the Rietveld method]

“Edit refinement commands”; On the page “Various” select “Fixed commands”;

In the case that the fixed command of form is “fixed all \*” is already in the panel, do nothing. If not:

Fix all parameters for all atoms (“\*” for “Atoms/Parameters” textbox); “Add”; OK; OK  
“Run Refine”

The refinement should converge to  $R_p = 11.6\%$ ,  $R(\text{obs}) = 7.5\%$

NEXT; YES to leave the for for Rietveld refinement

## 20. Testing different irreps to get the best single irrep model

[On the screen: Information]

[NEXT](#)

[On the screen: Representation analysis]

Representation analysis:					
Representation	Dimension	Shubnikov superspace group	Axes	Origin shift	
mDT1	2	P6/mmm.1'(00g)0000s	(1,0,0 0,1,0 0,0,1)	(0,0,0,0)	<input type="button" value="Details"/>
mDT2	2	P6/mmm.1'(00g)00sss	(1,0,0 0,1,0 0,0,1)	(0,0,0,0)	<input type="button" value="Details"/>
mDT3	2	P6/mmm.1'(00g)s00ss	(1,0,0 0,1,0 0,0,1)	(0,0,0,0)	<input type="button" value="Details"/>
mDT4	2	P6/mmm.1'(00g)s0s0s	(1,0,0 0,1,0 0,0,1)	(0,0,0,0)	<input type="button" value="Details"/>
mDT5	4	P2.1'(0b0)0s	(-1,0,0 0,0,-1 0,-1,0)	(0,0,0,0)	<input type="button" value="Details"/>
mDT6	4	P2.1'(0b0)ss	(-1,0,0 0,0,-1 0,-1,0)	(0,0,0,0)	<input type="button" value="Details"/>

This window has an information character. You can see here all irreps leading to magnetic ordering. The “details” buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.

[NEXT](#)

[On screen: List of kernels and epikernels]

**List of kernels and epikernels:**

Shubnikov superspace group	Axes	Origin shift	Representation
P6/mmm.1'(00g)0000s	(-1,0,0 1,1,0 0,0,-1)	(0,0,0,0)	MDT1
P6/mmm.1'(00g)00sss	(-1,0,0 1,1,0 0,0,-1)	(0,0,0,0)	MDT2
P6/mmm.1'(00g)s00ss	(-1,0,0 1,1,0 0,0,-1)	(0,0,0,0)	MDT3
P6/mmm.1'(00g)s0s0s	(-1,0,0 1,1,0 0,0,-1)	(0,0,0,0)	MDT4
P622.1'(00g)-t00s	(-1,0,0 1,1,0 0,0,-1)	(0,0,0,-1/6)	mLD1LD1
P622.1'(00g)h00s	(-1,0,0 1,1,0 0,0,-1)	(0,0,0,1/12)	mLD2LD2
Cmmm.1'(00g)0000s	(-1,-1,0 1,-1,0 0,0,1)	(0,0,0,0)	mLD1LD1
Cmmm.1'(00g)ss0s	(-1,-1,0 1,-1,0 0,0,1)	(0,0,0,0)	mLD1LD1
Cmmm.1'(00g)s00s	(-1,-1,0 1,-1,0 0,0,1)	(0,0,0,0)	mLD2LD2
Cmmm.1'(00g)s0s0s	(-1,-1,0 1,-1,0 0,0,1)	(0,0,0,0)	mLD2LD2
C222.1'(00g)0000s	(-1,-1,0 1,-1,0 0,0,1)	(0,0,0,0)	mLD1LD1
C222.1'(00g)00sss	(-1,-1,0 1,-1,0 0,0,1)	(0,0,0,0)	mLD2LD2
P2/m.1'(0b0)00s	(-1,0,0 0,0,-1 0,-1,0)	(0,0,0,0)	mLD1LD1
P2/m.1'(0b0)s0s	(-1,0,0 0,0,-1 0,-1,0)	(0,0,0,0)	mLD2LD2

Select from above kernels/epikernels one representative of a family of Shubnikov superspace groups for testing.

Select one of the hexagonal magnetic superspace groups based on average space group *P6/mmm*; NEXT;

This will pass all present hexagonal magnetic superspace groups of type *P6/mmm* to further testing. We assume that both magnetic atoms should have non-zero magnetic moment.

[On the screen: Select magnetic space group]

**Select magnetic superspace group:**

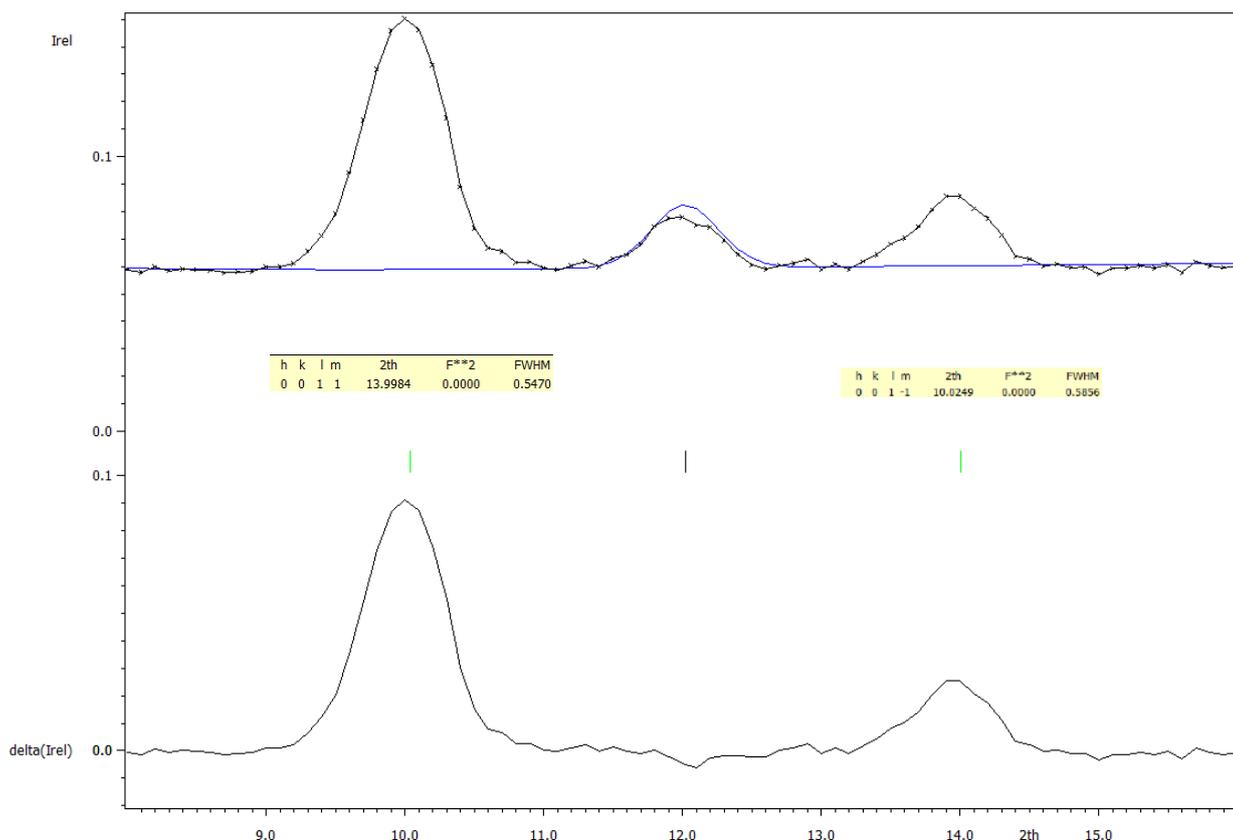
Shubnikov group	Atom	Moment	Global	sin#1	cos#1
P6/mmm.1'(00g)0000s	Dy1	(0,0,0)	(0,0,0)	(0,0,0)	(0,0,0)
P6/mmm.1'(00g)00sss	Mn1	(0,0,0)	(0,0,0)	(0,0,0)	(0,0,0)
P6/mmm.1'(00g)s00ss					
P6/mmm.1'(00g)s0s0s					

Information: The symbol "M" indicates that the component can have non-zero value.  
For more details press the button "Show details".  
Magnetic moments are expressed in the parent cell.

Only the second magnetic superspace group allows for non-zero magnetic moments for Mn and Dy atoms.

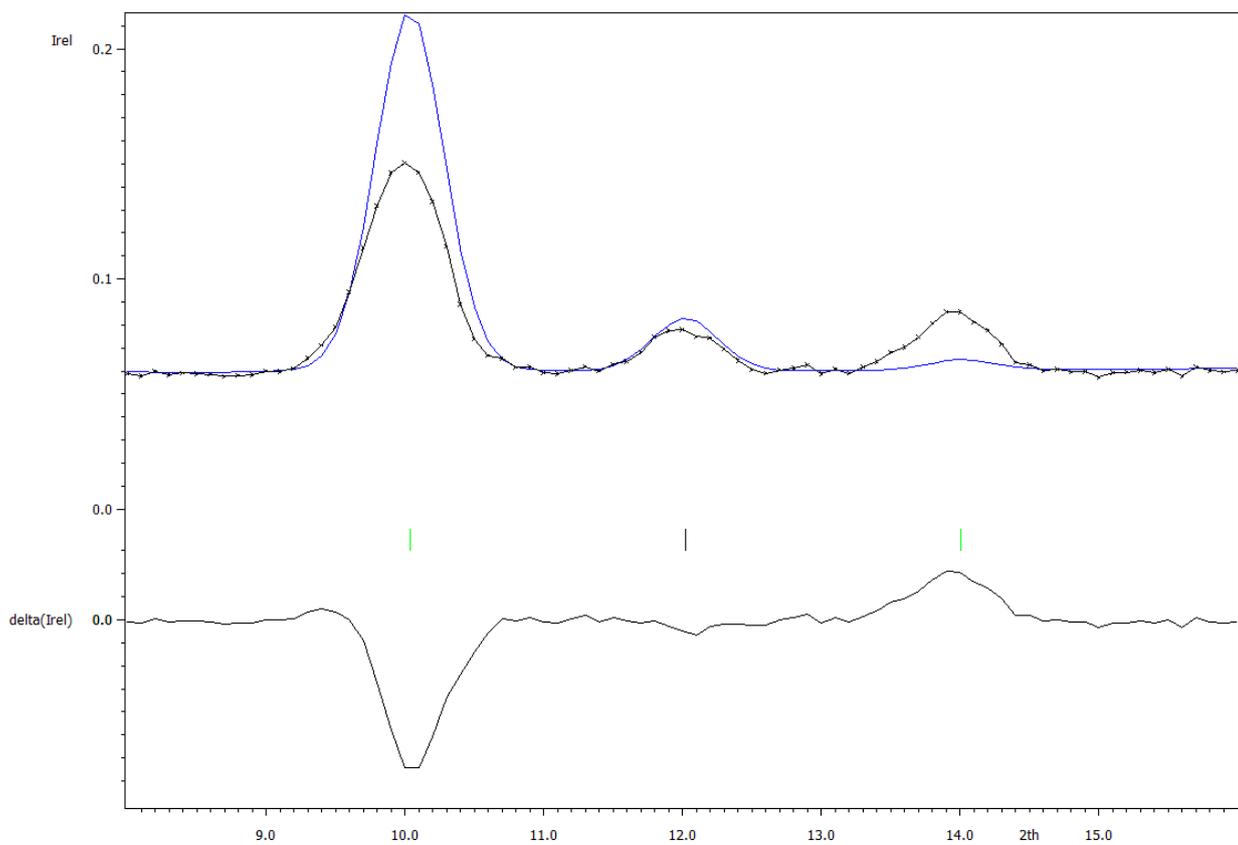
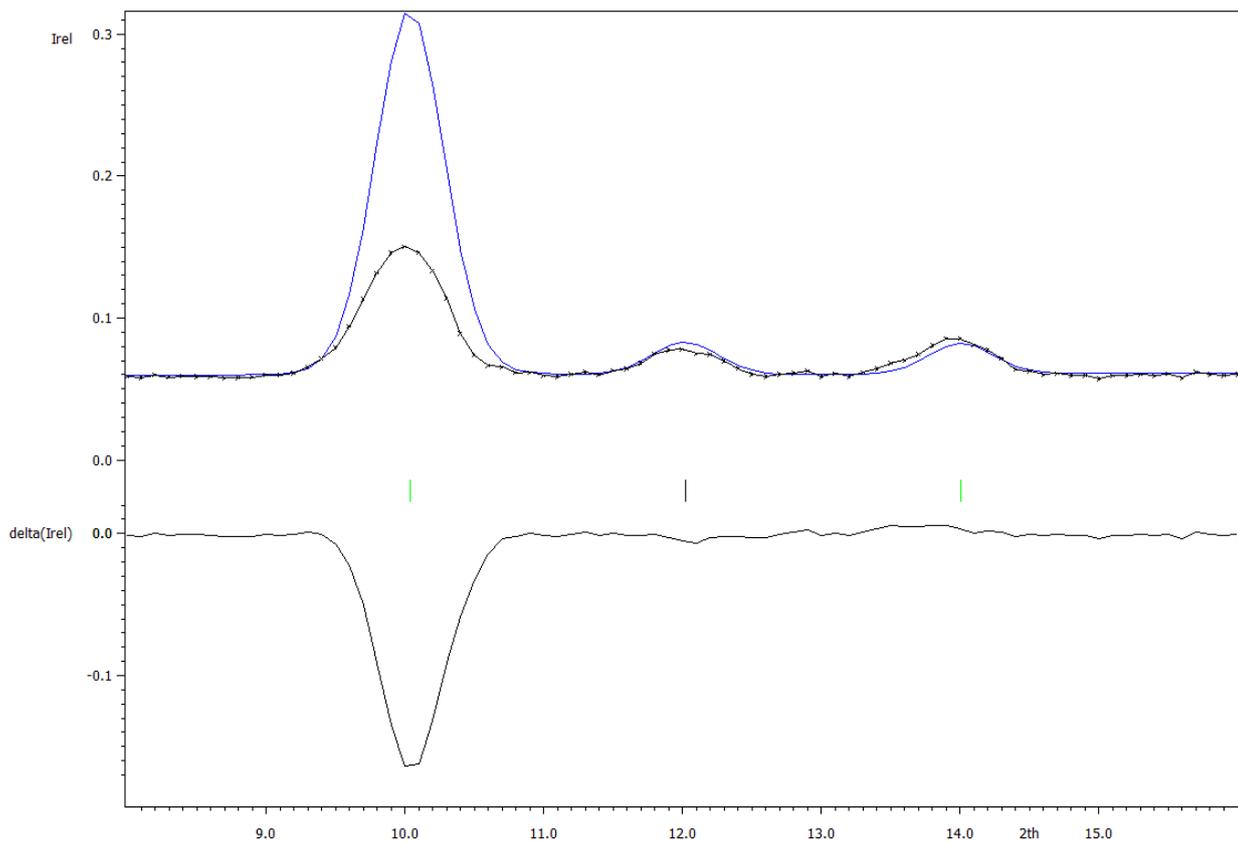
Select the second magnetic superspace group: *P6/mmm.1'(00g)00sss* and press "Start profile simulation";

Press "X exactly" and focus the region 8-16 degrees; Press "Fit Y":



Two dominant magnetic peaks in this region have zero intensity. This means that the tested model does not describe the magnetic ordering correctly. However, in making such conclusion we have to take into account that the simulation procedure uses randomly generated magnetic moments and that the result can be affected by an actual random choice. This is why we recommend repeating the simulation when some doubt exists. "Quit"; "Back" and return to the "List of kernels and epikernels" and select one of hexagonal superspace groups based on P622.

While the first one P622.1'(00g)t00s restricts the magnetic moments of the Dy atom to zero, the second one P622.1'(00g)-h00s allows non-zero magnetic moments for both magnetic atoms. The simulation profiles demonstrate that the intensity of both magnetic peaks in the interval (8-16) degs are generally non-zero:



## 21. Refinement of the magnetic structure in – P622.1'(00g)-h00s

[On the screen: Select magnetic superspace group]

Select the magnetic superspace group P622.1'(00g)-h00s

Press 'Continue with the selected magnetic superspace group'

[On the screen: Select structure name]

Use the default name i.e. dymn6ge6\_01 or any other; **OK**

[On the screen: Basic window of Jana2006]

Right-click the icon of Refine and select the page "Various"

Use the button "Restrictions" and ensure that all atoms (i.e. \*) are restricted to have identical ADP parameters.

The restriction "restric \* 13" has been set automatically when the program created the testing structure. To see the meaning of the restriction focus it by mouse and press "Load". "Load" opens the restriction for editing. Make sure that "Coordinates" and "Modulations" boxes are cleared and press "Rewrite" to close the editing mode.

OK

Select the page "Fixed commands" and (similarly like in the previous step) ensure that all atomic positions are fixed in their current values ("fixed xyz \*").

OK

Select the page "Basic" and check if the "Number of cycles" is set to 100 and the "Damping factor" to 0.1; **OK**; **Yes+start**;

Refinement converges with  $R_p \sim 4.9\%$ ,  $R(\text{obs}) \sim 4.1\%$ ,  $3.7\%$ ,  $4.9\%$  for all, nuclear and magnetic reflections, respectively.

Use "Profile viewer" and check the fit of the calculated powder profile

Observe that some main reflections like (1 0 1 0) around 25 degrees or (2 -1 1 0) at about 40 degrees are poorly fit. In order to exclude some additional nuclear effects we can allow the refinement of atomic positions:

Right-click the icon of Refine and select the page "Various". Use the button "fixed commands" and disable the command "fixed xyz". Run refine again.

Now the atom coordinates will also be refined. The refinement should end with  $R_p \sim 4.8\%$  and Bragg R factors  $R(\text{obs}) = 4.0\%$ ,  $3.5\%$  and  $4.9\%$  for all, main and satellite reflections, respectively. ("View of Refine"). The improvement is minimal. Some of the main reflections remain poorly fit systematically with too low intensity. This fact can lead to the conclusion that an additional magnetic ordering with  $k=0$  is present.

## 22. Refinement in the subgroups allowing magnetic wave (0,0,0)

[On the screen: Basic Jana window]

We try then the possibility that magnetic scattering occurs also at main reflections, i.e. an additional magnetic ordering with  $k=(0\ 0\ 0)$  is taking place. In the language of the symmetry group of the phase this implies to lower it, dropping the operation  $\{1'|0001/2\}$  associated with the existence of a single primary incommensurate wave vector.

There are several maximal subgroups without this operation. Then can be generated by the Jana tool "Tools→Transformations→Go to subgroup structure". As generators for the working group until now can be used:

$\{6+|0\ 0\ 0\ 5/6\}$ :  $x_1-x_2, x_1, x_3, x_4+5/6$

$\{2_{-xy}|0\ 0\ 0\ 0\}$ :  $x_2, x_1, -x_3, -x_4$

$\{1'|0001/2\}$ :  $x_1, x_2, x_3, x_4+1/2$

The possible maximal subgroups will then be generated by:

**P622(00g)-h00**

{6+|0 0 0 5/6}: x1-x2, x1, x3, x4+5/6, m

{2\_xy| 0 0 0 0}: x2, x1, -x3, -x4, m

**P6'22'(00g)t00**

{6+'|0 0 0 1/3}: x1-x2, x1, x3, x4+1/3, -m

{2\_xy| 0 0 0 0}: x2, x1, -x3, -x4, m

**P62'2'(00g)-h00**

{6+|0 0 0 5/6}: x1-x2, x1, x3, x4+5/6, m

{2'\_xy| 0 0 0 1/2}: x2, x1, -x3, -x4+1/2, -m

**P6'2'2(00g)t00**

{6+'|0 0 0 1/3}: x1-x2, x1, x3, x4+1/3, -m

{2'\_xy| 0 0 0 1/2}: x2, x1, -x3, -x4+1/2, -m

Make sure that your actual structure is the final refined structure from the previous step.

“Tools → Transformation → Go to subgroup structure”;

Press the “Refresh” button and select the generators:

x1-x2 x1 x3 x4+5/6 m

x2 x1 -x3 -x4 m

**Define subgroup**

Operator	Symbol	Direction
x2 -x1+x2 x3 x4+1/6 m	6-	(0,0,1)
x1-x2 x1 x3 x4+5/6 m	6+	(0,0,1)
x2 -x1+x2 x3 x4+2/3 -m	6 <sup>-1</sup>	(0,0,1)
x1-x2 x1 x3 x4+1/3 -m	6 <sup>+1</sup>	(0,0,1)
-x2 -x1 -x3 -x4+1/2 m	2	(1,-1,0)
-x2 -x1 -x3 -x4 -m	2'	(1,-1,0)
x2 x1 -x3 -x4 m	2	(1,1,0)
x2 x1 -x3 -x4+1/2 -m	2'	(1,1,0)
x1 x1-x2 -x3 -x4+1/6 m	2	(2,1,0)
x1 x1-x2 -x3 -x4+2/3 -m	2'	(2,1,0)
-x1+x2 x2 -x3 -x4+5/6 m	2	(1,2,0)
-x1+x2 x2 -x3 -x4+1/3 -m	2'	(1,2,0)

Space group : P622.1'(00g)-h00s    Axes : (1,0,0|0,1,0|0,0,1)    Origin : (0,0,0)

Subgroup :                                    Axes :                                    Origin :                                    Index :

Press the button “Complete subgroup”;

**Define subgroup**

Operator	Symbol	Direction
x1 x2 x3 x4 m	1	(0,0,0)
x1 x2 x3 x4+1/2 -m	1'	(0,0,0)
x1-x2 -x2 -x3 -x4+1/3 m	2	(1,0,0)
x1-x2 -x2 -x3 -x4+5/6 -m	2'	(1,0,0)
-x1 -x1+x2 -x3 -x4+2/3 m	2	(0,1,0)
-x1 -x1+x2 -x3 -x4+1/6 -m	2'	(0,1,0)
-x1 -x2 x3 x4+1/2 m	2	(0,0,1)
-x1 -x2 x3 x4 -m	2'	(0,0,1)
-x2 x1-x2 x3 x4+2/3 m	3+	(0,0,1)
-x1+x2 -x1 x3 x4+1/3 m	3-	(0,0,1)
-x2 x1-x2 x3 x4+1/6 -m	3+'	(0,0,1)
-x1+x2 -x1 x3 x4+5/6 -m	3-'	(0,0,1)

---

Space group : P622.1'(00g)-h00s    Axes : (1,0,0|0,1,0|0,0,1)    Origin : (0,0,0)

Subgroup : P622(00g)-h00    Axes : (1,0,0|0,1,0|0,0,1)    Origin : (0,0,0)    Index : 2

The selected subgroup is normal

NEXT; NEXT

[On the screen: Select one representative of the 2<sup>nd</sup> coset]

Select the first operation.

Generally, all selections would give the same result.

NEXT;

[On the screen: Specify the output structure]

Select “dymn6ge6\_01\_subgroup\_1” or any other

NEXT;FINISH;”Yes” to the question “Do you want to continue with the new structure?”

[On the screen: Basic window]

Run “Edit Atoms”; Select atoms Dy1 and Mn1; Press the button “Action”

Select “Reset modulation/magnetic parameters”

Deselect “Magnetic parameters k<>0”

Choose “Reset parameters randomly in the interval (-pmax,pmax)

OK;OK;”Yes” to the question “Do you want to rewrite changed files?”

Run “Refine”;

Repeat the procedure for all subgroups listed above

Use the “File→ Structure → History” to return to the final refined structure in P622.1'(00g)-h00s.

*P622(00g)-h00*

*R<sub>p</sub>=4.7%, R(obs)=4.4%,4.1%,5.1% for all, nuclear and magnetic reflections, respectively.*

*P6'22'(00g)t00*

*R<sub>p</sub>=4.6%, R(obs)=3.6%,3.1%,4.6% for all, nuclear and magnetic reflections, respectively.*

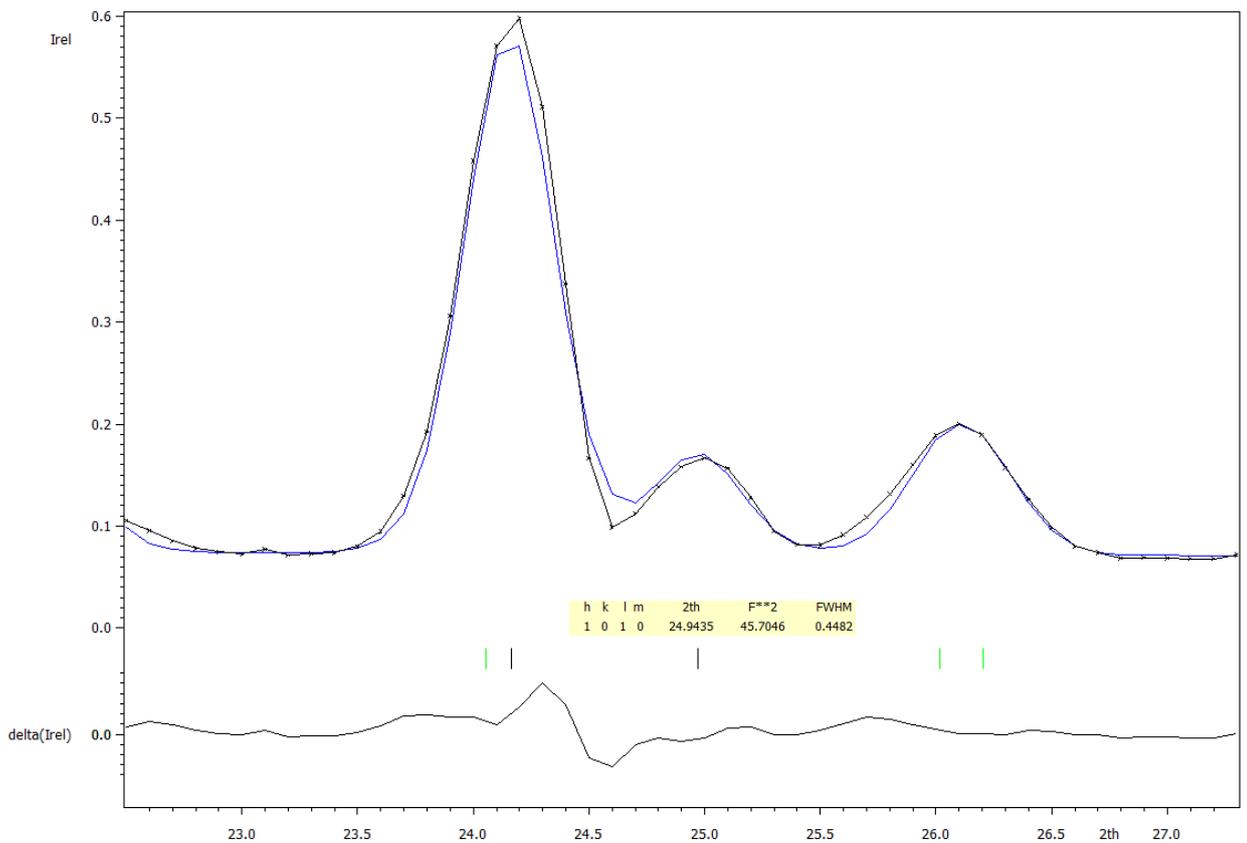
*P6'2'(00g)-h00*

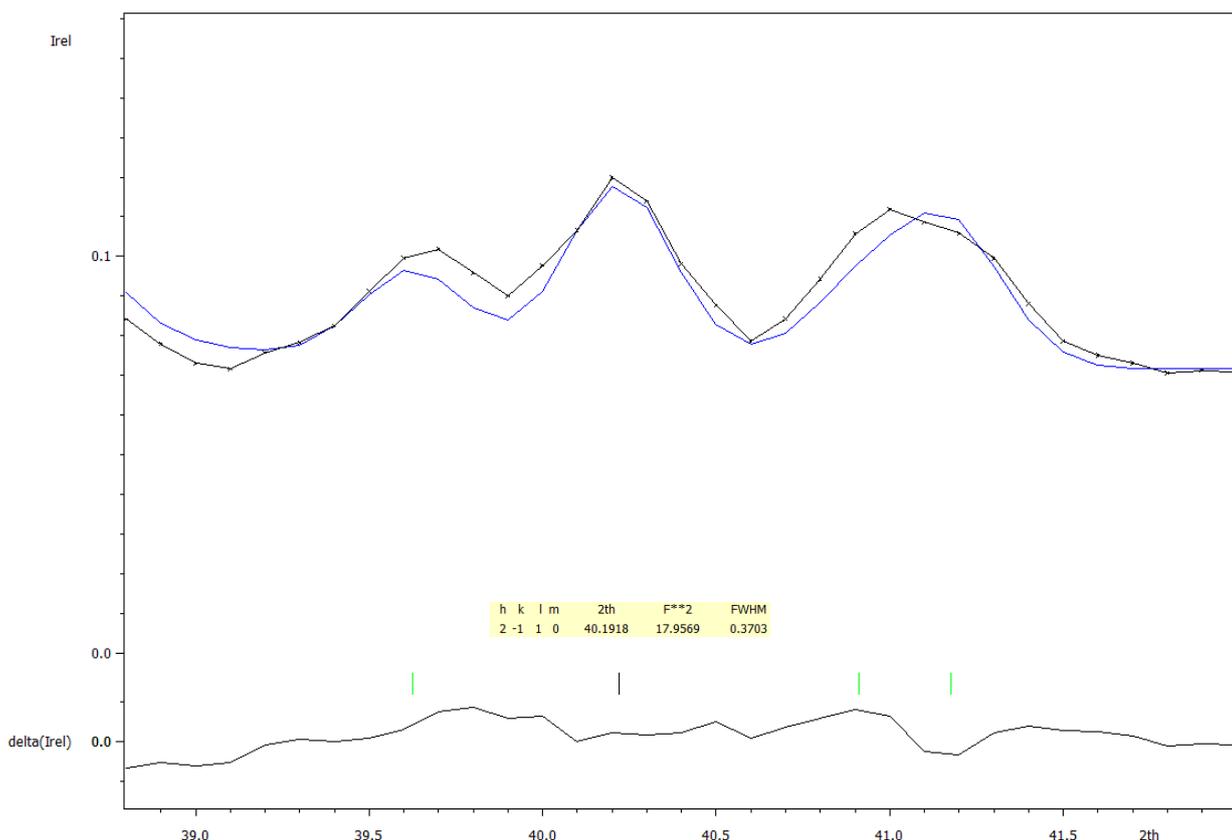
*R<sub>p</sub>=4.1%, R(obs)=3.0%,2.6%,3.7% for all, nuclear and magnetic reflections, respectively.*

*P6'2'2(00g)t00*

*R<sub>p</sub>=4.6%, R(obs)=4.0%,3.4%,5.1% for all, nuclear and magnetic reflections, respectively.*

*One of the symmetries clearly fits the data better. Observe that the strong misfit of some of the main reflections has disappeared.*





The final common  $U_{iso}$  is negative but its absolute value is very small.

Right-click the icon of Refine and select the page "Various"

Use the button "Fixed commands"

Select "Set individual"; File the edit box by the text " $U_{iso}[*]$ "; Define value "Set to" zero

Add; OK; OK; Press Button "Yes+start"

$R_p=4.1\%$ ,  $R(obs)=3.4\%, 3.2\%, 3.8\%$  for all, nuclear and magnetic reflections, respectively.

Run "EditM50"; Go to the page "Magnetic parameters"; Change the magnetic form factor for Dy to  $\langle j_0 \rangle + c \langle j_2 \rangle$  and Dy3+

OK; "Yes" to the question "Do you want to rewrite M50 file?"

Run "Refine"

$R_p=4.1\%$ ,  $R(obs)=3.0\%, 2.8\%, 3.4\%$  for all, nuclear and magnetic reflections, respectively.

### 23. Visualize the refined model with MVISUALIZE (Jmol) – Internet connection needed

[On the screen: Basic window]

"File → CIF utilities → Make mCIF file for MVisualize";

[On the screen: Define name for the out mcif file]

Define here the name of a mcif file with the file extension "mcif"

OK

[On the screen: INFORMATION]

OK

The Jana will now start your default internet browser on the home page of Bilbao

Crystallographic server. Select there the utility MVISUALIZE and follow their instructions.

## 24. Visualize the refined model with VESTA

[On the screen: Basic window]

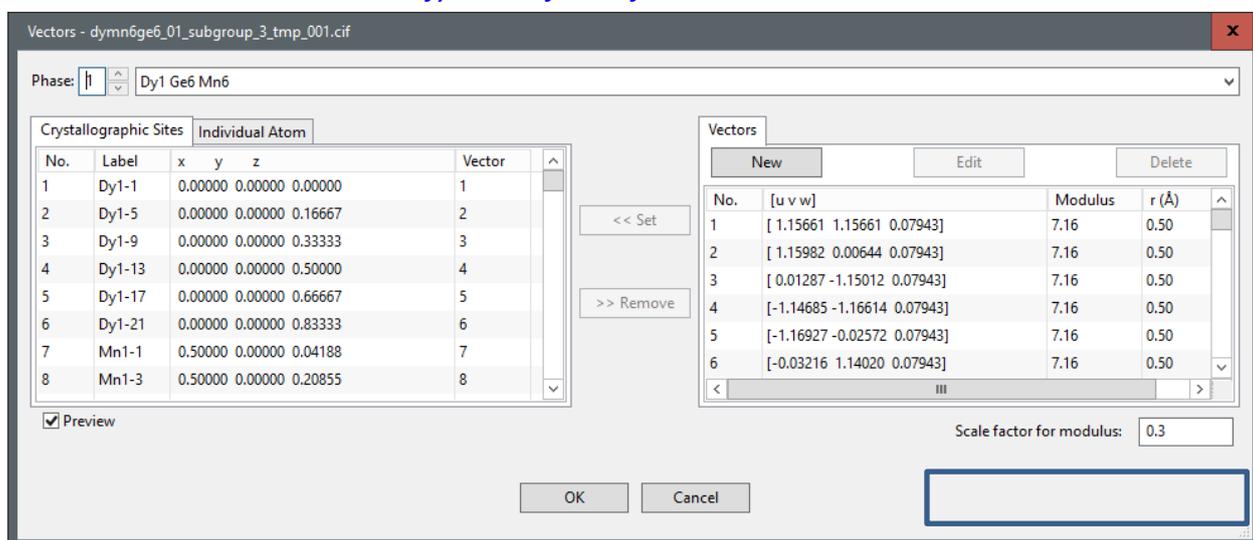
Double click on the icon "Plot structure"

Select "Draw approximant structure"; x from 0 to 1; y from 0 to 1; z from 0 to 6 (c\* component of the propagation vector is close to 1/6)

Select "Use Vesta to draw the magnetic structure"

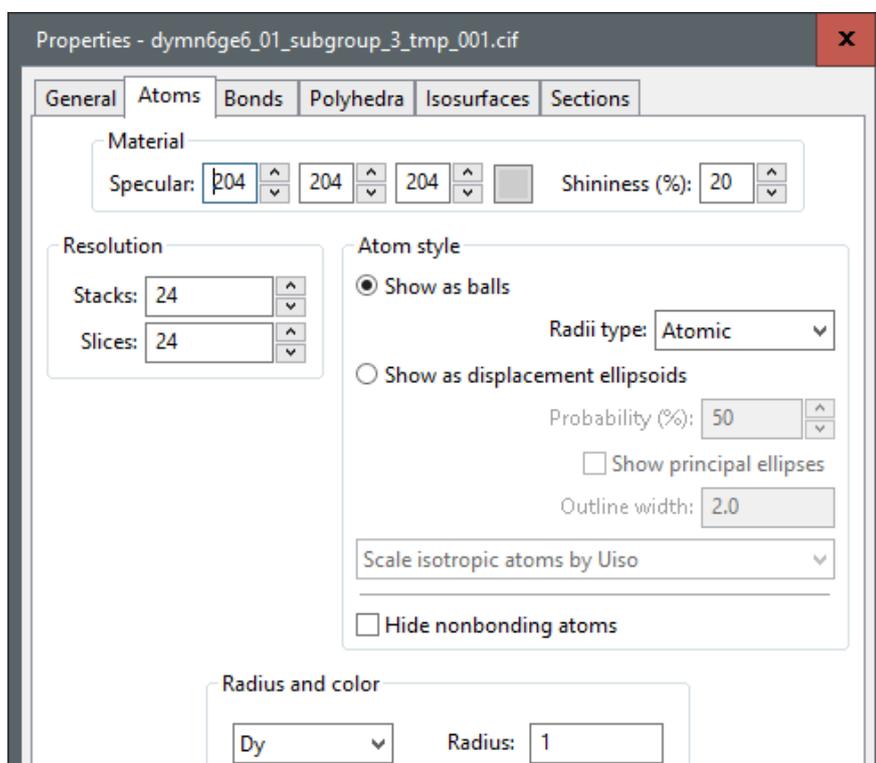
Press "Draw+return" or "Draw+continue"

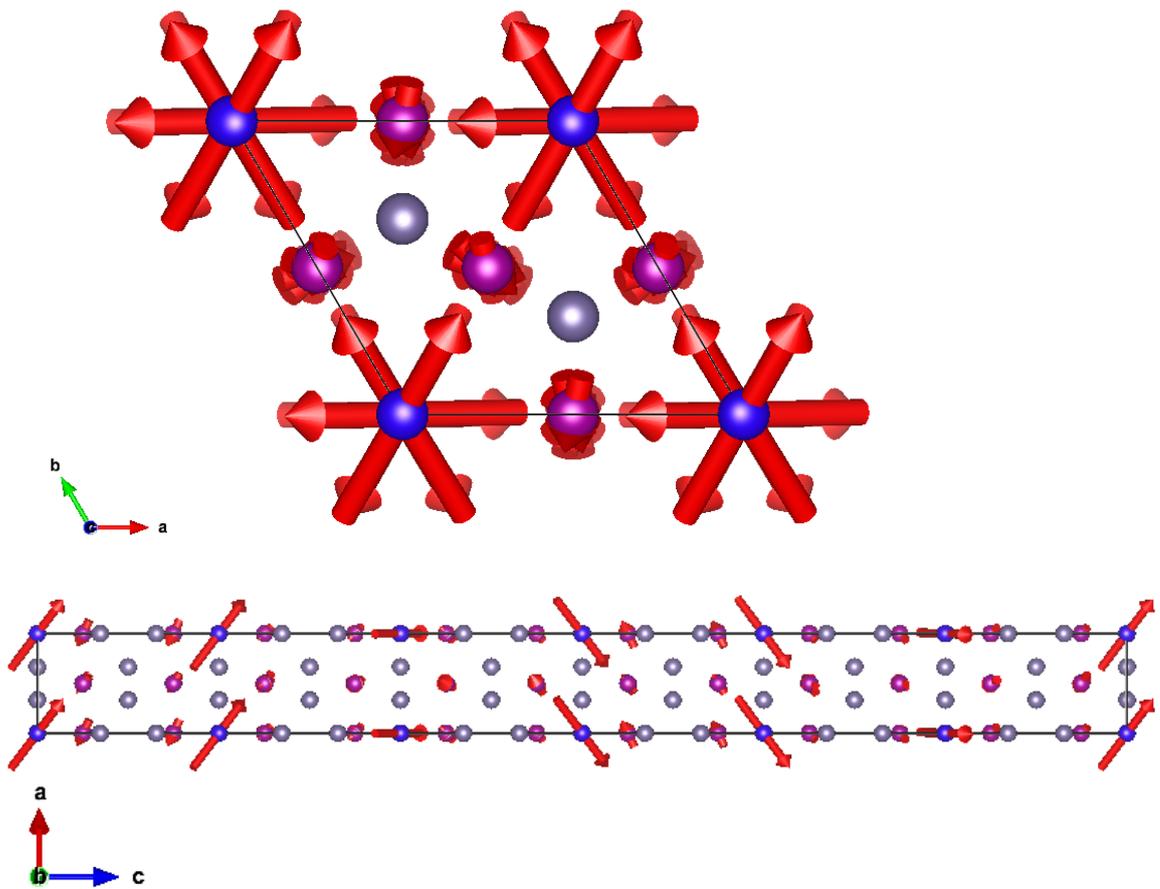
Select "Edit→Vectors" and modify "Scale factor for modulus" to 0.3



OK

Press button "Properties..."; Go the page "Atoms" and modify "Radius" for all atoms





## 25. Transformation to the standard setting as used in MAGNDATA - *Internet connection needed*

[On the screen: Basic window]

“Tools → Connect through internet to → Bilbao Crystallographic Server”

Select “MAGNDATA”; Enter the label of the structure “1.1.10”

Reference: Rodriguez-Carvajal, J et al., *EPJ Web of Conferences* (2012) **22** 00010

DOI: 10.1051/epjconf/20122200010

Atomic positions from: ICSD #57229

Parent space group (paramagnetic phase): P6/mmm (#191)

Propagation vector: k1 (0.000000, 0.000000, 0.1651)

Lattice parameters of the basic unit cell:

5.2081 5.2081 8.1522 90 90 120

Transformation from parent structure: (a,b,c;0,0,0)

[View matrix form]

Magnetic Superspace Group: P62'2'(00γ)h00

[View symmetry operations]

Magnetic Point Group: 62'2' (24.4.90)

[View symmetry operations]

Symmetry-adapted form of material tensors via

Average positions, magnetic moments and magnetic modulations of symmetry independent atoms:

From now on, magnetic atoms are in boldface and colored in red. Magnetic moments are expressed in units of  $\mu_B$

[Show only magnetic atoms]

[Show all the atoms]

Average atomic positions and magnetic moments of symmetry independent atoms

Label	Atom type	x	y	z	Multiplicity	Symmetry constraints on M	$M_{0x}$	$M_{0y}$	$M_{0z}$	M
Dy1	Dy	0	0	0	1	0,0, $m_z$	0.0	0.0	3.932	3.93
Mn1	Mn	0.5	0	0.2510	6	0,0, $m_z$	0.0	0.0	-1.149	1.15

Magnetic moment modulation parameters of symmetry independent atoms

Wave vector 1

Atom	Magnetic moment Fourier Cos coeffs						Magnetic moment Fourier Sin coeffs					
	Symmetry constraints			Numerical values			Symmetry constraints			Numerical values		
	x	y	z	x	y	z	x	y	z	x	y	z
Dy1	$\sqrt{3}M_x \sin 1$	0	0	6.195546	0.0	0.0	$M_x \sin 1$	$2M_x \sin 1$	0	3.577	7.154	0.0
Mn1	$M_x \cos 1$	$M_y \cos 1$	0	-1.877	-0.206	0.0	$M_x \sin 1$	$M_y \sin 1$	0	-0.846	-2.049	0.0

The result as derived step by step from the representation theory is expressed in a different chiral domain than used in MAGNDATA. Therefore, we should transfer it to the equivalent chiral domain.

[On the screen: Basic window]

“Tools → Transformation → Change enantiomorph”

Create a new structure with name e.g. “dymn6ge6\_01\_subgroup\_3\_chiral”

OK; Yes to continue with the new structure

Run EdiM50; Go the page “Symmetry”

Now the superspace group is the same as used in MAGNDATA however there is a non-zero origin shift in  $x_4$  equal  $1/6$ .

ESC

“Tools → Transformation → Origin shift”

Use shift to the point 0 0 0  $-1/6$

OK

The last point that has to be checked for a full comparison is if we are using in the same symmetry positions for the magnetic atoms Dy1 and Mn1. The positions of these atoms

from 1.1.10 are:

Dy1 (0,0,0) and Mn1 (0.5,0,0.251).

[On the screen: Basic window]

Run "Edit atoms"; Double click on Dy1 atom; Go to the page "Edit"

The coordinates are (1,1,1) and this means that we can just rewrite them to (0,0,0) as such transformation does not change the modulation functions.

In the case that the Mz0 is negative change it to positive.

Move to the atom Mn1

Its coordinates are (0.5,1,0.749). From the list of symmetry operations we can find that the symmetry operation:  $x_1-x_2, -x_2, -x_3, -x_4+1/2$  combined with the lattice translation (1,1,1,0) makes what is needed.

OK;

[On the screen: Select atoms to be used]

Select the atom Mn1; Press button "Action"; Select "Transform selected atoms"

Use the button "Fill by a symmetry operation"; Select  $x_1-x_2 -x_2 -x_3 -x_4+1/2 -m$ ; Modify the translation vector to 1 1 1 1/2

OK; OK; Yes to rewrite files

[On the screen: Basic window]

Run "Refine" to check that all transformation did not change the solution

[On the screen: Basic window]

"Edit/View → View of Refine"; Press "Go to" and select "Changes overview"

Dy1	ai	x	y	z	Uiso	
0	0.166668	0.000000	0.000000	0.000000	0.000000	0.00
1	0.166668	0.000000	0.000000	0.000000	0.000000	0.000000
su	0.000000	0.000000	0.000000	0.000000	0.000000	

---

Dy1	Mx0	My0	Mz0	
0	0.000000	0.000000	3.828030*	-0.01
1	0.000000	0.000000	3.827922	
su	0.000000	0.000000	0.121279	

---

Dy1	Mxsin1	Mysin1	Mzsin1	Mxcos1	Mycos1	Mzcos1	
0	3.517421*	7.034843	0.000000	6.092352	0.000000	0.000000	0.00
1	3.517436	7.034873	0.000000	6.092379	0.000000	0.000000	
su	0.054654	0.000000	0.000000	0.000000	0.000000	0.000000	

---

Mn1	ai	x	y	z	Uiso	
0	1.000000	0.500000	0.000000	0.251014*	0.000000	0.00
1	1.000000	0.500000	0.000000	0.251014	0.000000	
su	0.000000	0.000000	0.000000	0.000764	0.000000	

---

Mn1	Mx0	My0	Mz0	
0	0.000000	0.000000	-0.838416*	-0.04
1	0.000000	0.000000	-0.838840	
su	0.000000	0.000000	0.094546	

---

Mn1	Mxsin1	Mysin1	Mzsin1	Mxcos1	Mycos1	Mzcos1	
0	-1.203674	-2.383651*	0.000000	-1.435586	-0.388131	0.000000	0.01
1	-1.203557	-2.383534	0.000000	-1.435688	-0.388058	0.000000	
su	0.107789	0.103590	0.000000	0.127037	0.106534	0.000000	

		M <sub>0x</sub>	M <sub>0y</sub>	M <sub>0z</sub>	M
Dy1	MAGNDATA	0.0	0.0	3.93	3.93
	Jana	0.0	0.0	3.83(12)	3.83(12)
Mn1	MAGNDATA	0.0	0.0	-1.15	1.15
	Jana	0.0	0.0	-0.84(9)	0.84(9)

		cos			sin		
		M <sub>x</sub>	M <sub>y</sub>	M <sub>z</sub>	M <sub>x</sub>	M <sub>y</sub>	M <sub>z</sub>
Dy1	MAGNDATA	6.20	0.0	0.0	3.58	7.15	0.0
	Jana	6.09	0.0	0.0	3.51(5)	7.03	0.0
Mn1	MAGNDATA	-1.88	-0.21	0.0	-0.85	-2.05	0.0
	Jana	-1.43(12)	-0.39(10)	0.0	-1.20(11)	-2.38(10)	0.0

**26. Use of the option of polar coordinates for the moments to constraint further the Mn spin to have a circular modulation.**

[On the screen: Basic window]

“File → Structure → Save as”; Use e.g. “dymn6ge6\_01\_subgroup\_3\_final”

OK; No to the question “Do you want to continue with the new structure?”

[On the screen: Basic window]

Run “Edit atoms”

[On the screen: Select atoms to be used]

Double click on the atom Dy1; Activate option “in spherical coordinates”;

Go the “Edit” page;

For the magnetic moment  $k=0$  only  $M_{r0}$ -amplitude is a free parameter. Both angles  $M_{p0}$ - $\varphi$  angle and  $M_{t0}$ - $\vartheta$  angle are fixed by symmetry.

Uncheck the refine flags for angular components if active.

Press the button “Magnetic” to magnetic modulation waves.

The only free parameter is the amplitude  $M_{rsin1}$ . The  $\varphi$  angle is fixed for cos wave to 90 and for sin wave to 0. This means that the circular modulation is fully induced by the symmetry.

Uncheck the refine flags for angular components if active.

Go to the atom Mn1 and activate option “in spherical coordinates”;

Go the “Edit” page;

For the magnetic moment  $k=0$  only  $M_{r0}$ -amplitude is a free parameter. Both angles  $M_{p0}$ - $\varphi$  angle and  $M_{t0}$ - $\vartheta$  angle are fixed by symmetry.

Uncheck the refine flags for angular components if active.

Press the button “Magnetic” to magnetic modulation waves.

For Mn1, the modulation parameters except the  $\vartheta$  angle are symmetry free. In order to force a circular modulation, the constraints must be used:  $M_{rcos1}=M_{rsin1}$ ,  $M_{pcos1}=M_{psin1}-90$ .

These equations are only roughly satisfied by the previous refined model, as shown after the transformation.

Right click on the “Refine” icon; Select the page Various; Click on the button “Equations”;

Define the equations mentioned above:

Mp0[Dy1]=0  
 Mt0[Dy1]=0  
 Mrcos1[Dy1]=Mrsin1[Dy1]  
 Mpsin1[Dy1]=90  
 Mpcos1[Dy1]=0  
 Mtsin1[Dy1]=90  
 Mtcos1[Dy1]=90  
 Mp0[Mn1]=0  
 Mt0[Mn1]=180  
 Mrcos1[Mn1]=Mrsin1[Mn1]  
 Mpcos1[Mn1]= Mpsin1[Mn1]-90  
 Mtsin1[Mn1]=90  
 Mtcos1[Mn1]=90

You can do either one by one or you can use pre-prepared file "Equations-circular.txt". For the former method:

Press the button "Edit" and use the copy-paste method from the file "Equations-circular.txt".

OK;OK; Yes+start

$R_p=3.83\%$ ,  $R(\text{obs})=2.93\%, 2.43\%, 3.82\%$  for all, nuclear and magnetic reflections, respectively. Which means that it is not significantly worse than the full refinement – see point 9.

		$M_{0x}$	$M_{0y}$	$M_{0z}$	M
Dy1	MAGNDATA	0.0	0.0	3.93	3.93
	Jana	0.0	0.0	3.93(11)	3.93(11)
Mn1	MAGNDATA	0.0	0.0	-1.15	1.15
	Jana	0.0	0.0	-0.99(8)	0.99(8)

After transforming from polar to crystallographic coordinates

		cos			sin		
		$M_x$	$M_y$	$M_z$	$M_x$	$M_y$	$M_z$
Dy1	MAGNDATA	6.20	0.0	0.0	3.58	7.15	0.0
	Jana	6.17	0.0	0.0	3.56(5)	7.12	0.0
Mn1	MAGNDATA	-1.88	-0.21	0.0	-0.85	-2.05	0.0
	Jana	-1.85(10)	-0.17(9)	0.0	-0.86(9)	-2.04(8)	0.0

**General note: Two different strategies for handling refinement keys in Jana2006**

From Petříček, V., Dušek, M. & Palatinus, L. (2014) Z.Kristallogr. **229**, 345-352.

"All refinable parameters are divided into two groups: automatic and user-controlled ones. The

automatic parameters are those which can be usually refined without numerical problems: scale factors and extinction parameters; parameters describing position, ADP and their modulation for individual atoms as well as for molecules; background parameters of the powder profile; magnetic parameters. The user-controlled parameters are twin/phase volume fractions, atomic or molecular site occupancies, parameters of crenel modulation functions, parameters of multipole refinement and powder profile parameters for individual Bragg reflections. The automatic parameters are activated by default at the beginning of the refinement process while the user-controlled ones must be always explicitly activated by the user. The program always fixes the parameters which cannot be refined due to symmetry restrictions. In order to fix other automatic parameters the user is provided with a range of special fixing commands. This way is very useful for most cases because it minimizes mistakes in setting refinement flags. However, the program also allows switching to a completely manual mode, where all parameters are to be activated explicitly by the user, analogically to other refinement programs such as FullProf [29].”

**Handling of symmetry restrictions of magnetic moments in polar coordinates would be easier for most of users if the non-automatic procedure is used:**

The screenshot shows the 'Refine commands' dialog box with the following settings:

- Basic tab:**
  - Number of cycles: 100
  - Damping factor: 0.1
  - Use Marquart technique:
  - Use dynamical LS method:  => if R<sub>w</sub> is increased by 10% reduce the damping by a factor 2
  - Check for convergence:  => stop if max(change/s.u.) ≤ 0.05 in 1 consecutive cycles.
  - Disable atoms having too large isotropic ADP parameter:  => ADP(iso) limit for disabling 0.2
  - Automatic refinement keys:**  (highlighted)
  - Automatic symmetry restrictions:
  - Refinements on F(obs)\*\*2:
  - Apply electroneutrality:
  - Simulation run:
  - After last cycle call Fourier:
  - Correct for lambda/2 effect:
  - Correct for 3lambda effect:
  - Randomize atomic coordinates:  Random seed: [ ] Maximal random displacement in Ang: [ ]
  - Warning: the randomize procedure will applied just once during the next run.
- Select/Listing tab:**
  - Fudge factor: 0.001
- Various tab:**
  - Sigma weight:
  - Unit weight:
- Modulation tab:**
  - Instability factor: 0.01
  - Instability factor from reflection statistics:
  - Use Wilson's modification:
  - Apply Berar's correction:
  - Make only profile matching (le Bail refinement):
  - Frequency of le Bail decomposition: [ ]
  - Calculate only magnetic scattering:

Buttons: Esc, Ok

# Example 12.8: Cr<sub>2</sub>WO<sub>6</sub>

Commensurate magnetic structure –  $k=(0,0,0)$

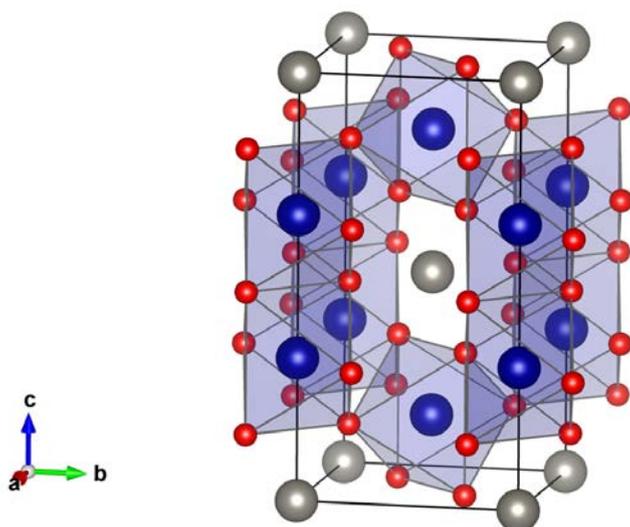
Revised: 6 May 2019

Neutron powder data measured at 4K on HB2A at HFIR,  $\lambda=2.4097\text{\AA}$   
Available at the Bilbao crystallographic server, database magndata, #0.75

References:

Zhu et al., PRL 113, 076406 (2014)  
PHYSICAL REVIEW B **92**, 094419 (2015)

Input files: **cr2wo6.dat** (powder profile data)  
**cr2wo6\_nuclear.cif** (nuclear structure)



Parent space group:  
 $P4_2/mnm$  (N. 136)

Propagation vector:  
 $k=(0,0,0)$

Magnetic site:  
Cr 4e (0,0,z)

## 27. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click cr2wo6

## 28. Import Wizard

Select “Magnetic parent structure: nuclear model from CIF”; NEXT

Right pane: select the input file cr2wo6\_nuclear.cif; OK

## 29. Define magnetic propagation vector and form factors

[On the screen: Define magnetic propagation vector and form factors]

Select “Number of non-zero magnetic propagation vectors” to 0

Select atom type Cr; check “Use as a magnetic atom”; select “Magnetic formfactor <j0>” Cr<sup>3+</sup>;

NEXT; FINISH

*The parent structure is created*

### **30. Import the reflection file**

*[On the screen: Specify type of the file to be imported]*

Select "Various CW format"; NEXT;

Check that the name of the input file is "cr2wo6.dat" and the format is "free format of 2th, l, [sig(l)]";

NEXT

*[On the screen: Complete/correct experimental parameters];*

Fill used wavelength 2.4097; Temperature 4; NEXT; FINISH

*[On the screen: Data repository]*

OK; YES to "Do you want to accept made changes?"

### **31. Refining of profile parameters by the le Bail technique.**

*[On the screen: Information]*

NEXT

*[On the screen: Refinement of the powder profile by the le Bail algorithm]*

"Show powder profile"

*The background is relatively smooth and it can be described without introducing manual background.*

"Quit";

"Edit profile parameters";

*[On the screen: Powder options]*

In page "Cell" activate refinement of a and c parameters;

In the page "Profile" check that the starting value of GW is 50 and activate its refinement;

In the page "Corrections" activate refinement of "shift" parameter and change the number of used Legendre polynomials to 8

OK; YES to save the changes

"Edit refinement commands"; In the page "Basic" change the number of cycles to 20; OK

"Run Refine";

*The refinement should converge to  $R_p \sim 17.5\%$ .*

"Edit profile parameters";

*[On the screen: Powder options]*

In the page "Profile" activate refinement of GU and GV

Change the peak-shape function to pseudo-Voigt and activate refinement LX

OK; YES to save the changes

"Run Refine"

*The refinement should converge to  $R_p \sim 7.2\%$ .*

"Show powder profile"

*Select the region  $2\theta$  from 10 to 20 degs – use the button "X exactly". The peak (0 0 1) has some asymmetry. "Quit";*

"Edit profile parameters";

*[On the screen: Powder options]*

In page "Asymmetry/Diffractometer"

Select "Berar-Baldinozzi correction"; Activate refinement of asym1, asym2, asym3, and asym4; "OK";

"Run Refine";

The refinement should end with  $R_p \sim 6.5\%$ .  
NEXT; YES to leave the form for le Bail refinement

### 32. Refinement of the scale parameter for the nuclear structure

[On the screen: Refinement of the nuclear structure by the Rietveld method]  
"Edit refinement commands"; On the page "Various" select "Fixed commands";  
In the case that the fixed command of form is "fixed all \*" is already in the panel, do nothing. If not:

Fix all parameters for all atoms ("\*" for "Atoms/Parameters" textbox); "Add"; OK; OK  
"Run Refine"

The refinement should converge to  $R_p = 14.2\%$ ,  $R(\text{obs}) = 6.8\%$   
NEXT; YES to leave the for for Rietveld refinement

### 33. Testing different irreps to get the best single irrep model

[On the screen: Information]

NEXT

[On the screen: Representation analysis]

Representation analysis:					
Representation	Dimension	Shubnikov space group	Axes	Origin shift	
mGM1+	1	P42/mnm	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
mGM2+	1	P42'/mnm'	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
mGM3+	1	P42/mn'm'	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
mGM4+	1	P42'/mn'm'	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
mGM5+	2	P2'/m'	(0,1,0 0,0,1 1,0,0)	(0,0,0)	Details
mGM1-	1	P42/m'n'm'	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
mGM2-	1	P42'/m'n'm'	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
mGM3-	1	P42/m'n'm	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
mGM4-	1	P42'/m'n'm'	(1,0,0 0,1,0 0,0,1)	(0,0,0)	Details
mGM5-	2	P2'/m	(0,1,0 0,0,1 1,0,0)	(0,0,0)	Details

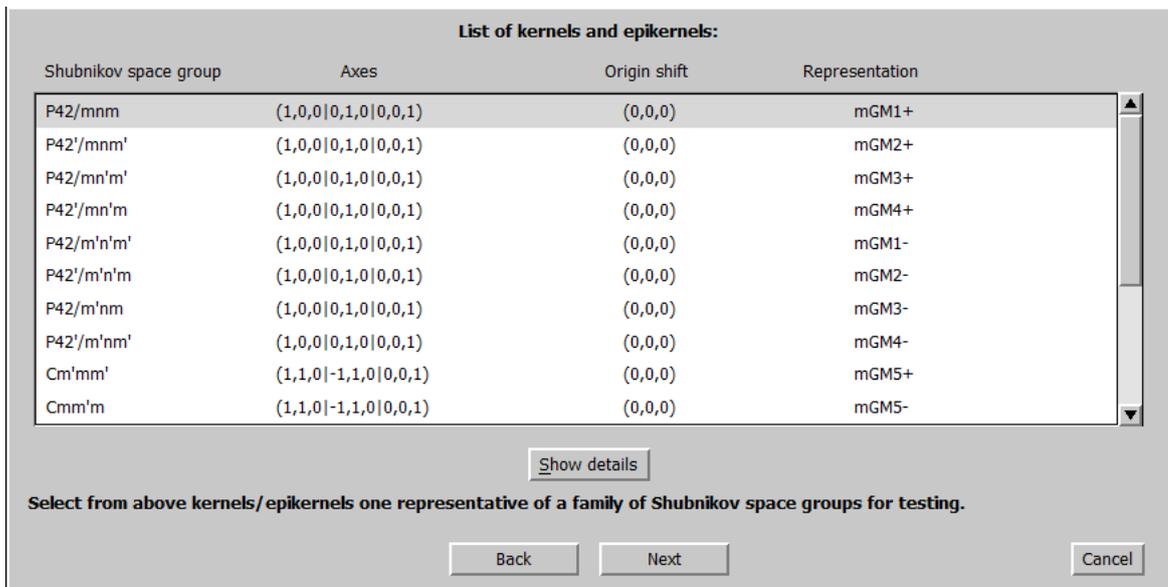
Display representations

Back Next Cancel

This window has an information character. You can see here all irreps leading to magnetic ordering. The "details" buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.

NEXT

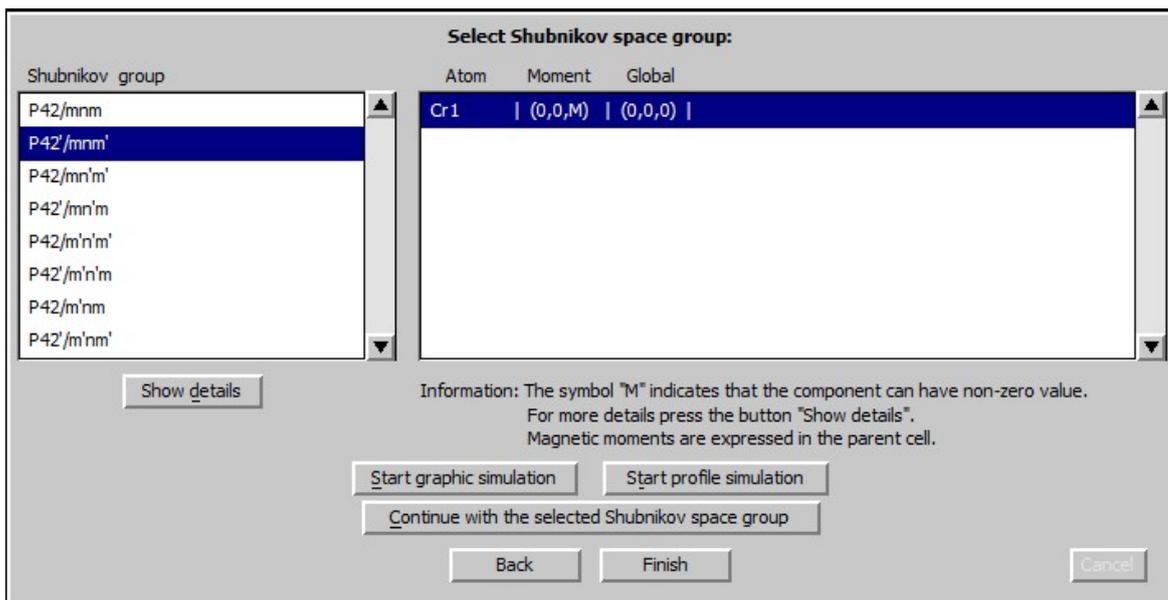
[On screen: List of kernels and epikernels]



Select one of the tetragonal Shubnikov space groups; NEXT;

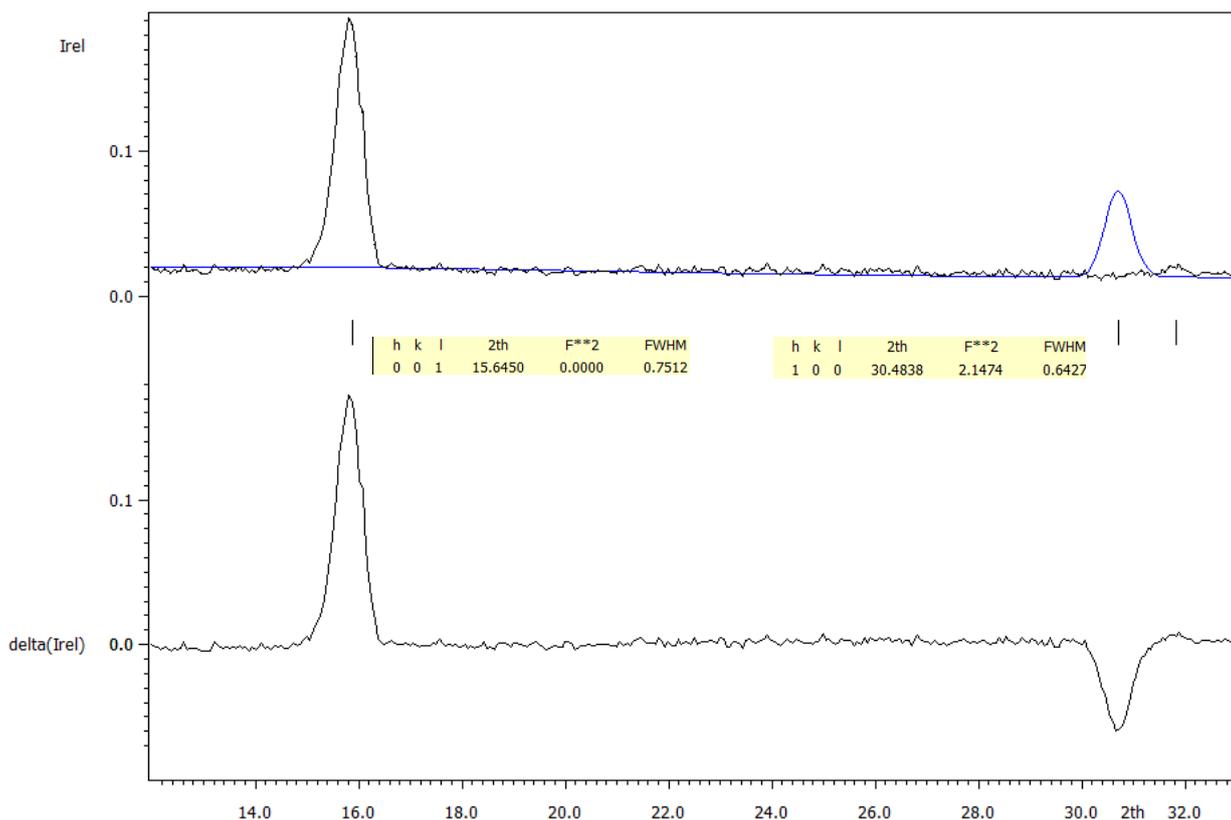
*This will pass all present tetragonal Shubnikov space groups of type P42/mnm to further testing. We assume that Cr magnetic atoms should have non-zero magnetic moment.*

*[On the screen: Select Shubnikov space group]*



Select the second Shubnikov superspace group: P42'/mnm' and press "Start profile simulation";

Press "X exactly" and focus the region 12-33 degrees; Press "Fit Y":



While for the strong magnetic reflection (0,0,1) the model gives zero, for the reflection (0,0,1) which seems to be very weak the model gives non-zero intensity. This can be reproduced for all tetragonal Shubnikov groups allowing non-zero magnetic moments for Cr atom –  $P42/mn'm'$ ,  $P42/m'n'm'$  and  $P42'/m'nm'$ . As a next step we should try orthorhombic space groups.

Quit;

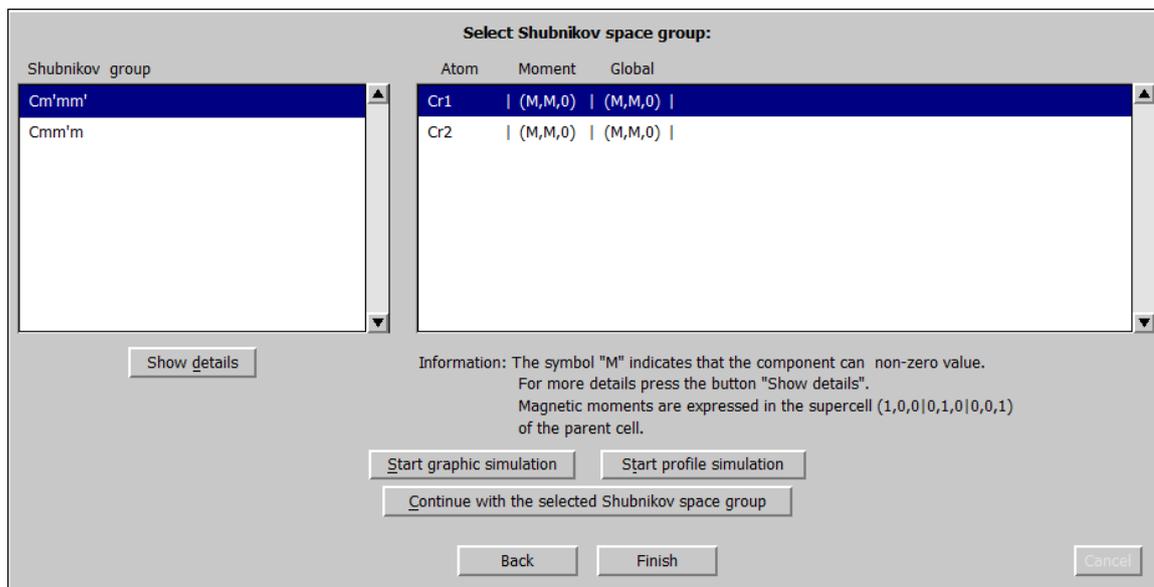
### 34. Testing orthorhombic subgroups

[On the screen: Basic window of the parent structure, with the representation analysis]

“Back → Select one of the orthorhombic C centered Shubnikov space groups;

The symbol of Shubnikov space group is related to the lattice defined by axes as expressed in the second column. However, the final transformation to the standard setting is offered only during the last step of the representation analysis to keep relationships of magnetic moments to the original call of the parent structure.

→ Next;



The first listed Shubnikov space group allows ferromagnetic ordering as seen from non-zero the global magnetic moment. This global magnetic moment can be suppressed only if additional condition to relate the magnetic moments of two independent Cr positions is applied. This makes this model less probable as no tendency to make ferromagnetic ordering was detected.

#### Switch to the second Shubnikov space group



The second Shubnikov space group has the global magnetic moment zero.

Select the first Shubnikov superspace group: Cm'mm' and press "Start profile simulation"; Press "X exactly" and focus the region 12-33 degrees; Press "Fit Y";

Both reflections (1,0,0) and (0,0,1) have generally non-zero intensity and this means that we cannot reject this space groups only from violation of systematically absent reflection as for the tetragonal case. However, in making such conclusion we have to take into account that the simulation procedure uses randomly generated magnetic moments and that the result can be affected by an actual random choice. This is why we recommend repeating the simulation when some doubt exists. This is also true for Cmm'm.

Select the Shubnikov space group Cm'mm'

Press 'Continue with the selected Shubnikov space group'

[On the screen: Select structure name]

Use the default name i.e. cr2wo6\_01 or any other; OK

YES to the question "Do you want to apply this transformation?"

This will transform the structure to the standard setting. Jana2006 can generally work at

non-standard setting.

[On the screen: Basic window of Jana2006]

Run "Edit profile" and activate refinement for a, b and c parameters;

Right-click the icon of Refine and select the page "Various"

Use the button "Restrictions" and ensure that all atoms (i.e. \*) are restricted to have identical ADP parameters.

The restriction "restric \* 12" has been set automatically when the program created the testing structure. To see the meaning of the restriction focus it by mouse and press "Load". "Load" opens the restriction for editing. Make sure that "Coordinates" box are cleared and press "Rewrite" to close the editing mode.

OK

Select "Fixed commands" and (similarly like in the previous step) ensure that all atomic positions are fixed in their current values ("fixed xyz \*").

OK

Select the page "Equation";

Introduce the equation  $b=a$  valid for diagonals in tetragonal lattice;

Select the page "Basic" and check that the "Number of cycles" is set to 100 and the

"Damping factor" to 0.1, "Use Marquart technique" check the Fudge factor 0.001; OK;

Yes+start;

Refinement converges with  $R_p \sim 13.1\%$ ,  $R(\text{obs}) \sim 11.3\%$ .

Return to the window of the parent structure;

Repeat the same process for the second orthorhombic C centered Shubnikov space group  $Cmm'm$  and use the default name i.e. cr2wo6\_02 or any other;

Refinement converges with  $R_p \sim 8.2\%$ ,  $R(\text{obs}) \sim 5.7\%$ .

Repeat the process also for  $Pnn'm'$  and  $Pnn'm$ ;

Use the same equation  $b=a$  as for the centered cell;

$Pnn'm'$  (allows ferromagnetic ordering) :  $R_p \sim 13.1\%$ ,  $R(\text{obs}) \sim 10.5\%, 7.7\%, 54.5\%$  for all, nuclear and magnetic reflections, respectively.

$Pnn'm$  (doesn't allow ferromagnetic ordering) :  $R_p \sim 8.2\%$ ,  $R(\text{obs}) \sim 5.2\%, 5.4\%, 3.1\%$  for all, nuclear and magnetic reflections, respectively.

### 35. Comparing of two best results $Pnn'm$ and $Cmm'm$

[On the screen: Basic Jana window]

Up to now atomic coordinates were kept fixed.

Select the structure cr2wo6\_02 (or any other) describing the  $Cmm'm$  model;

Right-click the icon of Refine and select the page "Various"

Select "Fixed commands" and disable the command "fixed xyz \*";

OK;OK; Yes+start;

Refinement converges with  $R_p \sim 6.7\%$ ,  $R(\text{obs}) \sim 2.3\%$  for 10 profile and 12 structural parameters

Repeat the process with  $Pnn'm$

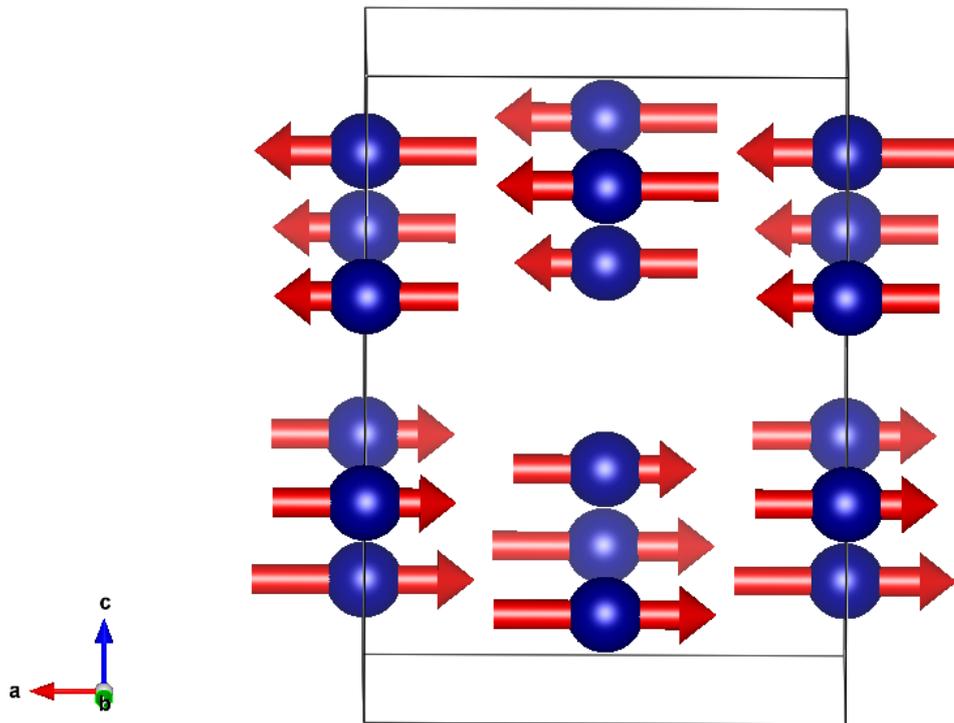
Refinement converges with  $R_p \sim 6.7\%$ ,  $R(\text{obs}) \sim 2.2\%, 2.1\%, 2.5\%$  for all, nuclear and magnetic reflections, respectively – number of 10 profile and 10 structural parameters

Select the structure cr2wo6\_02 (or any other) describing the  $Cmm'm$  model;

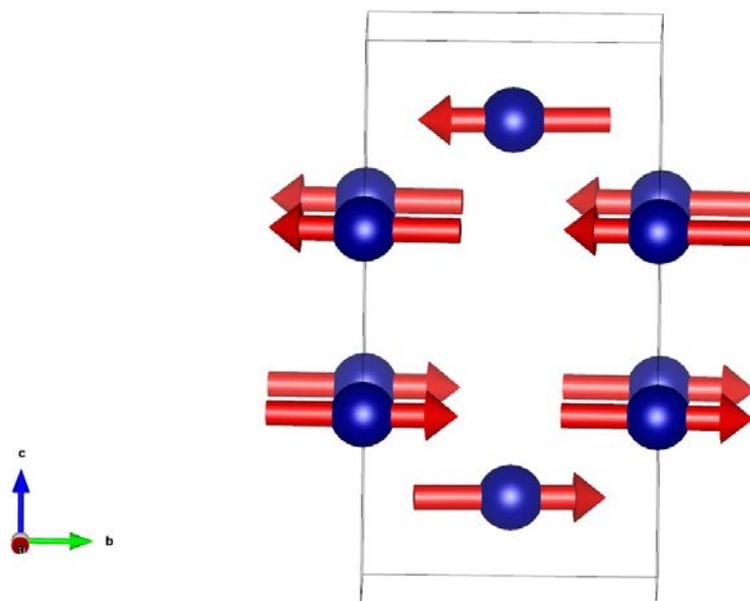
Double click on the icon "Plot structure"

Press the button "Atom filter" and select only Cr atoms;

Select "Use Vesta to draw the magnetic structure"



Select the structure `cr2wo6_04` (or any other) describing the  $Pnn'm$  model;  
 Double click on the icon "Plot structure"  
 Press the button "Atom filter" and select only Cr atoms;  
 Select "Use Vesta to draw the magnetic structure":



The model in Pnn'm gives slightly better R values but the difference is so small that it is difficult to make from it any final conclusion about the direction of the magnetic moment of Cr atoms.

### 36. Orthorhombic strain for Pnn'm and Cmm'm

While the P centered cell are identical with that used for the parent tetragonal cell the C centered cell is related to the original cell by equation:

$$\mathbf{a}_{C\text{-ortho}} = \mathbf{a}_{\text{tetra}} + \mathbf{b}_{\text{tetra}} \quad \mathbf{b}_{C\text{-ortho}} = -\mathbf{a}_{\text{tetra}} + \mathbf{b}_{\text{tetra}} \quad \mathbf{c}_{C\text{-ortho}} = \mathbf{c}_{\text{tetra}}$$

The orthogonal ordering of magnetic moments can have some influence to the cell parameters a and b which need not be same anymore. In order to test orthorhombic strain without mixing it with the refined magnetic structure we can use le Bail profile fitting.

[On the screen: Basic Jana window]

Select the structure cr2wo6\_02 (or any other) describing the Cmm'm model;

"File → Structure → Save as";

Select name e.g. cr2wo6\_02\_cell; OK; Yes to the question "Do you want to continue with the new structure?";

Right-click the icon of Refine and select the page "Basic";

Select "Make only profile matching (le Bail refinement)";

Go to the page "Various"; Press the button "Equation" and disable the equation b=a;

OK; OK; Yes;

Start "Edit profile"; Go to the page cell and activate there refinement of the b parameter and modify slightly its value to avoid full overlaps;

OK; Yes to rewrite changed files;

Run refinement;

Refinement converges with Rp~6.5%;

Yes to open listing;

Press "Go to" and select "Changes overview";

	a	b	c	alpha	beta	gamma	Volume	Density	
0	6.484911	6.485058*	8.857133	90.00000	90.00000	90.00000	372.4869	6.844531	-0.07
1	6.484925	6.485043*	8.857132	90.00000	90.00000	90.00000	372.4868	6.844533	-0.05
2	6.484937	6.485030*	8.857132	90.00000	90.00000	90.00000	372.4868	6.844533	-0.04
3	6.484947	6.485020	8.857132	90.00000	90.00000	90.00000	372.4868	6.844534	
su	0.002356	0.002346	0.000352	0.00000	0.00000	0.00000	0.0413	0.000758	

The cell parameters are: a=6.4849(23) and b=6.4850(23) which means that there is no strain within the accuracy following from the refinement.

Repeat the procedure with Pnn'm model;

Refinement converges with Rp~6.4%;

	a	b	c	alpha	beta	gamma	Volume	Density	
0	4.587633*	4.583685	8.857291	90.00000	90.00000	90.00000	186.2535	6.844164	0.03
1	4.587634	4.583685	8.857292*	90.00000	90.00000	90.00000	186.2535	6.844161	0.05
2	4.587635	4.583686	8.857294	90.00000	90.00000	90.00000	186.2537	6.844157	
su	0.000359	0.000332	0.000346	0.00000	0.00000	0.00000	0.0202	0.000744	

The cell parameters are:  $a=4.5876(3)$  and  $b=4.5837(3)$  which means that there is significant difference connected with orthorhombic strain .

### 37. Final model Pnn'm

The refined magnetic moment of the Cr atoms is:  $(0.19(14), 2.13(2), 0)$  Bohr magnetons, which means that the x component is negligible. In the final refinement we shall keep the x component 0.

[On the screen: Basic Jana window]

Select the structure cr2wo6\_04 describing the Pnn'm model;

"File → Structure → Save as";

Select name e.g. cr2wo6\_04\_final; OK; Yes to the question "Do you want to continue with the new structure?";

Right-click the icon of Refine and select the page "Various"

Press the button "Fixed commands" and select "Set individual";

Into the editing window "Atoms/parameters" write  $mx0[Cr1]$ ;

Add; OK; OK; Yes+start;

Refinement converges with  $R_p \sim 6.7\%$ ,  $R(\text{obs}) \sim 2.0\%, 2.0\%, 2.2\%$  for all, nuclear and magnetic reflections, respectively – number of 11 profile and 10 structural parameters.

# Example 13.1: TTB

Solution of a tetragonal-tungsten-bronze type structure from EDT (electron diffraction tomography) data. Complete procedure from data reduction to structure refinement.

Revised: 04 March 2015

**Chemical formula:**  $K_3Nb_{(5+x)}O_{15}$

Electron diffraction data was measured on a transmission electron microscope Philips CM120 with a precession device DigiStar. Accelerating voltage 120 kV.

Input data: directory dp with the set of experimental data

ttb.pts: input file for PETS – the data reduction of the beam stop

beamstop.xyz: file with the polygon defining the shape of the beam stop

ttb\_start.cif\_pets: result of the data processing. This file is provided so that this example can be solved without the data processing part, and to warrant reproducibility of the second part.

File ttb.cif\_pets is the output of the data reduction.

## 1. Preparing input file for PETS

*Make sure you correctly installed PETS and ImageJ. Check Chapter “Installation notes” (page 7) for details. File ttb.pts is the input to PETS. The file was prepared by the software used for the collection of the diffraction data, and most entries have been filled in. You have to enter two parameters: the information about the beam stop and the size of reflections.*

Open file ttb.pts in any plain-text editor (notepad, wordpad, notepad++, vim,...)

Open file dp/001.tif in ImageJ

In ImageJ go to “Image → Adjust → Brightness and Contrast”

Click the button “Auto” to adjust the contrast.

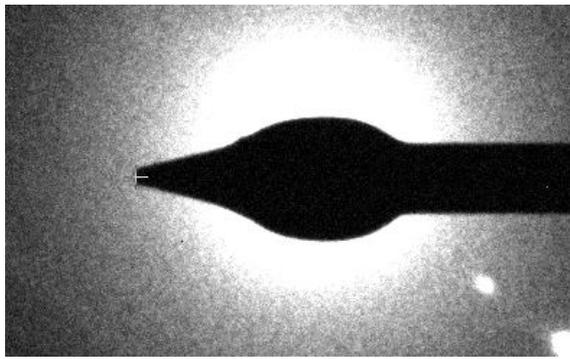
Go to “Image → Properties” and change the values of Pixel width and Pixel height from 0.005 to 1.

Measure the diameter of the reflections on the image.

*There are several ways to measure the diameter of the reflections, but the simplest and sufficient way is to place the cursor to the left of the reflection, remember or write down the x-coordinate, then place the cursor to the right of the reflection, again read the x-coordinate and subtract the two coordinates. The diameter should be large enough to encompass most of the reflections, but not too large, to prevent overlaps. Do not take into account the broad, weak TDS scattering around the strongest reflections! That would give you too large diameter. In this case, value 25 is a good choice.*

In ttb.pts, change the line “reflectionsizesize ??” to “reflectionsizesize 25”

In ImageJ, determine the coordinates of the tip of the beamstop (white cross on the following image):



You should get coordinates very close to 913 1014.

In `ttb.pts` change the line “`beamstop ??(yes/no)`” to “`beamstop yes beamstop.xyz 913 1014`”

File `beamstop.xyz` contains the coordinates of the polygon describing the beamstop relative to a reference point. 913 and 1014 are the x- and y-coordinates of the reference point, which is in this case the tip of the beamstop. The reference point can change from one experiment to another, and must be therefore determined by the user.

Save and close `ttb.pts`

## 2. Run PETS and prepare files for indexation

Make sure ImageJ is not running. If it is, close ImageJ.

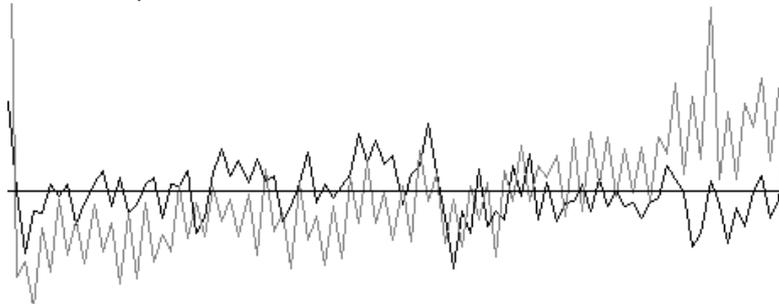
Run PETS with the file `ttb.pts`

There are several ways of running PETS. See installation notes for detailed description. A window with initial menu of PETS opens, and ImageJ starts displaying a black image with a white circle.

In the window of PETS, type `p[Enter]`

The peak hunting procedure starts. ImageJ sequentially displays diffraction images with circles at points found by PETS as significant peaks. Note that PETS follows the position of the primary beam, and corrects for small shifts. Note also the significant diffuse streaks. Although they seem very intense, it is just due to the enhanced contrast of the images. Compared to the Bragg intensities, the diffuse streaks are weak and do not disturb the structure solution.

At the end, the evolution of the x- and y-coordinates of the estimated primary-beam position is displayed (b&w inverted):



[On screen: main menu of PETS]

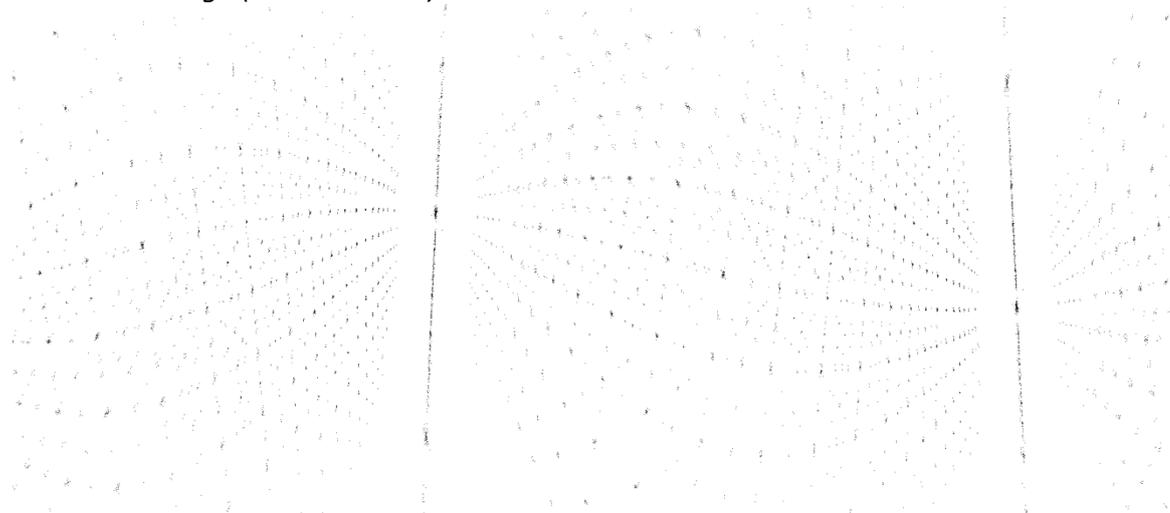
type `r[Enter]`

As the first step after peak hunting, PETS needs to refine the azimuthal angle between the horizontal axis and the projection of the tilt axis. This angle depends on experimental parameters, and needs to be refined for each data set. ImageJ displays a cylindrical projection of the difference space of the extracted peak positions. For correct azimuthal angle, the image contains sharp peaks aligned on sinusoidal curves. This step provides a first estimate of the data quality. At the end of the refinement, you should get message:

Final values of the parameters:

omega : 21.591

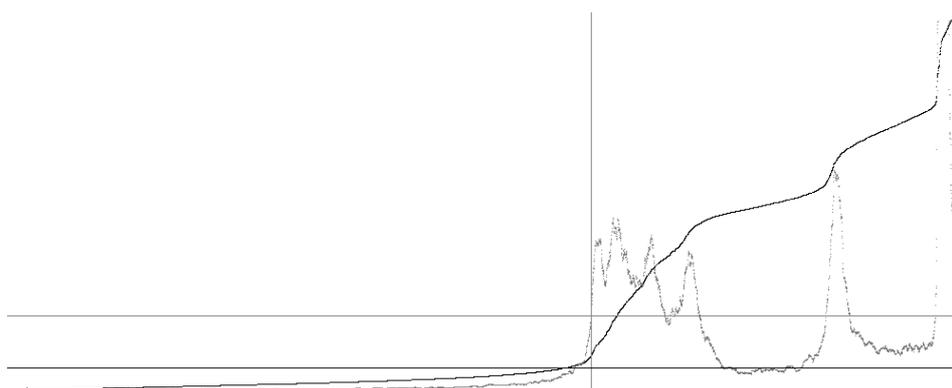
and see this image (b&w inverted):



[on screen: main menu of PETS]

type a[Enter]

PETS starts the analysis of the located peak positions. In the first step, distance distribution between peaks in the image plane is analyzed. A sorted plot of inter-peak distances is displayed (white curve on screen, black on the image below) with its derivative (grey curve):



For good quality data set, the white curve contains distinct steps, and, consequently, the grey curve has distinct peaks.

Press Enter

In the next step an autoconvolution of the diffraction pattern (difference space) is analyzed, and the groups of peaks in the autoconvolution (clusters) are replaced by the cluster centers. Again, a distance distribution is displayed, and clear-cut steps on the curve indicate a well-defined lattice.

Press Enter

Now the first step is finished and PETS prepared files needed for unit cell indexing. Keep the window of PETS open, you will need it later!

### 3. Indexing with Jana2006

Start Jana2006

By default, Jana2006 starts with the last structure open. It may be cumbersome to change the directory every time. You may create a dummy (empty) file `ttb.m40` in the example directory,

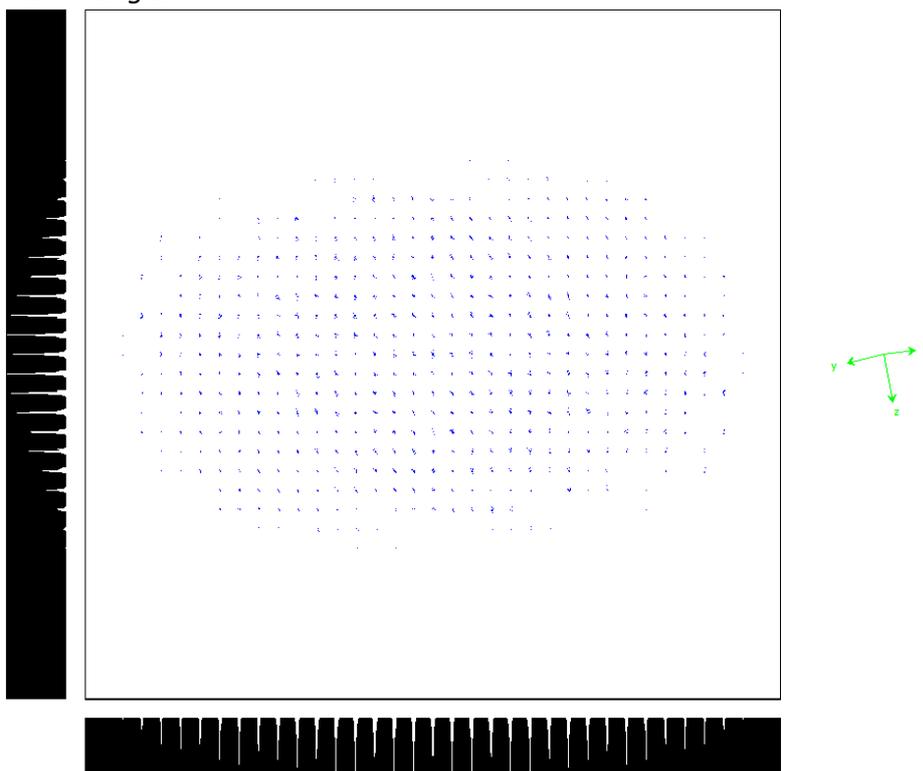
and use the command "Open with" from the file-manager context menu to launch Jana2006 directly in this directory.

"Tools → Graphics → Indexing"

Locate and open file `ttb.clust` by double clicking it

A 3D view of the reciprocal lattice opens. You can rotate the cloud by mouse. Use buttons and to switch between free rotation and rotation around z-axis. Rotate with the lattice and try to determine the crystal system and the special axes of the lattice.

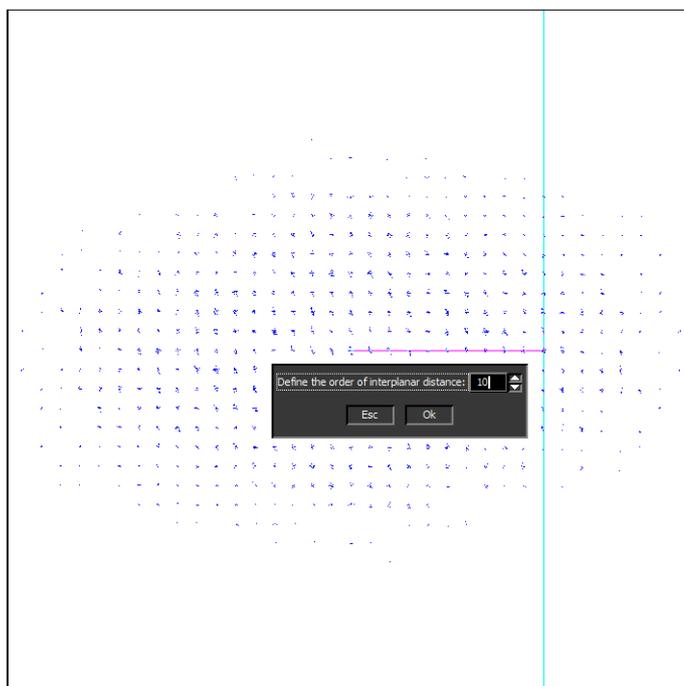
You should come to the conclusion that the lattice is tetragonal (warning – the lattice has a few projections that look tetragonal, but are not exactly tetragonal). The following image shows the view along  $c^*$ :



**IMPORTANT:** before you continue, make sure you have the same orientation of the lattice on your computer as displayed on the picture above (check the direction of the axes on the right). If not, you may obtain slightly different results in the rest of the tutorial. While not necessarily wrong, it makes following this tutorial more difficult.

Click the button in the lower-left corner

Click, hold the mouse button, and drag the marker to obtain the result on this image:



Note that the vertical red line is on the tenth vertical row of peaks. By this action you defined the direction and length of the (direct-space) basis vector **a**. Note: if you make a mistake and need to redo this step, make sure that the radio button **a** is selected under the main window, otherwise you will modify another cell parameter.

Repeat the action, this time drag the marker up vertically to define the vector **b**. Both vectors should have lengths close to 12.8 Å, and angle gamma is close to 90°.

Click "View direction", keep default selection "a", Click OK

The reciprocal space is now viewed along *a*, and *b* points to the right.

In analogy to the procedure above, select the direction and length of the vector *c* (*c* points up in this view).

When you are finished, at the bottom of the window you should see cell parameters close (within a fraction of angstrom and degree) to these values:



"Refine cell → Refine UB+cell"

The orienting matrix is refined. Note that 90.3% of all peaks were indexed.

OK; Quit

A file *ttb.smr* was now produced by Jana2006. This file contains the orientation matrix and the unit cell parameters.

Close Jana2006

#### 4. Integrate the intensities with PETS

Return to the window of PETS.

Type `u[Enter]`

PETS reads the orienting matrix from the *smr* file.

Type `i[Enter]`

The integration procedure starts. ImageJ displays images with circles drawn at positions predicted from the orienting matrix. A small circle inside large circle means that a peak with  $I > 3\sigma(I)$  was found. The small circle is located on the maximum of the intensity. A diamond means that a reflection is expected on upcoming frame(s), square indicates reflection present on previous frame(s).

When the integration finishes, files *ttb.cif\_pets* and *ttb.hkl* are created. Both can be used to import the data into Jana and to solve the structure.

## 5. Create reciprocal-space sections

In PETS, Type *h*[Enter]

Type *y*[Enter]

You just asked PETS to scan all images and reconstruct sections through reciprocal space at planes *hk0*, *hk1*, *hk2*, *h0l*, *h1l*, *h2l*, *0kl*, *1kl*, *2kl*. We will use these sections as an aid to determine the space group.

When the reconstruction finishes, type *q*[Enter] to close PETS. You may also close ImageJ.

## 6. Create new structure

**Important!** The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the file *ttb.cif\_pets* that you just created, but use the file *ttb\_start.cif\_pets* provided with the example files (Rename the file to *ttb.cif\_pets*). Using your own *cif\_pets* file is also possible, but your results may slightly differ from the results described in this tutorial.

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate the directory with input files

Right pane: double-click *ttb*

Right pane detects possible Jana files and shows one jobname for each group of files

## 7. Import Wizard

Select “Known diffractometer formats”; NEXT

Select “Pets electron diffractometer”

The file name automatically changes to *ttb.cif\_pets*, which is a file produced by PETS containing all important information, including the list of intensities.

NEXT

Leave all settings unchanged (note the wavelength of 120kV electrons!); NEXT

Leave all settings unchanged; NEXT

The program reads 3777 reflections from the file

OK

For absorption correction select “None or done before importing”; NEXT

FINISH; OK; YES to accept the data set

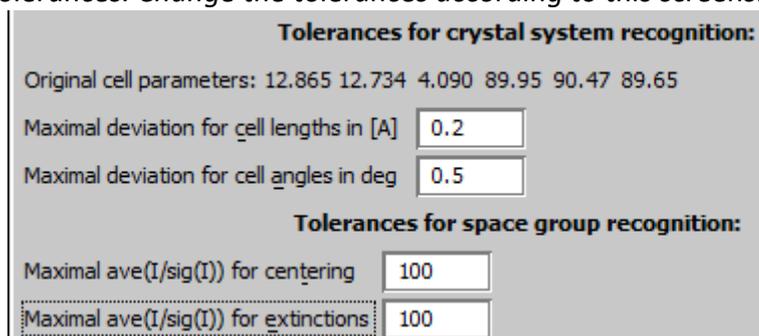
You just read in the cell parameters and the intensity list. If you do not have the data in the *cif\_pets* format, you can read them in from a general *hkl* file using the option “reflection file corrected for LP and absorption” at the beginning of the import wizard. You then have to input the radiation type, wavelength and cell parameters by hand.

## 8. Symmetry Wizard

NEXT to close the information window and start the wizard

Symmetry Wizard can be started separately by “File → Reflection file → Make space group

test. The default settings are prepared for x-ray diffraction. For electron diffraction we have to increase the tolerances. Change the tolerances according to this screenshot:



Leave other settings default; NEXT; OK

[On the screen: Select Laue symmetry]

Select tetragonal Laue class 4/mmm; NEXT

The internal R-values would be rather high for x-rays, but are normal for electron diffraction data, especially if measured in selected area mode.

[On the screen: Select cell centering]

Select primitive unit cell; NEXT

[On the screen: Select space group]

The window shows possible space groups.

The list of the strongest reflections contradicting the selected space group can be displayed by "Details" button.

It is difficult to select the correct space group. In particular, presence or absence of the b-glide is hard to assess, knowing that kinematically absent reflections may have significant intensities due to dynamical diffraction effect. Open the file h0l.bmp and h1l.bmp, and compare the intensities of reflections with  $h=2n$  (which should be absent in the h0l plane, but present in h1l). You will see that despite a number of violations, the b-glide absences are nevertheless clearly present in the h0l plane in comparison with the h1l plane. Space group with b-glide is thus a reasonable guess. Note that a wrong choice of the space group is not detrimental for the structure solution, because we will use Superflip, which will make additional check for the most probable space group.

Select P4/mbm; NEXT

Accept the space group in the standard setting; FINISH

Symmetry is saved in file ttb.m50.

## 9. Creating refinement reflection file

In this step program creates file ttb.m90 containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.

Proceed with the wizard, leaving all settings default

## 10. Structure Solution Wizard

OK to close the information window and start the wizard

[On the screen: window of Structure solution] Structure solution wizard can be executed separately through "Run → Solution". Jana2006 does not contain solution procedures, it calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2006.

In "Formula" textbox type just the list of chemical elements: K Nb O

*Superflip does not need information about chemical elements but they will be required for peak assignment based on electron density map calculated by Superflip. If Jana2006 is used for peak assignment, a list of expected chemical elements is sufficient. If you know the expected formula, you may enter it and use EDMA for peak picking (at the bottom of the window). If the formula is correct, EDMA often gives cleaner and more complete interpretations of the solution.*

Click the checkbox next to "Use a specific random seed".

Leave other settings default; Press "Run solution"

*The specific random seed is used just to guarantee reproducibility of the results. For standard work random seed need not be defined.*

*[On the screen: window of Superflip appears with iteration running. After ten runs, open the listing of Superflip log file in "Open the listing"]*

*Superflip performed ten solution attempts, and picked the best one. Its characteristics are displayed near the bottom of the listing:*

Properties of the saved density:

```
Run Rvalue Peaks Symm. Der.SG
8 24.46 2.71 3.24 P4/mbm
```

*The space group proposed by Superflip is the same as our initial guess. The space-group selection is confirmed. Small symmetry agreement factor (column Symm.) indicated good quality of the solution. In cases of doubts or difficult problems, it is worth checking the statistics, especially the symmetry analysis, for each of the ten runs, and seeking for the most probable one.*

Press "Close" to leave the listing

Press "Accept last solution"

*The program creates file ttb.m40 with atoms of the structure model*

## 11. Verification and completion of the structure solution

Go to "Contour → New plot → OK → Run 3D maps"

*VESTA opens with a density shown as isosurfaces, and an atomic model overlaid. Rotate the view to inspect the structure. Do you think it is complete?*

*You should come to the conclusion that the model is correct, all atoms were assigned correct chemical type, only one oxygen (between two atoms Nb2 is missing.*

Decrease the isosurface level to see weaker features in the density ("Properties → Isosurfaces", set isosurface level to 1)

*You can see that there is a peak between the two Nb atoms, it just was not interpreted by Jana2006 as an atom. Take-home message: it is always worth checking the density (i.e. the raw result from Superflip), because it may contain features not considered in the interpreted structure model.*

Quit VESTA (do not save the file), quit Contour.

Start "Parameters → Atoms → New → Peaks from last Fourier calculation"

*A list of maxima found in the density is displayed. In the right pane, the distances of the maximum to the nearest atoms are displayed. First eight maxima correspond to atoms interpreted by Jana2006. Max9 is a ghost peak, too close to Nb1. Max10 is at a correct distance from two Nb2 atoms – this is the oxygen atom missing in the model.*

Click "Include selected peak", type O\* in the field for name; OK; Finish; Yes to include the new atom in the model

You may now check the structure in Diamond to convince yourself that the structure is complete and chemically reasonable.

## 12. Initial Refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine.

[On the screen: refinement options]

Change the number of cycles to 100; OK

Choose “Yes+start”

Refinement converges with R value about 20.0%. At this moment you may check the refinement listing with a lot of information about the refinement procedure and results.

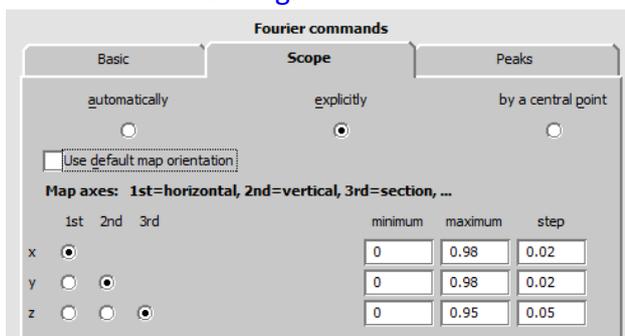
## 13. Adding missing, partially occupied atom

[On the screen: basic window of Jana]

Right click the icon Fourier

On the first card, select F(obs)-F(calc) – difference Fourier

Modify the setting on the second card to agree with this screenshot:



OK; Yes+Start; No; No

Jana just calculated a difference Fourier map.

View the map in VESTA: “Contour → New plot → OK Run → 3D maps”

You will see that the difference map is dominated by one positive peak in the middle of an empty cage of oxygens. This position tends to be partially occupied in some TTB structures. In this case, the partial atom is Nb.

Add the missing atom. The procedure is the same as when you added the missing oxygen atom after the solution. This time, the first maximum in the list is the correct maximum.

When defining the atom, do not forget to define the name as Nb\* and type as Nb. Define “Occupancy reduction” 0.2

OK; Finish; Yes

Now we will allow the occupancy of the niobium atom to be refined:

Double click “Edit atoms”; double click Nb3; on card “Edit” check the check box next to the parameter “ai”; OK; OK; Yes

Double click Refine

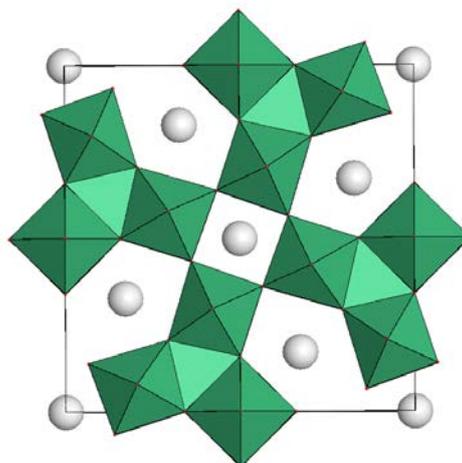
The model refines to R-value about 19.4%. The improvement is very small, because the occupancy of the Nb3 atom is very small, too, actually less than 10%.

This data set is exceptionally good. Normally, partial occupancies of atoms cannot be refined reliably from electron diffraction data. Even here the refined occupancy must be taken only as a rough indicator.

At this moment the structure is essentially finished. You may try to refine anisotropic displacement parameters of the heavy atoms. The R-value decreases to ~18.3%. Again, with

*this data set such refinement is possible, and the resulting parameters are reasonable. In many other cases, anisotropic displacement parameters refine to unrealistic or even non-positive definite values.*

### **The resulting structure**



# Example 13.2: Kaňkite

Solution of kaňkite – a hydrated Fe-bearing arsenate.

Revised: 3 December 2013

**Expected chemical formula:**  $\text{Fe}^{+++}\text{AsO}_4 \cdot 3.5\text{H}_2\text{O}$

Electron diffraction data measured on a transmission electron microscope Philips CM120 with precession device DigiStar. Accelerating voltage 120 kV.

Input data: directory dp with the set of experimental data,

kankite.pts: input file for PETS – the data reduction program

beamstop.xyz: file with the polygon defining the shape of the beam stop

kankite\_start.cif\_pets: result of the data processing. This file is provided so that this example can be solved without the data processing part, and to warrant reproducibility of the second part. File kankite.cif\_pets is the output of the data reduction.

## 1. Data reduction using PETS

*The data processing part follows exactly the procedure described in example 13.1. Please follow that tutorial. Here only key results are provided for your control, and comments are provided for stages that require special attention.*

*Parameters filled in the prepared file kankite.pts:*

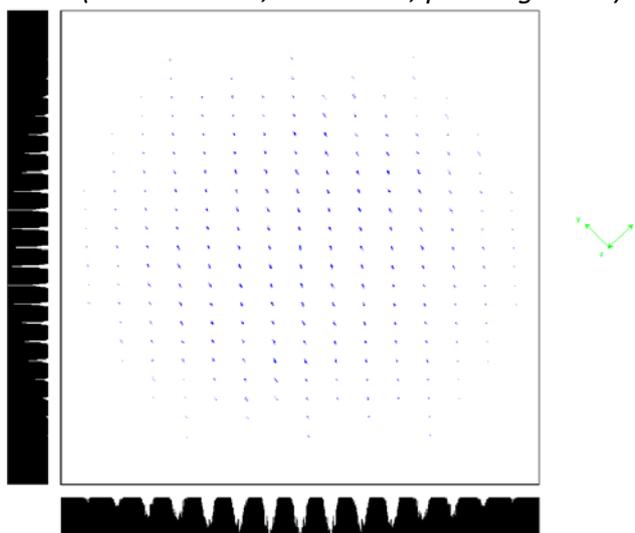
reflectionsize 25

beamstop yes beamstop.xyz 927 1025

*Refined azimuthal angle omega of the tilt axis:*

omega : 11.752

*Unit cell is monoclinic, C-centered. The following screenshot is the view of the reciprocal lattice along the monoclinic axis **b** ( $a^*$  horizontal,  $c^*$  vertical, pointing down):*



*The direction and length of the  $b$ -axis is difficult to determine. The lattice is obscured by quite a lot of noise. This noise comes from the diffuse nature of the reflections along  $b^*$  and from the mosaicity of the crystal. If such noise is present, it is amplified by the data processing preceding the creation of the file .clust. In such cases it is useful to check the correctness of*

the cell determination in the file .xyz. This file contains only the peak positions in reciprocal space, not their autoconvolution. It is thus cleaner, but much less complete.

Click “New plot”

Locate and open the file kankite.xyz

You will see that the plot is less complete, but the noise is less abundant.

Final refined cell parameters (refined against the peaks in kankite.clust):

a	5.684	b	21.300	c	9.136	alpha	89.78	beta	92.75	gamma	89.93
---	-------	---	--------	---	-------	-------	-------	------	-------	-------	-------

Quit the indexing plugin to create file kankite.smr with the orienting matrix, and continue data processing in PETS by typing u[Enter] to read in the orienting matrix, and i[Enter] to integrate the intensities.

You will note significant overlap of integration boxes (white circles) in the images displayed by ImageJ. This is, however, not a real problem, because the lattice is C-centered, and every second reflection is systematically absent.

PETS produced file kankite.cif\_pets, which will be imported in Jana2006 in the next step.

Type h[Enter] and y[Enter] to produce standard sections through reciprocal space.

With this step the data processing in PETS is finished.

Type q[Enter] to close PETS. You may also close ImageJ.

## 2. Create new structure

**Important!** The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the file kankite.cif\_pets that you just created, but use the file kankite\_start.cif\_pets provided with the example files (Rename the file to kankite.cif\_pets). Using your own cif\_pets file is possible, but your results may slightly differ from the results described in this tutorial.

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate the directory with input files

Right pane: double-click kankite

Right pane detects possible Jana files and shows one jobname for each group of files

## 3. Import Wizard

Select “Known diffractometer formats”; NEXT

Select “Pets electron diffractometer”

The file name automatically changes to kankite.cif\_pets, which is a file produced by PETS containing all important information, including the list of intensities.

NEXT

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

The program reads 5921 reflections from the file

OK

For absorption correction select “None or done before importing”; NEXT FINISH; OK; YES to accept the data set

You just read in the experimental parameters, cell parameters and the intensity list.

## 4. Symmetry Wizard

NEXT to close the information window and start the wizard

Symmetry Wizard can be started separately by "File → Reflection file → Make space group test. The default settings are prepared from x-ray diffraction. For electron diffraction the tolerances should be increased. Change the tolerances according to this screenshot:

The screenshot shows a dialog box titled "Tolerances for crystal system recognition:" and "Tolerances for space group recognition:". The "Original cell parameters" are listed as 5.684 21.300 9.136 89.78 92.75 89.93. Under "Tolerances for crystal system recognition:", the "Maximal deviation for cell lengths in [Å]" is set to 0.2 and the "Maximal deviation for cell angles in deg" is set to 0.5. Under "Tolerances for space group recognition:", the "Maximal ave(I/sig(I)) for centering" is set to 100 and the "Maximal ave(I/sig(I)) for extinctions" is set to 100.

Leave other settings default; NEXT

Jana detected a seven times larger unit cell with orthorhombic metric. This is not likely to be the correct unit cell.

NEXT

[On the screen: Select Laue symmetry]

Select monoclinic Laue symmetry; NEXT

The internal R-value of 13.21 % is very good for electron diffraction data.

[On the screen: Select cell centering]

From the table the fact that the cell is C-centered is not obvious at all. This is due to the overlap of the reflection positions during the integration. But we know the centering from the data reduction and indexing step. You may convince yourself about the correctness of the centering by inspecting the reciprocal space sections  $hk0$ ,  $hk1$  and  $hk2$  generated by PETS.

Select C-centering; NEXT

[On the screen: Select space group] The window shows possible space groups. It is not obvious, if the c-glide is present or not. Out of 60 reflections forbidden by the c-glide 33 have observed intensity. Again, you should use the reciprocal-space sections to check for the c-glide. However, do not use the  $h0l$  section! Due to the short  $b^*$  axis and large mosaic spread, this section contain "ghosts" from neighboring sections, and the systematic absences are obscured. Inspection of the  $0kl$  and  $2kl$  section shows clearly that the reflections of the type  $h0l: l=2n$  are absent, and c-glide is thus most likely present.

At this point we cannot decide, which of the choices  $Cc$  or  $C2/c$  is correct. Centrosymmetric space groups are, in general, more frequent, and we will use it as a first guess.

Select  $C2/c$ ; NEXT

Note that a wrong choice of the space group is not detrimental for the structure solution, because we will use Superflip, which will make additional check for the most probable space group.

Accept the space group in the standard setting; FINISH

Symmetry is saved in file kankite.m50.

## 5. Creating refinement reflection file

In this step program creates file `ttb.m90` containing the data set merged by symmetry and with discarded forbidden reflections. `M90` will be used for refinement.

Proceed with the wizard, leaving all settings default

The internal R-value decreased from 13.21% To 10.02% due to the exclusion of the systematically absent reflections.

## 6. Structure Solution Wizard

OK to close the information window and start the wizard

[On the screen: window of Structure solution]

Structure solution wizard can be executed separately through "Run → Solution". Jana2006 does not contain solution procedures, it calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2006.

In "Formula" textbox type the expected formula: Fe<sub>2</sub> As<sub>2</sub> O<sub>15</sub>

In "Formula units" textbox type 4

This value gives a reasonable value of density: 3.01 g/cm<sup>3</sup>

Click the checkbox next to "Use a specific random seed" and leave the value 111.

The specific random seed is used just to guarantee reproducibility of the results. For standard work, random seed need not be defined.

Click the radio button "EDMA – take as it is"

EDMA is an external program for interpretation of electron densities. It can take the chemical formula and interpret the density using this formula.

Leave other settings default; OK

[On the screen: window of Superflip appears with iteration running. After ten runs, listing of Superflip log file is displayed]

Superflip performed ten solution attempts. Check the space groups derived by Superflip from each of the attempts. The most frequently proposed space group is Cc (eight of ten attempts). Inversion center and two-fold axis have much worse symmetry agreement factors. It is likely that the correct space group is Cc and not C2/c.

Press CLOSE to leave the listing

Press "Discard the result"

Back in the structure solution window, change the space group to Cc and recreate the refinement reflection file

OK

[On the screen: Superflip runs again, this time creating output in Cc. EDMA is used to interpret the density]

"Accept the result"

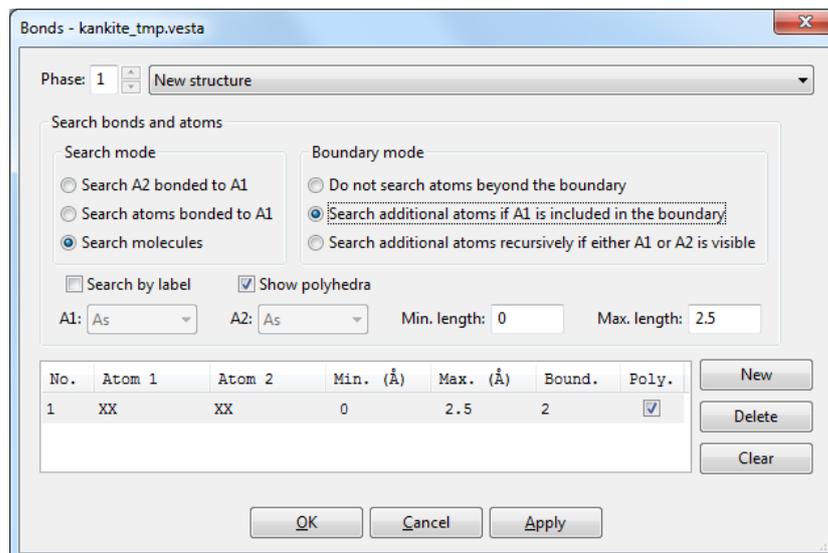
The result is a file kankite.m40 with atoms of the structure model.

## 7. Verification and completion of the structure solution

Go to "Contour → New plot → OK → Run 3D maps"

VESTA opens with a density shown as isosurfaces, and an atomic model overlaid. Rotate the view to inspect the structure. Try to recognize the structural motifs. The main expected motifs are AsO<sub>4</sub> tetrahedra and FeO<sub>6</sub> octahedra. The analysis will be simpler if you display the bonds between atoms:

Go to Edit → Bonds, and set up the options according to this screenshot:



It is also useful to show only positive isosurfaces (Properties > Isosurfaces). Viewing the structure solution in VESTA has the advantage that you can directly check, if the raw density was correctly interpreted. In this case, atom As1 should be Fe, and Fe1 should be As. You may inspect the model also in Diamond. You should come to the conclusion that the model is almost complete. Two oxygen atoms are missing (around Fe2) and five oxygen atoms in the list (O10, O11, O12, O14 and O15) are ghost peaks.

## 8. Delete ghost atoms and change atomic types

Double click icon Edit atoms

Select atoms O10, O11, O12, O14 and O15 (Click while holding Ctrl)

“Action → Delete atoms → Yes to all”

Select atom As1

“Action → Edit/Define atoms → Type → Fe”

Repeat the assignment process to atom Fe1 (type As)

OK

“Select all → Action → Rename selected atoms to “atom\_type”+number”

OK; Yes

## 9. Structure refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine.

[On the screen: refinement options]

Set Number of cycles to 100; OK Choose “Yes+start”

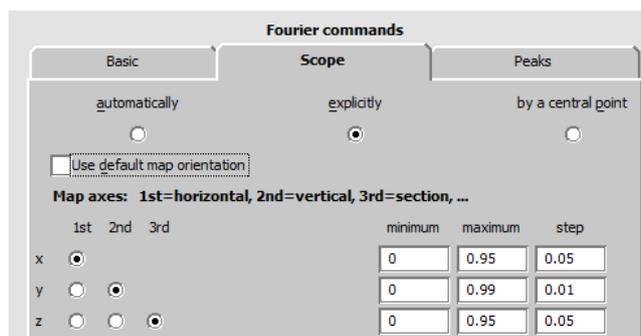
Refinement converges to an R value about 19%

## 10. Adding the missing atom [On the screen: basic window of Jana]

Right click the icon Fourier

On the first card, select F(obs)-F(calc) – difference Fourier

Modify the setting on the second card to agree with this screenshot:



OK; Yes+Start; No; No

Jana just calculated a difference Fourier map.

View the map in VESTA: "Contour → New plot → OK → Run 3D maps"

You will see that the difference map is dominated by two positive peaks around the atom Fe2. These maxima correspond to the two missing atoms.

Close VESTA and return to the main window of Jana2006

"Parameters → Atoms → New → Peaks from last Fourier calculation"

A list of maxima found in the density is displayed. In the right pane, the distances of the maximum to the nearest atoms are displayed. The first two maxima correspond to the missing oxygen – they have the right distance to Fe2.

Select Max1, click "Include selected peak", type O\* in the field for name; OK;

Select Max2, click "Include selected peak", type O\* in the field for name; OK;

Finish; Yes to include the new atoms in the model

Double click the icon Refine to refine the completed model.

The structure refines to 15.89%. At this moment the refinement is finished. It is possible to refine anisotropic ADP parameter of the atoms. The R-value drops to 11.63%, but the ADPs are unrealistic – they have an extremely large component along **b**. This effect comes from the data quality – reflections with high k-index are systematically weakened.

## 11. Identification of OH and H2O groups

The data quality is by far not good enough to see directly the hydrogen atoms. However, we can estimate the positions of OH and H2O groups by the coordination and bond-valence sums of the oxygen atoms.

Right-click icon Dist

Click button "Define coefficients for bond valences"

Define pair of atoms Fe, O; Click "From file → Fe3+ O2- (fourth in the list) → OK → Add"

Repeat for pair As – O, select the entry As5+ O2- from the list → OK → Add

OK;

[On screen: main dialog window of the Dist module]

Uncheck checkbox "dmax derived from atomic radii and typical distances"

OK; Yes+start; Yes to open the listing

At the end of the listing you will find the following table of bond-valence sums:

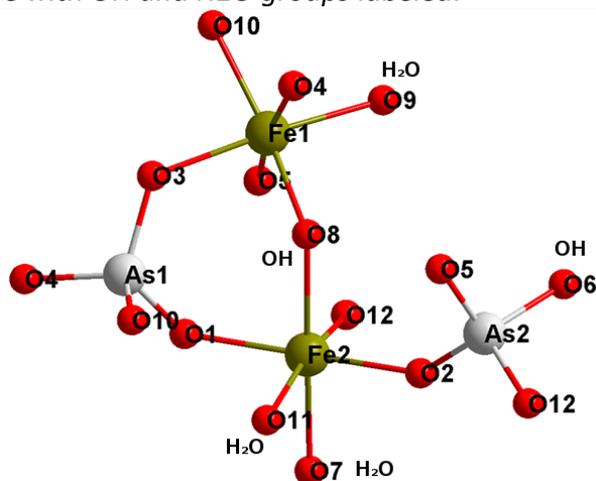
```

Bond valence for : Fe1 2.48(6)
Bond valence for : As1 4.32(12)
Bond valence for : As2 5.46(19)
Bond valence for : Fe2 2.33(6)
Bond valence for : O1 1.42(8)
Bond valence for : O2 1.86(8)
Bond valence for : O3 1.53(7)

```

Bond valence for : O4 1.46(4)  
 Bond valence for : O5 2.08(15)  
 Bond valence for : O6 0.99(5)  
 Bond valence for : O7 0.35(3)  
 Bond valence for : O8 0.90(5)  
 Bond valence for : O9 0.40(2)  
 Bond valence for : O10 1.53(5)  
 Bond valence for : O11 0.326(18)  
 Bond valence for : O12 1.75(8)

You can see three types of oxygen atoms. Most of oxygens have bond-valence sums above 1.4, two around 0.9 (O6 and O8) and three very low – below 0.5 (O7, O9, O11). O6 and O8 correspond to OH groups, and O7, O9, O11 are water molecules coordinating Fe atoms. This is a view of the structure with OH and H<sub>2</sub>O groups labeled:



Thus, the published formula is not correct. The correct formula is  $Fe_2(OH)(AsO_4)(AsO_3OH) \cdot 3H_2O$  or  $Fe_2As_2O_7(OH)_2 \cdot 3H_2O$



# Example 13.3: Orthopyroxene

## Refinement of atomic occupancies from electron diffraction data using dynamical diffraction theory

Revised: October 2015

### Background information:

Orthopyroxene (opx) is a rockforming mineral – iron-magnesium silicate  $(\text{Fe,Mg})_2\text{Si}_2\text{O}_6$ ,  $Pbca$ ,  $a=18.268$ ,  $b= 8.868$ ,  $c=5.202$ . It contains two symmetry-independent octahedral sites with Mg and Fe. The distribution of Mg and Fe in these two sites depends on the crystallization conditions, and it can therefore be used to infer information about the formation of the rock.

Orthopyroxene often forms only microcrystalline aggregates or intergrowths with other minerals. It is thus desirable to determine the occupancies of Fe and Mg on the two sites from individual micro- or nano-crystals of opx.

Electron diffraction data were measured on FEI Tecnai G<sup>2</sup> 20 operated at 200 kV with precession device DigiStar.

Input data: `opx_001.tif`: the experimental diffraction pattern, zone axis  $[001]$  of orthopyroxene.

`opx_001.pts`: input file for PETS with experimental information

`opx_xray.cif`: cif file with the model of the opx structure refined against x-ray data set.

`opx_001_dyn_start.cif_pets`: result of data processing with PETS. This file is provided so that this example can be solved without the data processing part.

### 1. Data reduction using PETS

*File `opx_001.pts` contains instructions for PETS. Open the file and check the instructions.*

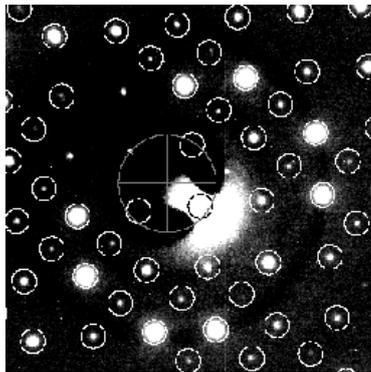
*Compared to tomographic data, the input is much simpler in this case – the tilt-axis azimuth need not be defined, and the orientation angles can be set to 0.*

*Note the line “background 32768”. The `tif` file was obtained by conversion of a `dm3` file (Digital Micrograph format). By default, the zero level of such file is at  $2^{15}=32768$ . The byword `background 32768` corrects for this shifted zero level.*

Start PETS with the file `opx_001.pts`

Type `p`[Enter]

*PETS will extract peaks from the image and save them in file `opx_001.cor`. Check the image shown by `ImageJ`. The central part is shown here:*



*The encircled black cross shows the predicted position of the primary beam. Obviously, the automatic location of the center failed. We have to provide the center explicitly.*

Type q[Enter] to quit PETS.

Open the file opx\_001.tif in ImageJ

Go to “Image → Properties” and change the values of Pixel width and Pixel height from 0.005 to 1.

Read the coordinates of the direct beam.

*The coordinates are close to 1990 1393*

Close ImageJ

Open file opx\_001.pts in a plain-text editor (e.g. Notepad) and modify the line “center AUTO” to “center 1990 1393”

Save and close opx\_001.pts.

Start PETS again with the updated file opx\_001.pts

Type p[Enter]

*This time the center is located properly.*

*We will not use the peak-processing functions of PETS, because the amount of data is not sufficient. We will use directly the file opx\_001.cor produced by PETS after the peak hunting.*

Start Jana2006

Go to “Tools → Graphics → Indexing”

Locate the example directory and select file opx\_001.cor; OK

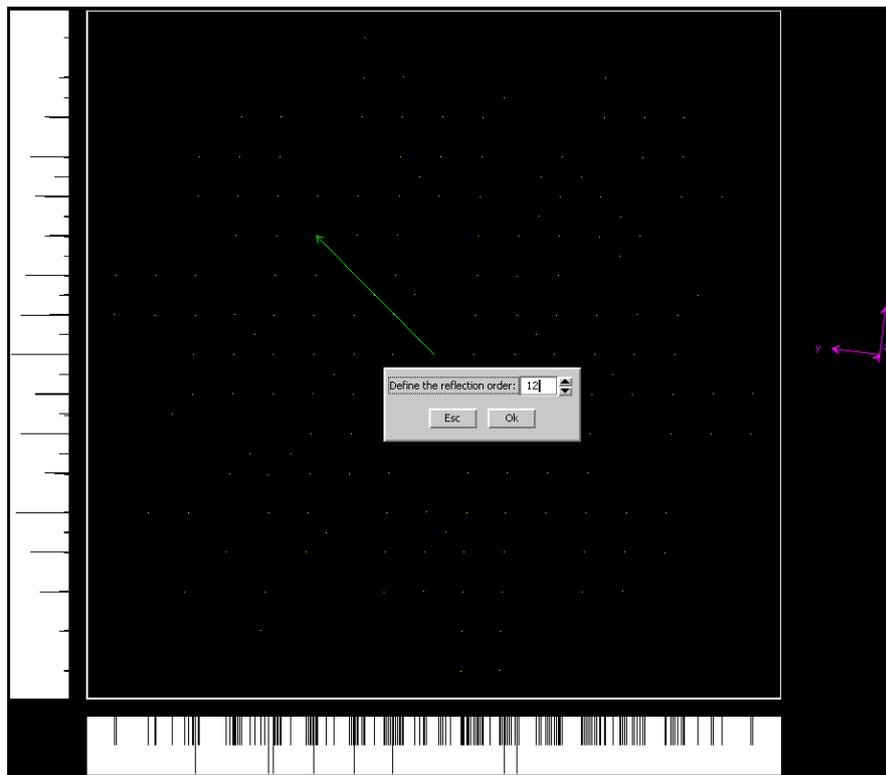
*You will see a plot of located peaks. The peaks form only a 2D layer. We have to use a 2D indexing option of the indexing plugin to index the layer.*

Click the button “2d section ON”

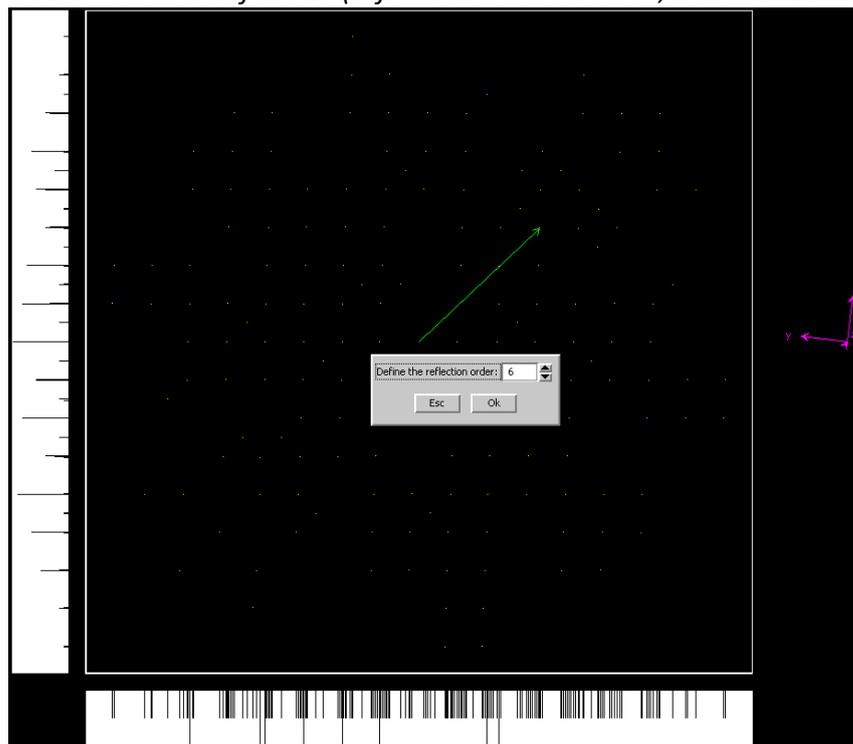
*Jana2006 finds the best plane through the peaks, and fixes the view on this plane.*

Click on the “indexing” button  in the lower left corner.

*Now if you drag the mouse with left button pressed, you will move an arrow on the screen. By this arrow, you should locate a reflection, of which you know the indices. This is a little tricky, because the plane [001] contains systematically absent reflections (due to the a-glide), and, in addition, a pseudo n-glide. You should locate the vector **a** according to the following screenshot. Note that reflection 12 0 0 was selected:*



Similarly, vector **b** is located as follows (reflection 0 6 0 selected, hence order 6):



If you get lost, open the original diffraction pattern in ImageJ and compare the distribution of reflections with the peak positions in Jana2006.

Once the two vectors are defined, the selected 2D cell can be refined:

“Refine cell → Refine UB+cell”

You should obtain a result very close to the following 2D cell:

parameters:	18.4044	8.8784	89.4196
s.b.:	0.0095	0.0034	0.0363

OK to quit the refinement dialog

This cell must be converted to a 3D cell to produce an orientation matrix:

Click "2d section OFF"

A dialog for the 2D to 3D transformation appears

Type the cell parameters: 18.268 8.868 5.202 90 90 90

In the line labeled "(h,k,l) for 2d axial direction #1" type 1 0 0

In the line labeled "(h,k,l) for 2d axial direction #2" type 0 1 0

Click "Calculate"

You should obtain the following result:

**Define cell parameters and 2d axes**

Cell parameters: 18.268 8.868 5.202 90 90 90

(h,k,l) for 2d axial direction #1: 1 0 0

(h,k,l) for 2d axial direction #2: 0 1 0

Calculate

2d cell as measured: 18.4044 8.8784 89.420

2d cell as follows from cell parameters: 18.2680 8.8680 90.000

Orientation matrix:

0.033681	0.087012	0.000084
0.042636	-0.071520	-0.000042
0.000005	0.000053	-0.193058

Final cell parameters: 18.408 8.880 5.180 90.00 90.00 88.89

Esc Ok

OK; Quit

Now you have an orientation matrix that you can read back to PETS, and extract intensities.

[On screen: window with PETS, main menu]

Type u[Enter]

PETS read in the orientation matrix calculated by Jana2006.

Type d[Enter]

D stands for "integration for dynamical refinement". PETS extracts all intensities up to  $d^*=1.4$ , and produces file `opx_001_dyn.cif_pets`.

## 2. Import structure in jana2006

**Important!** The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the file `opx_001_dyn.cif_pets` that you just created, but use the file `opx_001_dyn_start.cif_pets` provided with the example files. Before continuing, make a copy of the file and name it `opx_001_dyn.cif_pets`. Using your own `cif_pets` file is also possible, but your results may slightly differ from the results described in this tutorial. Now we will import the file `opx_001_dyn.cif_pets` in Jana2006.

Start Jana2006

"File → Structure → New"

In the left pane, locate the example directory

In the right pane, double click the label `opx_001_dyn`  
 Select “Single crystal: known diffractometer format”; NEXT  
 Select “Pets – electron diffractometer”; NEXT; NEXT; NEXT; OK; NEXT; FINISH; OK; Yes  
 You have just imported the data from `cif_pets` using default options. At this point Jana offers symmetry determination wizard, but we will escape the standard procedure, which is not useful for us.

Cancel; Cancel to cancel the symmetry wizard and the production of reflection file.

Now we have to import the structure model from the provided CIF file:

“File → Import model from → CIF”

Locate file `opx_001.cif` and double click it

OK to accept the new model

Cancel to avoid production of the refinement reflection file

If we accepted to produce the refinement reflection file at this stage, it would be prepared for kinematical refinement. We will use dynamical refinement.

### 3. Setting up dynamical refinement

[On screen: Main windows of Jana2006]

“Parameters → Electron diffraction”

You should see this dialog:

This dialog contains experimental information relevant for the dynamical refinement, and information about the zone axis (or several zone axes, if there are more zone axes imported). Most options are now blank, because the reflection file for dynamical refinement has not yet been prepared.

Check the box next to “Use dynamic approach”

OK to create refinement reflection file

Follow the wizard and accept default choices

[On screen: Electron diffraction dialog]

Now we have to find initial values for the sample thickness, scale factor and orientation. As a first quick check, we will calculate only the thickness curve, using fixed orientation. This

calculation is much faster than the optimization of orientation, and it provides first estimated of the data quality.

Click “except of scale optimize also: Thickness → Run optimization”

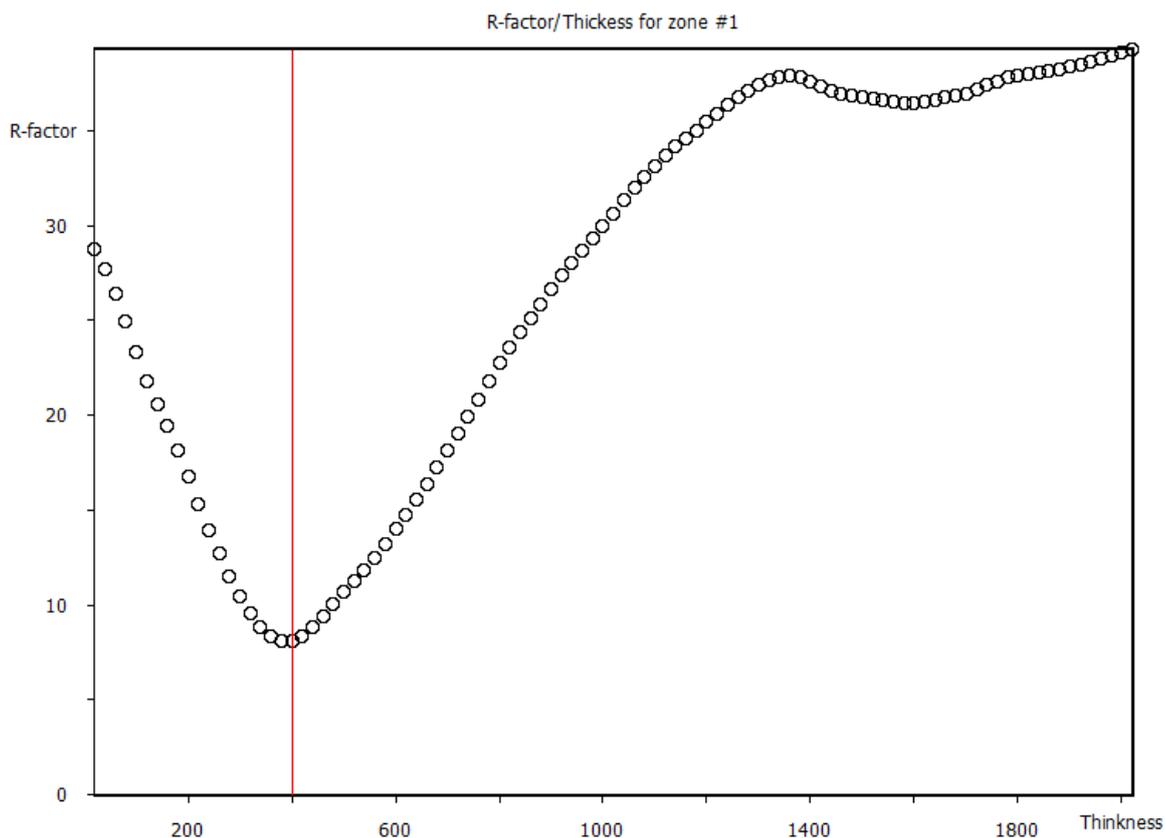
Jana2006 generates reflections and calls Dyngo.exe. Dyngo.exe calculates the reflection intensities using dynamical diffraction theory.

[On screen: Electron diffraction dialog]

Next to the indication of the zone number you see the best R-value:  $R(\text{all})=8.1174\%$ . This is a very promising value and indicates that already now the fit of the model to the data is quite good.

Click “Show thickness plots”

You should obtain the following plot:



This plot shows a clearly defined minimum at the thickness 400 Å. This together with the low R-value shows that the starting point for the refinement is reasonable.

Quit the display of the thickness plot

Click “except of scale optimize also: orientation → Run optimization”

The orientation of the experimental pattern is never perfect. Dyngo finds the parameters of the misalignment of the zone axis from the perfect orientation predicted by the orientation matrix. This calculation requires repeated evaluations of reflection intensities and may take some time. You may follow the progress of the simplex algorithm in the window of Dyngo.

After the optimization, the zone axis parameters look like this:

EDScale	2680.311	<input checked="" type="checkbox"/>	EDThick	400	<input checked="" type="checkbox"/>
EDPhi	180	<input type="checkbox"/>	EDTheta	0.15	<input type="checkbox"/>

The R-value decreased only slightly to 7.9963%. Value 0.15 of EDtheta means that the diffraction pattern was recorded at an angle of 0.15 degrees away from the perfect

orientation.  $ED\Phi$  is the azimuth of the tilt axis. Given the large precession angle, this value is within the precision of the method, and means that the pattern was essentially perfectly oriented.

Quit the Electron diffraction dialog and confirm changes in the m42 file.

#### 4. Dynamical least-squares refinement

We will first refine only the scale and thickness.

“Right-click Refine → Various → Fixed commands”

In the line labeled “Atoms/parameters” type \* (star)

Click the arrow next to “Add”

You have fixed all structure parameters of all atoms. An exception is the atomic occupancy, which is not fixed by this command, but we did not explicitly allow its refinement either, and therefore the occupancies will remain, for the moment, fixed, too.

OK; OK; Yes+Start

Refinement converges smoothly to an R-value of 7.28%.

Now we will allow the refinement of occupancies.

“Right-click Refine → Various → Restrictions”

In the line labeled Atoms/molecules type “Fe1 Mg1”

Click radio button next to “Occupancies: keep overall sum”

Click the arrow next to “Add”

Repeat the action for the pair “Fe2 Mg2”

OK; OK; Yes to save the changes, but do not start the refinement

We have now restricted the occupancies of the two atoms to sum to 1. Only one occupancy for each pair will be refined.

Now we have to allow the refinement of occupancies of Fe1 and Fe2:

Double click the icon “Edit atoms”

Double click atom Fe1

On the card “Edit” check the box next to the parameter “ai”; OK

Repeat for atom Fe2

OK to close the Edit atoms dialog

Double click Refine to start refinement

Refinement converges smoothly. R-value decreases only very little to 7.25%.

Refined occupancies are  $o(\text{Fe1})=0.050(11)$ ,  $o(\text{Fe2})=0.52(11)$ . The occupancies refined from the same sample with x-ray data are  $o(\text{Fe1})=0.035(3)$ ,  $o(\text{Fe2})=0.552(3)$ . In general, the refinement against electron diffraction data is in a good agreement with the refinement against bulk material using x-rays.

If you wish, you may convince yourself that even from more distant starting values of the occupancies the refinement will converge to the same values. You may, however, need to use smaller damping factor (right-click Refine → Damping factor) to avoid oscillation or locking in a false minimum, if you start from too distant values.

#### 5. Kinematical least-squares refinement

We will perform a kinematical refinement for comparison.

[On screen: main window of Jana2006]

“File → Structure → Save as”

Type “opx\_001\_kin” in the window under the right pane; OK; Yes

We saved the structure under another name to preserve the dynamical refinement.

“Parameters → Electron diffraction”

Uncheck the box next to “Use dynamic approach”; Yes to save changes

Accept the proposal to recreate the refinement file and follow the instructions. Leave all settings default.

Double click “Refine” to start refinement

*With a few clicks we switched from dynamical to kinematical refinement. The refinement R-value is 31.03%, and the refined occupancies are  $o(\text{Fe1})=0.280(87)$  and  $o(\text{Fe2})=0.435(90)$ .*

# Example 13.4: Silicon

Complete procedure from structure solution to dynamical structure refinement from three zone-axis patterns.

Revised 11 December 2013

Input data: si\_ZAPs.cif\_pets: a cif\_pets file containing the orientation matrix, positional angles and intensity information from three zone-axis patterns collected on the same sample – a wedge-shaped silicon single crystal. The file was obtained from raw diffraction patterns using the procedure analogical to example 13.1.

## 1. Import data to Jana2006

Start Jana2006

“File → Structure → New”

In the left pane, locate the example directory

In the right pane, double click green label si\_ZAPs

Select “Single crystal: known diffractometer format”; NEXT

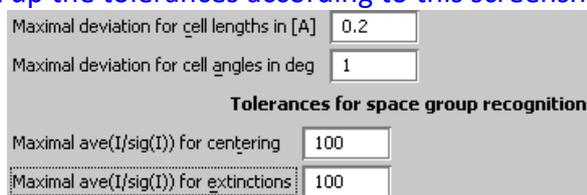
Select “Pets – electron diffractometer”; NEXT; NEXT; NEXT; OK; NEXT; FINISH; OK; Yes

You have just imported the data from cif\_pets using default options.

As a next step Jana starts the symmetry determination wizard. The data set we have is not really complete, but we may nevertheless attempt to proceed with the wizard:

Next to start the wizard

On the next screen, set up the tolerances according to this screenshot:



The screenshot shows a dialog box with the following settings:

Maximal deviation for cell lengths in [Å]	0.2
Maximal deviation for cell angles in deg	1
<b>Tolerances for space group recognition:</b>	
Maximal ave(I/sig(I)) for centering	100
Maximal ave(I/sig(I)) for extinctions	100

Next; OK;

You now look at a table of  $R_{int}$  values for various Laue classes. The cubic Laue classes have acceptable  $R_{int}$  values, and there is little doubt the structure is indeed cubic.

Select Laue class m-3m; Next

The data were already integrated assuming F-centering, therefore there are zero reflections matching the F-centering absences in the data set.

Select centering F; Next

On the next screen a list of possible space groups is presented. For the space group Fd-3m, 7 out of 24 forbidden reflections have  $I > 3\sigma(I)$ . However, looking at the details (click the button “Details”) you will find that these reflections are in fact only two - 0 0 2 and 0 0 6. The d-glide is thus likely to be present. Indeed, the space group of silicon is Fd-3m.

Select “Fd-3m”; Next; Finish

In the next step we prepare a “standard” reflection file suitable for structure solution.

Next; OK; OK

[On screen: the window with three radio buttons for the choice of the handling of scales] Jana treats can data from each zone axis on a separate scale. For the structure solution and kinematical refinement, we will, however, assume that the data are on the same scale. The number of common reflections is insufficient to determine a reliable common scale.

Select "Ignore scale flags"; Next; Next; OK; Finish

## 2. Structure solution and kinematical refinement

[On screen: Information window explaining that the next step is structure solution]

OK to open the structure solution dialog

Type Si in the dialog box for formula; change the number of formula units to 8

Leave all settings default

OK to start solution by Superflip

Superflip runs and produces a structure solution.

When Superflip exits, accept the solution

Plot structure in Diamond to make sure it has been correctly solved

Right-click Refine; change number of cycles to 100; OK; Yes+start

Jana2006 refines the structure using kinematical calculation of diffracted intensities. The structure refines to the following values (note that there are only 13 symmetry independent reflections!):

```
R factors : [13=13+0/2], Damping factor: 1.0000
GOF(obs)= 45.83 GOF(all)= 45.83
R(obs)= 23.25 wR(obs)= 41.88 R(all)= 23.25 wR(all)= 41.88
Last wR(all): 49.75 46.57 44.61 43.45 42.29 41.98 41.90 41.88
Maximum change/s.u. : 0.0304 for scale1
```

Open the refinement listing (Edit → View of Refine) and check the statistics.

The displacement parameter of silicon refines to -0.0106.

## 3. Origin shift

The default origin of the space group  $Fd-3m$  is at the point  $-43m$ , which does not contain inversion center. For the dynamical refinement it is desirable to have the origin in the inversion center, if possible. We will now shift the origin of the unit cell to the inversion center:

[On screen: Main window of Jana2006]

"Tools → Transformations → Origin shift"

Type "1/8" in all three fields; OK

## 4. Initiation of dynamical refinement

[On screen: Main window of Jana2006]

The displacement parameter of silicon did not refine to physically meaningful value. Before initiating the dynamical refinement it is good to reset it to a more correct value. It is not strictly necessary in this example, but it is generally a good practice.

Double click the icon Edit atoms

Double click Si1

On the card Edit, change Uiso to 0.005

OK; OK; Yes

[On screen: Main window of Jana2006]

"Parameters → Electron diffraction"

You will see the following dialog:

Parameters for electron diffraction data

Orientation matrix: U11 0.00621 U12 0.00283 U13 0.18318  
U21 0.13491 U22 0.12349 U23 -0.00635  
U31 -0.12065 U32 0.13477 U33 0.00175

Maximal diffraction vector g(max): 2 Number integration steps: 128  
Maximal excitation error: 0.01 Use dynamic approach:   
Omega: 0 Select zones for refinement Define zones of equal thicknesses

ED4Jana commands:

Optimize orientation Optimize thickness and scale Optimize thickness, scale and orientation  
Show thickness plots

Zone#: 1 R(all)= -----  
H -0.99515 K 1 L 0.00196 prec.angle 2  
alpha -2.97 beta -0.57  
EDScale 1  EDThick 400  EDXNorm 0  EDYNorm 0   
EDPhi 0  EDTheta 0

Esc Ok

Default excitation error is too small for the current data – it must be increased:

Change Maximal excitation error to 0.03

Check the box next to “Use dynamic approach”

OK to create refinement reflection file

Follow the wizard and accept default choices

[On screen: Electron diffraction dialog]

Now we have to find initial values for the sample thickness, scale factors and orientations of all three zones. As a first quick check, if the data quality is acceptable, we will calculate only the thickness curve, using fixed orientation. This calculation is much faster than the optimization of orientation, and it provides a first estimate of the data quality.

Click “Optimize thickness and scale”

Jana2006 generates reflections and calls Dyngo.exe for each zone separately. Dyngo.exe calculates the reflection intensities using dynamical diffraction theory. Wait until Dyngo.exe terminates.

[On screen: Electron diffraction dialog]

Click “Show thickness plots”

Go through the thickness plots. You should see three curves with more-or-less well defined minima between 500 and 1000 Å. The best R-values are around 15%. This is a good start, but it is still not satisfactory. It is necessary to optimize the orientations:

Quit the display of the thickness plot

Click “optimize thickness, scale and orientation”

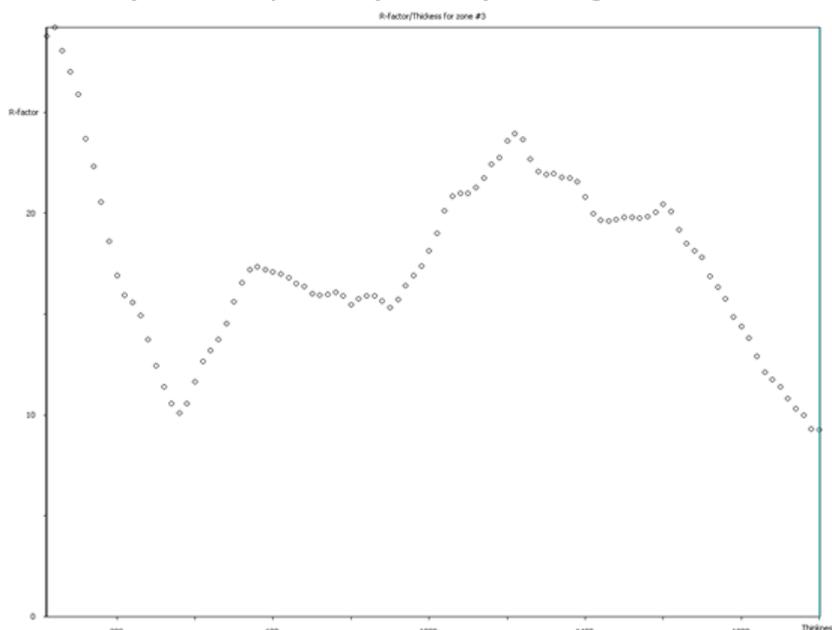
This option optimizes all three parameters simultaneously, using a simplex algorithm. This calculation requires repeated evaluations of reflection intensities and is thus much longer than just the thickness optimization. Wait until all three runs of Dyngo finish.

[On screen: Electron diffraction dialog]

Check the refined tilt angles. EDtheta is the azimuth of the tilt, EDphi is the amplitude. You will see that the refined misorientations range between 0.13 and 0.39 degrees – very reasonable values.

Click “Optimize thickness and scale”

Repeat the thickness orientation to view the updated thickness curves. When viewing the thickness curves again, you will see much better defined minima. However, for zone 3 you will find the following curve:



There is a clear and reasonable minimum at  $t=350 \text{ \AA}$ , but the lowest R-value is found for the thickness of  $2000 \text{ \AA}$ . It is necessary to manually reset the thickness to  $350 \text{ \AA}$  before the refinement.

Quit; Locate zone 3 and set the thickness according to the following screenshot:

Zone#: 3		R(all)= 9.2662%	
H 0.01239	K 1	L -0.00472	prec.angle 2
alpha 42.5	beta 0.67		
EDScale 1658.773 <input checked="" type="checkbox"/>	EDThick 350 <input checked="" type="checkbox"/>	EDXNorm 0 <input type="checkbox"/>	EDYNorm 0 <input type="checkbox"/>
EDPhi -85.59474 <input type="checkbox"/>	EDTheta 0.270805 <input type="checkbox"/>		
Esc		Ok	

The data are now checked and ready for least-squares refinement.

OK; Yes to exit the Electron diffraction dialog

## 5. Structure refinement

[On screen: Main window of Jana2006]

The dynamical refinement tends to be unstable with default damping factor, it is thus better to decrease it:

Right click "Refine"

Set damping factor to 0.2

OK; Yes+Start

The dynamical refinement starts. You may follow the progress in the window of Jana2006. You may also interrupt the refinement or change the parameters the same way as for the standard refinement.

The refinement converges after 21 cycles to  $R(\text{obs})=6.8\%$ . (Compare with 23% obtained with kinematical refinement).

*Uiso(Si1) refines to -0.0010(19). This is a much better value than the result of kinematical refinement, but it is, of course, not satisfactory. A detailed investigation shows that even if only one zone-axis at a time is used for the refinement, Uiso(Si1) remains slightly negative. It is thus probably a problem related to the experiment. Unfortunately, the sample used for the data collection was damaged, and we could not remeasure the data. Previous measurements on the same samples yielded correct Uiso around 0.005, but these measurements were single-zone only, and they are thus not so well suited for demonstration of the complete procedure.*

*By repeating the optimization of orientation and rerefining the structure, the R-value can be decreased even more to 5.0%. However, Uiso(Si1) remains negative.*



# Example 13.5: Ni<sub>2</sub>Si

Solution of nickel silicide Ni<sub>2</sub>Si by PEDT (precession electron diffraction tomography) data. Complete procedure from data reduction to structure refinement using the dynamical approach.

Revised: February 2019

## Chemical formula: Ni<sub>2</sub>Si

Electron diffraction data was measured on a transmission electron microscope Philips CM120 with a precession device DigiStar. Accelerating voltage of 120 kV.

Input data:

directory dp-150 with the set of experimental data (reflection images)

directory img with the set of experimental images from the crystal tilt

Ni<sub>2</sub>Si.pts: input file for PETS

Ni<sub>2</sub>Si\_start.cif\_pets: result of the data processing. This file is provided so that this example can be solved without the data processing part, and to warrant reproducibility of the solution and refinement part. File Ni<sub>2</sub>Si.cif\_pets will be the output of the data reduction.

Ni<sub>2</sub>Si\_start\_dyn.cif\_pets: result of the data processing for dynamical refinement. This file is provided so that the dynamical approach can be used without the processing part, and to warrant the reproducibility of the refinement.

### 1. Preparing input file for PETS

*Make sure you correctly installed PETS and ImageJ. Check Chapter "Installation notes" (page 7) for details. File Ni<sub>2</sub>Si.pts is the input to PETS. The file was prepared by the software used for the collection of the diffraction data, and most entries have been filled in. You have to enter two parameters: the information about beam stop and the size of reflections.*

Open file Ni<sub>2</sub>Si.pts in any plain-text editor (notepad, wordpad, notepad++, vim,...)

Open file dp-150/001.tif in ImageJ

In ImageJ go to "Image → Adjust → Brightness and Contrast"

Click the button "Auto" to adjust the contrast

Go to "Image → Properties" and change the values of Pixel width and Pixel height from 0.005 to 1

Measure the diameter of the reflections on the image

*There are several ways to measure the diameter of the reflections, but the simplest and sufficient way is to place the cursor to the left of the reflection, remember or write down the x-coordinate, then place the cursor to the right of the reflection, again read the x-coordinate and subtract the two coordinates. The diameter should be large enough to encompass most of the reflections, but not too large, to prevent overlaps. Do not take into account the broad, weak TDS scattering around the strongest reflections! That would give you a too large diameter. In this case, value 25 is a good choice.*

In Ni<sub>2</sub>Si.pts, change the line "reflectionsizesize ???" to "reflectionsizesize 25"

This measurement was performed without beamstop (microdiffraction). In Ni<sub>2</sub>Si.pts change the line "beamstop ??(yes/no)" to "beamstop no"

Save and close Ni2Si.pts

## 2. Run PETS and prepare files for indexing

Make sure ImageJ is not running. If it is, close ImageJ.

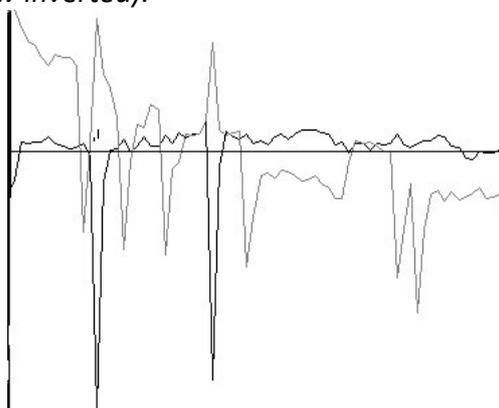
Run PETS with the file Ni2Si.pts

There are several ways of running PETS. See installation notes for detailed description. A window with initial menu of PETS opens, and ImageJ starts displaying a black image with a white circle.

In the window of PETS, type p[Enter]

The peak hunting procedure starts. ImageJ sequentially displays diffraction images with circles at points found by PETS as significant peaks. Note that PETS follows the position of the primary beam, and corrects for small shifts. Note also the significant diffuse streaks. Although they seem very intense, it is just due to the enhanced contrast of the images. Compared to the Bragg intensities, the diffuse streaks are weak and do not disturb the structure solution.

At the end, the evolution of the x- and y-coordinates of the estimated primary-beam position is displayed (b&w inverted):



[On screen: main menu of PETS]

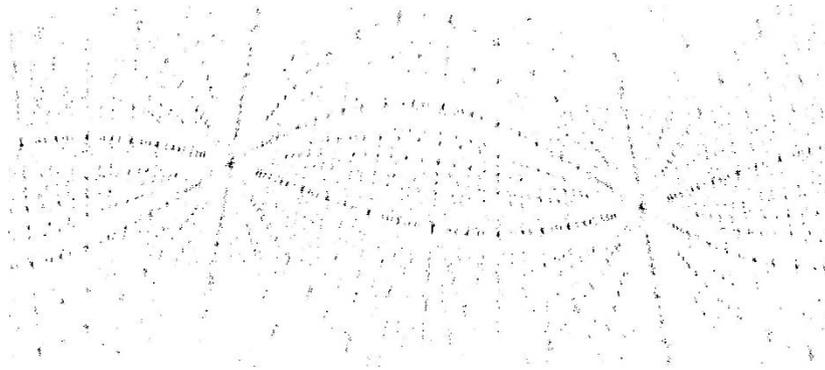
type r[Enter]

The next step after peak hunting is the refinement of the azimuthal angle between the horizontal axis (x axis of the micrograph) and the projection of the tilt axis. This angle depends on experimental setup, and needs to be refined for each data set. ImageJ displays a cylindrical projection of the difference space of the extracted peak positions. A correct azimuthal angle refinement results in the image containing sharp peaks aligned on sinusoidal curves. This step provides a first estimation of data quality. At the end of the refinement the omega angle should be close to 13°.

On the screen:

```
Final values of the parameters:  
omega : 13.165
```

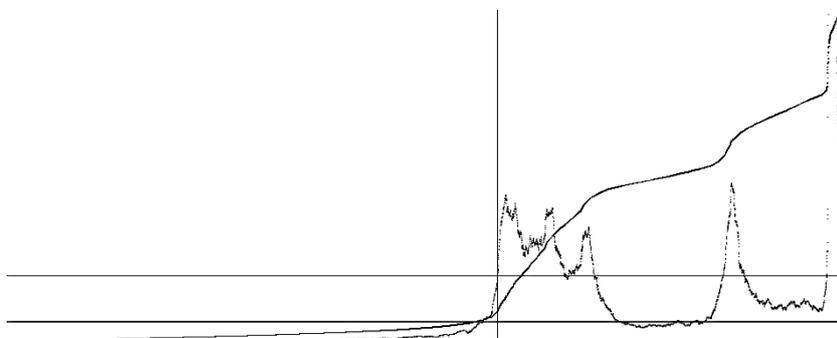
and see this image (b&w inverted):



[on screen: main menu of PETS]

type a[Enter]

PETS starts the analysis of the peak positions obtained in the peak hunting procedure. In the first step, distance distribution between peaks in the image plane is analyzed. A sorted plot of inter-peak distances is displayed (white curve on screen, black on the image below) with its derivative (grey curve):



For good quality data set, the white curve contains distinct steps, and, consequently, the grey curve has distinct peaks.

Press Enter

In the next step an autoconvolution of the diffraction pattern (difference space) is analyzed, and the groups of peaks in the autoconvolution (clusters) are replaced by the cluster centers. Again, a distance distribution is displayed, and clear-cut steps on the curve indicate a well-defined lattice.

Press Enter

Now the first step is finished and PETS prepared the files needed for unit cell indexing. Keep the window of PETS open, you will need it later!

### 3. Indexing with Jana2006

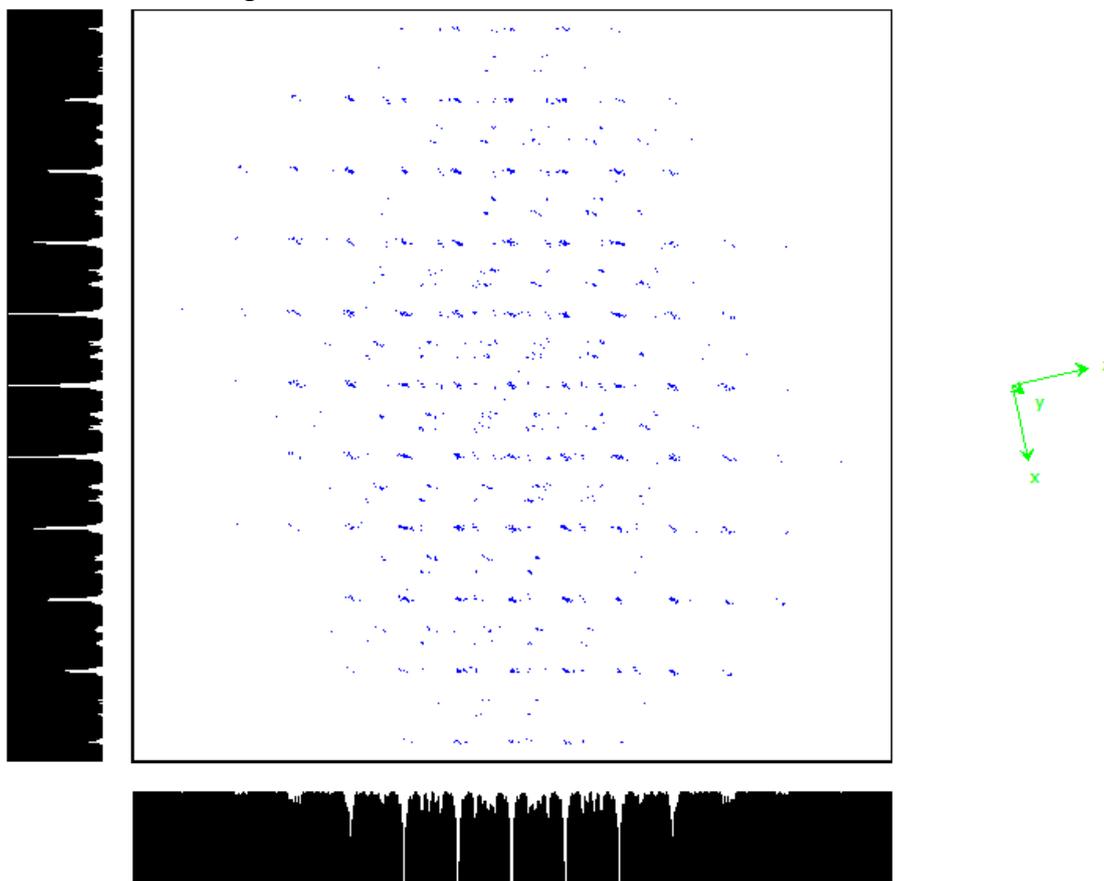
Start Jana2006

By default, Jana2006 starts with the last structure open. It may be cumbersome to change the directory every time. You may create a dummy (empty) file Ni2Si.m40 in the example directory, and use the command "Open with" from the file-manager context menu to launch Jana2006 directly in this directory.

"Tools → Graphics → Indexing"

Locate and open file Ni2Si.clust by double clicking it

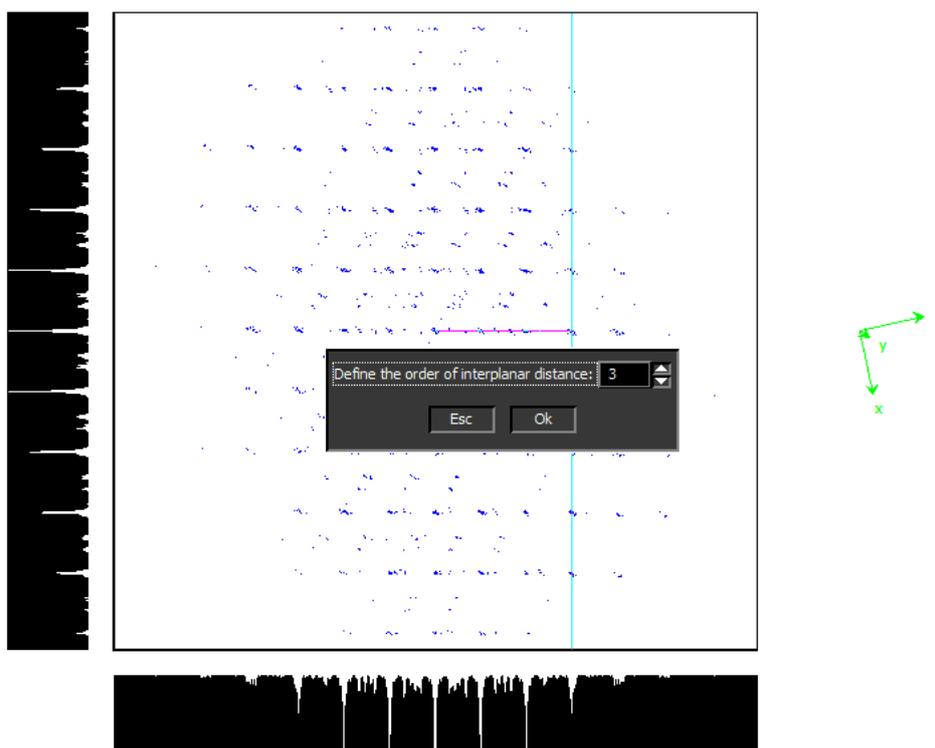
A 3D view of the reciprocal lattice opens. You can rotate the cloud by mouse. Use buttons  and  to switch between free rotation and rotation around z-axis. Rotate with the lattice and try to determine the crystal system and the special axes of the lattice. You should come to the conclusion that the lattice is orthorhombic. The following image shows the view along  $c^*$ :



**IMPORTANT:** before you continue, make sure you have the same orientation of the lattice on your computer as displayed on the picture above (check the direction of the axes on the right). If not, you may obtain slightly different results in the rest of the tutorial. While not necessarily wrong, it makes following this tutorial more difficult.

Click the button  in the lower-left corner and choose the radio button for  $a$  vector setting (right to the  button).

Click, hold the mouse button, and drag the marker to obtain the result on this image:



Set the order of the interplanar distance to 3.

Note that the vertical red line is on the third vertical row of peaks. By this action you defined the direction and length of the (direct-space) basis vector **a**. Note: if you make a mistake and need to redo this step, make sure that the radio button **a** is selected below the main window, otherwise you will modify another cell parameter.

Repeat the action, this time drag the marker up vertically to define the vector **b**.

Vector **a** should have length close to 5.00 Å, vector **b** should have length close 3.73 Å, angles alpha and beta should be close to 90°.

Click "View direction", select "a", Click OK

The reciprocal space is now viewed along **a**, and **c** points up.

In analogy to the procedure above, select the direction and length of the vector **c**.

When you are finished, at the bottom of the window you should see cell parameters close (within a fraction of angstrom and degree) to these values:



"Refine cell → Refine UB+cell"

The orientation matrix is refined. Note that 44.9% of all peaks were indexed.

OK; Quit

The file Ni2Si.smr was now produced by Jana2006. This file contains the orientation matrix and the unit cell parameters.

Close Jana2006

#### 4. Integrate the intensities with PETS

Return to the window of PETS.

Type u[Enter]

PETS reads the orienting matrix from the Ni2Si.smr file.

Type i[Enter]

The integration procedure starts. ImageJ displays images with circles drawn at positions predicted from the orienting matrix. A small circle inside large circle means that a peak with  $I > 3\sigma(I)$  was found. The small circle is located on the maximum of the intensity. A diamond means that a reflection is expected on upcoming frame(s), square indicates reflection present on previous frame(s).

When the integration finishes, files `Ni2Si.cif_pets` and `Ni2Si.hkl` are created. Both can be used to import the data into Jana and to solve the structure.

## 5. Create reciprocal-space sections

In PETS, Type `h`[Enter]

Type `y`[Enter]

You just asked PETS to scan all images and reconstruct sections through reciprocal space at planes `hk0`, `hk1`, `hk2`, `h0l`, `h1l`, `h2l`, `0kl`, `1kl`, `2kl`. We will use these sections as an aid to determine the space group.

When the reconstruction finishes, type `q`[Enter] to close PETS. You may also close ImageJ.

## 6. Create new structure

**Important!** The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the file `Ni2Si.cif_pets` that you just created, but use the file `Ni2Si_start.cif_pets` provided with the example files (Rename the file to `Ni2Si.cif_pets`). Using your own `cif_pets` file is also possible, but your results may slightly differ from the results described in this tutorial.

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate the directory with input files

Right pane: double-click `Ni2Si`

Right panel detects possible Jana files and shows one jobname for each group of files

## 7. Import Wizard

Select “Known diffractometer formats”; NEXT

Select “Pets electron diffractometer”

The file name automatically changes to `Ni2Si.cif_pets`, which is a file produced by PETS containing all important information, including the list of intensities.

NEXT

Leave all settings unchanged (note the wavelength of 120kV electrons!); NEXT

Leave all settings unchanged; NEXT

The program reads 614 reflections from the file

OK

For absorption correction select “None or done before importing”; NEXT

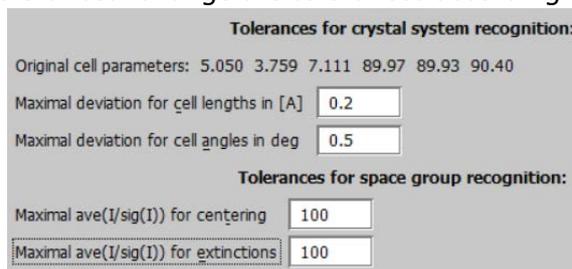
FINISH; OK; YES to accept the data set

You just read in the cell parameters and the intensity list. If you do not have the data in the `cif_pets` format, you can read them in from a general `hkl` file using the option “reflection file corrected for LP and absorption” at the beginning of the import wizard. You then have to input the radiation type, wavelength and cell parameters by hand.

## 8. Symmetry Wizard

**NEXT** to close the information window and start the symmetry wizard.

Symmetry Wizard can be started separately by “File → Reflection file → Make space group Test”. The default settings are prepared for x-ray diffraction. For electron diffraction we have to increase the tolerances. Change the tolerances according to this screenshot:



Leave other settings default; **NEXT**; **OK**

[On the screen: Select Laue symmetry]

Select orthorhombic Laue class mmm; **NEXT**

The internal R-values would be rather high for x-rays, but are low for electron diffraction data.

[On the screen: Select cell centering]

Select primitive unit cell; **NEXT**

[On the screen: Select space group]

The window shows possible space groups.

The list of the strongest reflections contradicting the selected space group can be displayed by “Details” button.

It is difficult to select the correct space group. In particular, presence or absence of the glide is hard to assess, knowing that kinematically absent reflections may have significant intensities due to dynamical diffraction effect. In this case the missing wedge leaves almost no information in  $hk0$  reciprocal-space section. Open images  $0kl$  and  $1kl$  and check the intensities with  $k+l=2n+1$  (which should be absent in the  $0kl$  plane, but present in  $1kl$ ). You will see that despite some violations and the missing information in the center of the image, the  $n$ -glide absences are nevertheless clearly present in the  $0kl$  plane in comparison with the  $1kl$  plane. Space group with  $n$ -glide is thus a reasonable guess.

Note that a wrong choice of the space group is not detrimental for the structure solution, because we will use Superflip, which will make additional check for the most probable space group.

Select Pnma; **NEXT**

Accept the space group in the standard setting; **FINISH**

Symmetry is saved in file Ni2Si.m50.

## 9. Creating refinement reflection file

In this step program creates file Ni2Si.m90 containing the data set merged by symmetry and with discarded forbidden reflections. .m90 will be used for refinement.

Proceed with the wizard, leaving all settings default

## 10. Structure Solution Wizard

**OK** to close the information window and start the solution wizard

[On the screen: window of Structure solution] Structure solution wizard can be executed separately through “Run → Solution”. Jana2006 does not contain solution procedures, it

*calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2006.*

In “Formula” textbox type just the list of chemical elements: Ni Si

*Superflip does not need information about chemical elements but they will be required for peak assignment based on electron density map calculated by Superflip. If Jana2006 is used for peak assignment, a list of expected chemical elements is sufficient. If you know the expected formula, you may enter it and use EDMA for peak picking (at the bottom of the window). If the formula is correct, EDMA often gives cleaner and more complete interpretations of the solution.*

Click the checkbox next to “Use a specific random seed” and enter the value 111.

Leave other settings default; “Run solution”.

*The specific random seed is used just to guarantee reproducibility of the results. For standard work random seed need not be defined.*

*[On the screen: window of Superflip appears with iteration running. After ten runs, listing of Superflip log file is displayed]*

*Superflip performed ten solution attempts, and picked the best one. Its characteristics are displayed near the bottom of the listing:*

```
Properties of the saved density:
  Run Rvalue Peaks Symm. Der.SG
   10  51.46  2.23  1.37  Pnma
```

*The space group proposed by Superflip is the same as our initial guess. The space-group selection is confirmed. Small symmetry agreement factor (column Symm.) indicated good quality of the solution. In cases of doubts or difficult problems, it is worth checking the statistics, especially the symmetry analysis, for each of the ten runs, and seeking for the most probable one.*

Press “Close” to leave the listing

Press “Accept last solution”

*The program creates file Ni2Si.m40 with atoms of the structure model*

## **11. Verification of the structure solution**

Go to “Contour → New plot → OK → Run 3D maps”

*VESTA opens with a density shown as isosurfaces, and an atomic model overlaid. Rotate the view to inspect the structure. Do you think it is complete?*

*You should come to the conclusion that the model is correct, correct elements were assigned to all maxima.*

Quit VESTA (do not save the file), quit Contour.

You may now check the structure in Diamond to convince yourself that the structure is complete and chemically reasonable.

## 12. Initial Refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine.

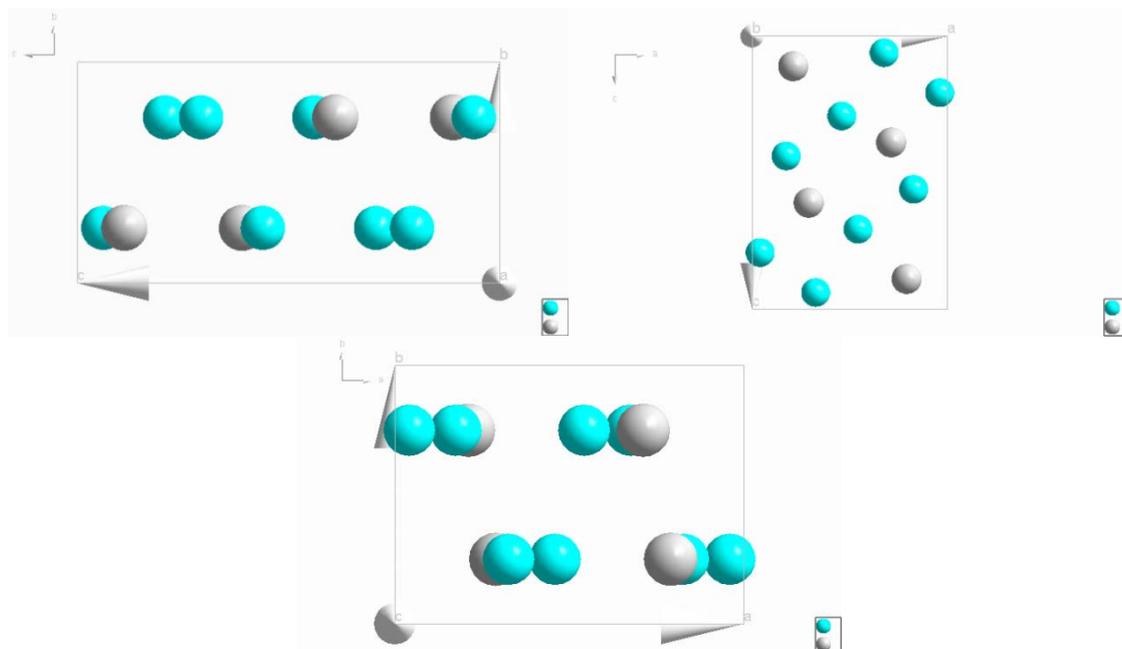
[On the screen: refinement options]

Change the number of cycles to 100; OK

Choose "Yes+start"

Refinement converges with R value about 11.07%. At this moment you may check the refinement listing with a lot of information about the refinement procedure and results. As you can see, the refinement is already very good for electron diffraction. R values are low, all the ADPs were positive definite. Refinement of anisotropic atomic displacements would decrease the residue value ( $R=8.79\%$ ), but the ratio reflections per parameter is already low.

### The resulting structure



## 13. Preparation of reflection file for the dynamical refinement

Open Ni2Si.pts again. Type "o" to read the peak table, "u" to read the orientation matrix and "d" to integrate the intensities for the dynamical refinement.

The integration for the dynamical refinement considers each diffraction image separately. The result is a list with the hkl indices, the measured intensity with the respective sigma and the number of the frame in which the intensity is present. PETS creates the file Ni2Si\_dyn.cif\_pets with all these information, which will be used in Jana2006. Note that the same hkl reflection might be present in several frames, with different intensity due to the multiple scattering relative to different crystal orientation and thickness at this condition.

Quit PETS and go back to Jana2006. “Structure→Save as” and save a new structure Ni2Si\_dyn for the dynamical refinement. Continue with the new structure.

*This will be the structure with the dynamical refinement*

“File→Reflection file→Import/modify the reflection file→Reimport”

*Again, if you want to be sure that you can exactly reproduce the following part of the tutorial, use the file Ni2Si\_start\_dyn.cif\_pets provided with the example files. Rename this file to Ni2Si\_dyn.cif\_pets.*

Select the Ni2Si\_dyn.cif\_pets as the new reflection file. NEXT, NEXT, NEXT.

Now, Jana reads 4825 reflections from all the frames.

OK, NEXT, Finish, OK, Yes, Cancel.

*It is not necessary to average the intensities, because the intensities will be used independently for each frame during the dynamical refinement.*

#### 14. Starting the dynamical refinement

*[On the screen: basic window of Jana]*

“Parameters”, “Electron diffraction”.

*[On the screen: Parameters for electron diffraction data]*

Enable “Use dynamic approach”. OK, NEXT, OK, OK, OK, Finish.

*Notice that now, 1673 reflections are symmetrically independent from the 4825 reflections read. From these, 12 were rejected because they violate the systematic extinctions. You can see these information in the file .rre. In this same file you can see the completeness of the data (63% for theta full (0.76 °).*

*[On the screen: Parameters for electron diffraction data]*

*The default values for the selection of the intensities are:  $g(\max)=2$ , maximal excitation error  $Sg(\text{matrix})=0.01$ , maximal excitation error  $Sg(\text{refine})=0.1$  and  $Rsg=0.4$ .*

#### 15. Optimization of thickness

Enable “Except of scale optimize also: Thickness”, “Run optimizations”.

*[On the screen: Intensity calculation for optimizing of thickness].*

*Dyngo calculates  $wR$ -factor for the thickness varying from 0 to 2000 Å.*

“Show thickness plots”. Check the variation of the thickness of the crystal for the frames. Quit.

*Most frames have well defined  $wR$ -factor minima for one thickness. However, some frames either have poorly defined minimum or the minimum is defined for very different thickness. For example frames 13, 18, 22 and 44 have a plateau for thickness between 0 and 400 Å. Frame 36 have minimum at very high thickness (around 1500 Å). Check the problematic frames. You will notice that for most frames there is no problem with the reflection image, in this case, and for some of them 1 or 2 reflections are stronger the all the rest. Notice also that the maximum  $R$ -factor is 17.64% for the last frame. You can check the  $wR(\text{all})$  going through the zones in the main window of “parameters for electron diffraction data” or while seeing the graphs. The different thickness is not a problem now, but if the frame would have some problem (the crystal mostly moved from the beam, for example) it could be removed from the refinement.*

#### 16. Defining all the zones with the same thickness

“Define zones of equal thickness”. “Select all”, OK.

*The crystal is a nanowire and the thickness is mostly constant along the sample. However, the thickness changes according to the tilt of the sample, because the nanowire lies roughly perpendicular to the tilting axis of the sample holder. Then, it is possible to define the same thickness for all the frames but still refine the variations of the thickness according to the tilting of the sample.*

*There are two ways of defining the same thickness of the crystal for all the frames. You can either estimate a reasonable thickness, based on the plots of  $wR$  versus thickness, and type it for all frames, or run 0 cycle of refinement and average the thickness. It will be used the first option here. From the plots the minima are well defined mostly for EDThick under 200 Å. Also based on the image of the crystal (it can be measured using imageJ) 150 (15 nm) for EDThick is a reasonable value.*

“Select zones for editing → Select all → OK” and type 150 for “EDThick”. OK, Yes.

Right-click on icon “Refine”, change the number of cycles to 100 and the damping factor to 0.3 in order to avoid instability of the refinement.

*The refinement runs 23 cycles, each cycle takes less than 2 minutes (depending on your computer). You can see the details of the refinement in the file Ni2Si.ref (Edit/View → View of Refine). The refinement converges with  $R=7.79\%$ . However, the ratio reflections per parameter refined is around 5 (454/84) and it is advisable to increase it. It can be done by changing RSg (selecting more reflections for the refinement).*

*Another important thing to check is the number of observed reflections per zone. Also in the Ni2Si.ref file, you can see “R-factors for individual zones”, where it is shown the list of zones with the respective R-factors and number of reflections.*

## 17. Optimization of orientation

Save a new structure “File → save as → Ni2Si\_dyn\_ori”, OK, Yes.

“Parameter → electron diffraction”, change the “Limit on RSg” to 0.75

Enable “Run optimizations except of scale optimize also: Orientation”, “Run optimization”.

[On the screen: Intensity calculation for optimizing of orientation].

*Check the EDTheta for the frames. As said before, the orientation of the crystal during the measurement plays an important role in the dynamical scatterings. Typically, a deviation of  $0.5^\circ$  is already considered high. The frames with high misorientation are: 8, 24, 32, 41, 60, 61, 62 and 73. If you check these frames, most have few reflections (because the unit cell is small), the reflections are mostly weak (the nanowire is very thin) and some frames have 1 or 2 peaks visibly stronger than the rest. These stronger reflections dominate the optimization and hamper the correct estimative of orientation. Frames with EDTheta larger than  $0.5^\circ$  will be removed from the refinement.*

“Select zones for refinement”

Disable the frames 8, 24, 32, 41, 60, 61, 62 and 73 (Ctrl + left mouse button).

OK, OK, Yes. Double click on “Refine”.

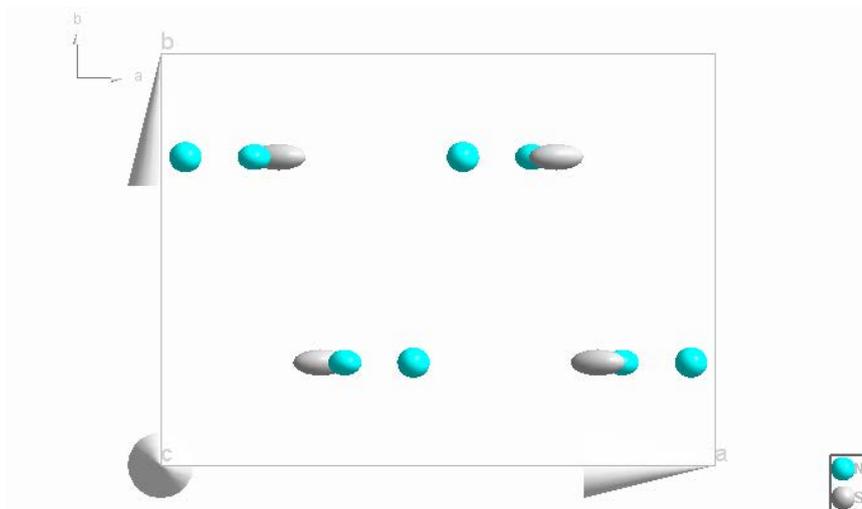
*The refinement converges with  $R=7.11\%$  after 13 cycles. Since there are more reflections, it is possible to refine the anisotropic displacement parameters.*

## 18. Refinement of anisotropic atomic displacement parameters

Save the structure as Ni2Si\_dyn\_ori\_aniso, "Edit atoms→select all→double click in one of the atoms→ADP parameter(s): harmonic", OK, OK, Yes  
[On the screen: Mains window of Jana2006].  
Double-click on icon "Refine".

Now the refinement converges with  $R = 6.52\%$  after 15 cycles. If you check the ellipsoid model, you will see that Si is elongated along  $a^*$ , which was the noisiest direction when defining the unit cell.

**Final structure model:**



# Example 13.6:

## Orthopyroxene from EDT

A complete procedure from structure solution to dynamical structure refinement from electron diffraction tomography data.

Revised: 13 October 2015

Warning: this is a complex and time-consuming example. The computations in the last stages may take up to several hours.

Input data: directory dp with the set of experimental data,  
opx.pts: input file for PETS – the data reduction program  
opx\_start.cif\_pets and opx\_dyn\_start.cif\_pets: results of the data processing. These files are provided so that this example can be solved without the data processing part, and to warrant reproducibility of the second part. Files opx.cif\_pets and opx\_dyn\_start.cif\_pets is the output of the data reduction.

### 1. Data reduction using PETS

*The data processing part follows exactly the procedure described in example 13.1. Please follow that tutorial. Here only key results are provided for your control, and comments are provided for stages that require special attention. Be aware that the peak search and integration take a long time, because the original images are rather large.*

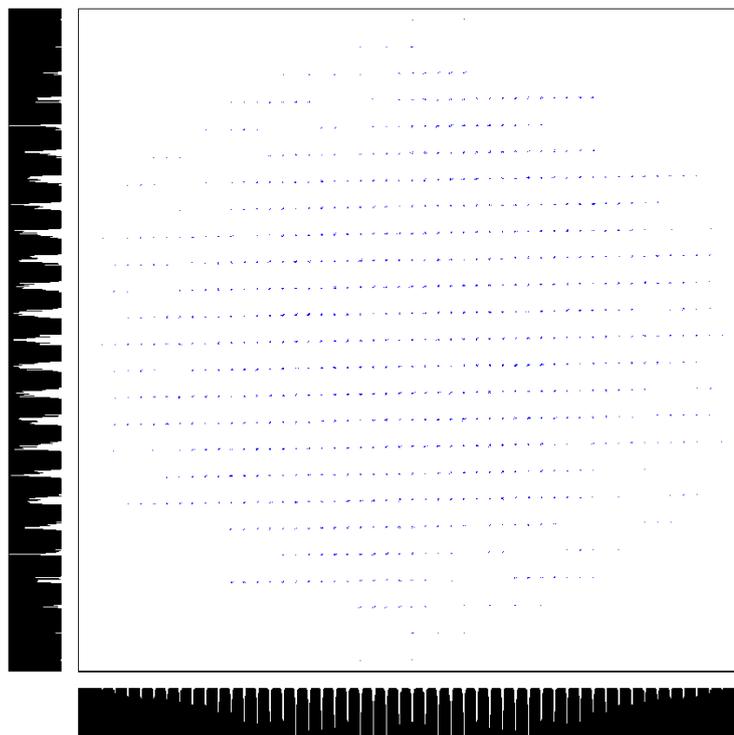
*Parameters filled in the prepared file opx.pts:*

```
reflectionsize 30  
beamstop no
```

*Refined azimuthal angle omega of the tilt axis:*

```
omega : 57.922
```

*Unit cell is orthorhombic, primitive. The following screenshot is the view of the reciprocal lattice along the axis c (a\* horizontal, b\* vertical):*



Final refined cell parameters (refined against the peaks in *opx.clust*):

a	18.463	b	8.881	c	5.239	alpha	90.03	beta	89.98	gamma	90.94
---	--------	---	-------	---	-------	-------	-------	------	-------	-------	-------

Quit the indexing plugin to create file *opx.smr* with the orienting matrix, and continue data processing in PETS by typing `u[Enter]` to read in the orienting matrix, and `i[Enter]` to integrate the intensities.

PETS produced file *opx.cif\_pets*, which contains intensities suitable for structure solution and kinematical refinement. We have to produce another intensity set for dynamical refinement: In PETS type `d[Enter]`

PETS will make another integration, this time producing file *opx\_dyn.cif\_pets*.

Type `h[Enter]` and `y[Enter]` ]to produce a standard set of sections through reciprocal space.

The sections will be useful for confirming the space group.

With this step the data processing in PETS is finished.

Type `q[Enter]` to close PETS. You may also close ImageJ.

## 2. Create new structure

**Important!** The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the files *opx.cif\_pets* and *opx\_dyn.cif\_pets* that you just created, but use the files *opx\_start.cif\_pets* and *opx\_dyn\_start.cif\_pets* provided with the example files (Rename the files to *opx.cif\_pets* and *opx\_dyn.cif\_pets*). Using your own *cif\_pets* files is possible, but your results may slightly differ from the results described in this tutorial.

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate the directory with input files

Right pane: double-click *opx*

### 3. Import Wizard

Select "Known diffractometer formats"; NEXT

Select "Pets electron diffractometer"

The file name automatically changes to *opx.cif\_pets*, which is a file produced by PETS containing all important information, including the list of intensities.

NEXT

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

The program reads 5232 reflections from the file

OK

For absorption correction select "None or done before importing"; NEXT

FINISH; OK; YES to accept the data set

You just read in the experimental parameters, cell parameters and the intensity list.

### 4. Symmetry Wizard

NEXT to close the information window and start the wizard

Symmetry Wizard can be started separately by "File → Reflection file → Make space group test."

The default settings are prepared from x-ray diffraction. For electron diffraction the tolerances should be increased so that Jana properly detect that the cell is orthorhombic. Change the tolerances according to this screenshot:

The screenshot shows a dialog box titled "Tolerances for crystal system recognition:" and "Tolerances for space group recognition:". The top section shows "Original cell parameters: 18.525 8.906 5.259 90.04 90.00 89.06". Below this, there are two input fields: "Maximal deviation for cell lengths in [Å]" with a value of 0.2, and "Maximal deviation for cell angles in deg" with a value of 1. The bottom section, "Tolerances for space group recognition:", has two input fields: "Maximal ave(I/sig(I)) for centering" with a value of 100, and "Maximal ave(I/sig(I)) for extinctions" with a value of 100.

Leave other settings default; NEXT; OK

[On the screen: Select Laue symmetry]

Select orthorhombic Laue symmetry; NEXT

The internal R-value of 23.68% is quite acceptable for EDT data.

[On the screen: Select cell centering]

The numbers in the table indicate that the only acceptable lattice type is primitive. In general it is a good practice to check the centering in the reciprocal-space reconstructions.

Select centering P; NEXT

[On the screen: Select space group]

The window shows possible space groups. It can be quite tricky to determine the correct space group form EDT data, as the systematic absences can be violated in electron diffraction. You should use the reconstructions of the reciprocal-space layers to check, if you can see some systematic absences. From the inspection of the section *hk0.pgm* (open the file in ImageJ) the presence of the *a*-glide is quite obvious. The *b*-glide and *c*-glide conditions in the files *0kl.pgm* and *h0l.pgm* are violated by a couple of weak reflections, but still their presence is very likely. *Pbca* is therefore a good first guess.

Select *Pbca*; NEXT

*Note that a wrong choice of the space group is not detrimental for the structure solution, because we will use Superflip, which will make additional check for the most probable space group.*

Accept the space group in the standard setting; FINISH

*Symmetry is saved in file opx.m50.*

#### 5. **Creating refinement reflection file**

*In this step the program creates file opx.m90 containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.*

Proceed with the wizard, leaving all settings default.

#### 6. **Structure Solution Wizard**

OK to close the information window and start the wizard

*[On the screen: window of Structure solution]*

*Structure solution wizard can be executed separately through "Run → Solution".*

*Jana2006 does not contain solution procedures, it calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2006.*

In "Formula" textbox type the expected formula: Fe Mg Si<sub>2</sub> O<sub>6</sub>

In "Formula units" textbox type 8

Click the checkbox next to "Use a specific random seed" and leave the value 111.

*The specific random seed is used just to guarantee reproducibility of the results. For standard work, random seed need not be defined.*

Click the radio button "EDMA – fixed composition"

*EDMA is an external program for interpretation of electron densities. It can take the chemical formula and interpret the density using this formula.*

Leave other settings default; OK

*[On the screen: window of Superflip appears with iteration running. After ten runs, listing of Superflip log file is displayed]*

*Superflip performed ten solution attempts. Check the space groups derived by Superflip from each of the attempts. In eight out of ten cases the proposed space group is Pbca. It is thus likely (though not guaranteed!) that Pbca is indeed the correct space group.*

Press CLOSE to leave the listing but stay in the dialog "Structure solution

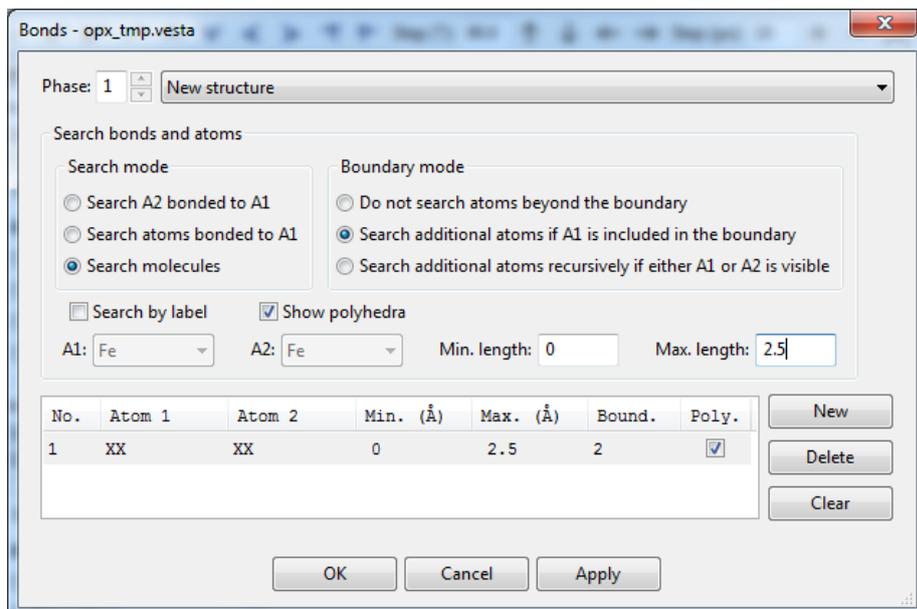
*The result is a file opx.m40 with atoms of the structure model.*

#### 7. **Verification of the structure solution**

Click "Draw 3D map"

*VESTA opens with a density shown as isosurfaces, and an atomic model overlaid. Rotate the view to inspect the structure. Try to recognize the structural motifs. The main expected motifs are SiO<sub>4</sub> tetrahedra and (FeMg)O<sub>6</sub> octahedra. The analysis will be simpler if you display the atomic bonds:*

Go to Edit → Bonds, and set up the options according to this screenshot:



Viewing the structure solution in VESTA has the advantage that you can directly check, if the raw density was correctly interpreted. In this case, the solution is very good and all atoms are properly located. The only problem is that some cations have been assigned a wrong atomic type. By inspecting the structure you should come to the conclusion that the following two atoms need to be changed:

Mg1 -> Si

Si2 -> Mg or Fe – we will choose Mg for the moment

Quit VESTA (do not save changes)

Click “Accept last solution”

## 8. Change the atomic types

Double click icon Edit atoms

Double click atom Si1

Change its name to Mg2

Change its atomic type to Mg

OK

Repeat the procedure for the atom Mg1 and rename it to Si2

Close the dialog for editing atoms and confirm changes

## 9. Structure refinement

[On the screen: basic window of Jana]

Double click the icon Refine.

Refinement converges smoothly to an R value about 25%.

The octahedral positions are not exclusively occupied by iron or magnesium, but by both elements. We have to refine the mixed occupancy in these sites.

[On the screen: basic window of Jana]

Double click icon Edit atoms

Right-click atom Fe1 → Split atomic position

Set up the dialog according to the following screen shot:

**Split atomic position for : Fe1**

Name of the split atom:

Atomic type:  ▼

Relative occupancy of the split atom:

Shift of the split atom:

Generate restrict commands for REFINE

Restrict the split atoms to have identical positions

Apply

Repeat the procedure with Mg2 to generate atom Fe2 at the same position.

*The procedure generated a pair of atoms with restricted ADP parameters and coordinates and with a restricted sum of occupancies. The only small problem (although rather esthetic than real) is that in one pair the Fe atom is the “Master” and Mg the “slave”, while for the other pair it is vice versa. We will modify the restrictions to be both the same.*

*[On the screen: basic window of Jana]*

Right-click Refine → Various → Restrictions

Load the restriction on atoms Mg2 and Fe2

Exchange the order of atoms in the restriction (type Fe 2 Mg2 in the line “Atoms/molecules), so that Fe is the “master” atom. Rewrite the restriction. When finished, the dialog should look like this:

restrict Fe1 1 Mg1  
restrict Fe2 1 Mg2

Load ▼

Make identical:  Coordinates    Occupancies:  keep overall sum  
 ADP parameters                     not restricted

Atoms/molecules

OK; OK; Yes (do not start refinement yet!)

*Now we have restricted the atomic pairs, but the occupancies are still fixed and would not be refined. We have to allow their refinement explicitly:*

Double click the icon “Edit atoms”

Double click atom Fe1

On the card “Edit” check the box next to the parameter “ai”;

Repeat for atom Fe2

OK to close the Edit atoms dialog

Double click Refine to start refinement

Refinement converges to R-value of 24.25%. The refined atomic occupancies are:

Fe1: 0.44(5)

Fe2: 0.44(5)

Note that the equal occupancies and their e.s.d. is a pure coincidence and not a result of some restriction or symmetry.

## 10. Set up dynamical refinement

At this moment there is very little we can do with the kinematical refinement. We have a satisfactory refinement, the structure makes sense, the occupancies have been refined, but their accuracy cannot be estimated from the kinematical refinement. Furthermore, some ADPs are negative. We will now proceed to the structure refinement using dynamical diffraction theory.

File → Structure → Save as

Save the structure as opx\_dyn

Answer Yes to the question if you want to continue with the new structure

File → Reflection file → Import/modify the reflection file

Reimport; Browse for the file opx\_dyn.cif\_pets; NEXT; NEXT; NEXT; OK; NEXT; Finish; OK;

Yes

You have just replaced the previous reflection data with new data set suitable for dynamical refinement.

Cancel to avoid the production of refinement reflection file

If we continued, we would have produced a symmetry-averaged file for kinematical refinement. For dynamical refinement the intensities on each frame must be kept separate.

We will now enable the dynamical refinement option:

Go to “Parameters → Electron diffraction”

Check the checkbox “Use dynamical approach”

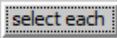
Proceed with creation of the reflection file, leave all settings default.

At this point we are ready to start dynamical calculations. Because the calculations are very time consuming, we will not, in this example, use all 90 zones, but only nine selected zones.

Click “Select zones for refinement”; In the line below the table, set the following:



From the zone#	10	select each	10	th zone
----------------	----	-------------	----	---------

Click the button ; OK

Only zones 10, 20, 30, 40, 50, 60, 70, 80 and 90 are now selected for refinement.

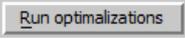
The data collection was performed on one crystal and there is also no reason to expect that the thickness varies for each zone. We will therefore restrict the thickness to the same value for all zones:

Click “Define zones of equal thicknesses; Select all; OK

Dyngo – the external executable that performs the heavy calculations – can run in a parallel mode. In the field “Number of threads” you can decide, how many parallel threads Dyngo may use. For the fastest performance set this number to the number of cores of your processor. **Important!** Most Intel processors indicate twice as many threads available than

they have cores due to the hyper-threading technology. Do not set the number of threads to the number of threads available on your processor, but to the number of true distinct cores!

As a first step we have to check, if our model fits the data sufficiently well to start the refinement. For that, we will run thickness optimization. This procedure is relatively fast, and for each selected zone it calculates an R-value as a function of thickness. For good data set and reasonable starting model, this curve should have a minimum at a meaningful thickness, and all curves should indicate approximately the same thickness.

Check the checkbox next to “Thickness” and click 

Jana calls Dyngo for each zone. When the calculation is finished, each selected zone has next to the zone number in the dialog the best R-value, e.g.:

Zone #:   R(all)= 13.3208%

All zones' R-values are lower than 20%, some of them even lower than 10%. This is a pretty good start.

Click “Show thickness plots”

Now you can view the curves R-value vs. thickness for all zones. In most cases the curve has a well-defined minimum, only in zones 30 and 70 the minimum is at the lowest thickness. The best thickness varies in a relatively broad interval, but the minima are broad, and our structure model is far from perfect at this stage, so this is not surprising.

Quit the viewer of the thickness curves

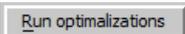
We want the thickness to be the same for all zones in the refinement. Now the thicknesses are all different and we should reset them to a common most appropriate value. The best practice seems to be a visual estimation of the “typical” thickness in the thickness plots. In this case 500 angstroms seems to be a good guess. Do not worry about the inaccuracy of such guess – the thickness is a very robust parameter and it will refine to the correct value even from a quite distant start.

Click “Select zones for editing”; “Select all”; OK

Double click the yellow field EDThick and type “500” in the field

This procedure reset the thickness of all zones to 500 angstroms.

We have to recalculate the scale factors for each zone, because the scale changes with changing thickness:

Click the button  without any other checkbox checked (neither thickness nor Orientation)

When the calculation finishes, click OK to close the electron diffraction dialog.

You can now start the structure refinement.

[On the screen: basic window of Jana]

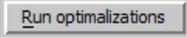
Double click the icon Refine

After the first cycle the refinement R-value Robs is 13.13%. After 5 cycles the refinement should converge to an R-value of 8.29%.

In the next step we will optimize the orientation of each zone. Due to the inaccuracy of goniometer positioning and orientation matrix, the positional angles of each diffraction pattern are not exactly correct, and a correction should be found.

Go to “Parameters → Electron diffraction”

Check the checkbox next to “Orientation”

Click the button 

*An optimization procedure starts that finds the best zone-axis orientation for each pattern. Wait until the calculation finishes. Now you can now run a few more cycles of structure refinement.*

Click OK to close the form “Electron diffraction”

Double click the icon Refine

*The refinement converges after 10 cycles to an R-value of 5.10%. Inspection of the structure model shows that the occupancies of Fe1 and Fe2 refined to 0.33(3) and 0.06(2), respectively. This is still relatively far from the values from x-ray refinement, which are 0.432(3) and 0.157(3). However, there are only 188 observed reflections in this limited dataset for the refinement of 52 parameters. The data to parameter ratio is thus poor. If all 90 zones are included in the refinement and the whole procedure is repeated with them, the final result is:*

*Robs=5.89%*

*occ(Fe1)=0.389(7)*

*occ(Fe2)=0.148(7)*



# Example 20.1: CeAsSe

Merohedric twin with extinction imported from SHELX to Jana2006.

**Chemical formula: CeAsSe**

**Reference:** Structure provided by Max Planck Institute for Chemical Physics of Solids

Input files: CeAsSe.hkl, CeAsSe.ins

## 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate the directory with input files

Right pane: double-click CeAsCe

## 2. *Importing structure from SHELX*

*[On the screen: Specify type of the file to be imported]*

Select “Structure – from SHELX”; Next

In File manager double-click CeAsSe.ins

*The program reads the structure, detects the presence of CeAsSe.hkl and starts import of reflections*

Go through the usual steps of the Import Wizard

Rint = 4.69%

## 3. *Checking the twinning of the imported structure*

Start EditM50

The twinning check box must be selected

Press “Matrices”

The twinning matrix should be 0 1 0 | -1 0 0 | 0 0 1

Leave EditM50

Start “Parameters → Twin fractions”

The parameter “twvol2” must be 0.46346

Activate refinement of “twvol2”

Save the changes and leave to the basic window

## 4. *Refinement*

Run refinement

It converges with R=3.2%

Open refinement listing, GoTo Statistics

Higher R value for the strongest reflections indicates that extinction correction is needed

Close the refinement listing

Start “Parameters → Extinction”

Activate Isotropic extinction with Gaussian model

Save changes and leave to the basic window

Repeat refinement

It converges with R=2.75%. The reason extinction has not been imported from the ins file is that SHELX and Jana use different parameters for extinction correction



# Example 20.2: HfPdGe

Six-fold twin with reflections in HKLF5 format, imported from SHELX to Jana2006.

**Chemical formula:** HfPdGe

**Reference:** Structure provided by Max Planck Institute for Chemical Physics of Solids  
Input files: HfPdGe.hkl, HfPdGe.ins

## 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate the directory with input files

Right pane: double-click HfPdGe

## 2. *Importing structure from SHELX*

*[On the screen: Specify type of the file to be imported]*

Select “Structure – from SHELX”; Next

In File manager double-click HfPdGe.ins

*The program reads the structure, detects the presence of HfPdGe.hkl, automatically recognizes HKLF5 format and starts import of reflections*

Go through the usual steps of the Import Wizard

Rint = ----

## 3. *Checking the twinning of the imported structure*

Start EditM50

The twinning check box must be selected, number of twin domains should be six

Press “Matrices”

The twinning matrices are all unit matrices because for HKLF5 data they have just a formal meaning

Leave EditM50

Start Parameters → Twin fractions

The parameters “twvol2”, .... “twvol6” must contain the numbers from the BASF commands of the ins file.

Activate refinement of all twin volume fractions

Save the changes and leave to the basic window

## 4. *Refinement*

Run refinement

It converges with R=4.1% for 60 parameters. There were very large changes of the twin fractions during the refinement because probably the order of twin fractions in SHELX and Jana differs.

Open refinement listing, GoTo Statistics

There is no indication of extinction and at the bottom of the listing no warnings.





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## Notes

The *Rint* statistics seems to suggest tetragonal symmetry. However, the lattice is C-centered (as will be confirmed on the next slide) and this excludes the tetragonal symmetries.

Select centering **C** unit cell; **NEXT** (Step 3)

[On the screen: Select space group]

Select **Cmmm**; **NEXT**

Leave all settings unchanged; **FINISH**

**Step 2**

Crystal system	Point group	Rint(obs/all)	#averaged	Redundancy
Tridinic	-1	8.70/8.72	973/1067	3.685
Monoclinic-setting "a"	2/m	10.13/10.15	589/633	6.212
Monoclinic-setting "b"	2/m	9.52/9.54	536/576	6.826
Monoclinic-setting "c"	2/m	9.88/9.90	587/630	6.241
Orthorhombic	mmm	10.41/10.42	350/371	10.598
Tetragonal	4/m	10.31/10.33	415/443	8.876
Tetragonal	4/mmm	10.67/10.68	294/310	12.684

**Step 3**

Centering	obs/all	ave(I/sig(I))
<input type="radio"/> P	0/0	0.000/0.000
<input type="radio"/> A	1718/1999	12.036/10.624
<input type="radio"/> B	1718/1999	12.036/10.624
<input checked="" type="radio"/> C	0/0	0.000/0.000
<input type="radio"/> I	1717/1964	14.047/12.499
n.a. R-obverse	2256/2623	13.658/11.998
n.a. R-reverse	2251/2619	13.649/11.989
<input type="radio"/> F	1718/1999	12.036/10.624

Warning: The cell centering need not be one you expect from collection as the program first transform the cell to the reduced form. Moreover after your selection the program makes another transformation whenever the centering is not the standard one.

Creating refinement reflection file

**NEXT** to confirm threshold 3sigma; **OK**; **OK**

[On the screen: settings for merging of reflections]

**NEXT**

The program reports *Rint* 10.41% for 350 observed reflections merged from 371 observed reflections.

**OK**;

Select "Accept the new data block and calculate coverage"; **FINISH**; **OK**

Structure solutions wizard

[On the screen: Structure solution]

In "Formula" textbox type list of chemical elements: **U Ge Fe**

Select "**Use Superflip**";

Check "**Repeat Superflip: Number of runs**" leave **10**

Leave other settings default; press "**Run solution.**"

[On the screen: the window of Superflip replaced after reaching the convergence with a listing of Superflip]

Press **CLOSE** to leaving the listing

Press **Accept last solution**

Refinement

Start **EditM50**;

Go to page Composition; enter **2** for "Formula units," press "**Formula from M40.**"

**OK**; **YES**; **OK**; **YES**;

## Notes

It displays formula **U3 Ge7 Fe2** (for Z=2) which correspond to the expected composition. If some atoms are missing in your case, run refinement and use a difference Fourier map to find missing atoms.

**INFORMATION**

Formula from M40 : U3 Ge7 Fe2  
Molecular weight = 1333.91  
Calculated density = 10.2477 g.cm<sup>-3</sup>  
Absorption coefficient  $\mu(\text{Mo-K}\alpha)$  = 83.063 mm<sup>-1</sup>

**Run Refine;**

Notes

*R factors [371=350+21/13]*  
*GoF(obs)  $\approx$  5.11;*  
*R(obs)  $\approx$  7.44; wR(obs)  $\approx$  9.70; R(all)  $\approx$  7.74; wR(all)  $\approx$  9.74*

Start **Edit atoms;**

Press "**Select all**" then "**Action**" and select "**Edit/Define atoms.**"

Change the ADP parameter(s) from isotropic to **harmonic** (anisotropic);

**OK; OK; YES**

**Run Refine;**

Notes

*R factors [371=350+21/27]*  
*GoF(obs)  $\approx$  4.57;*  
*R(obs)  $\approx$  6.15; wR(obs)  $\approx$  8.49; R(all)  $\approx$  6.35; wR(all)  $\approx$  8.51*  
**Warning** due to Negative ADP of atoms

Start **EditM50;**

Go to page Composition; press "**Calculate density.**"

**OK; OK;**

Notes

*Molecular weight = 1333.91*  
*Calculated density = 10.2477 g.cm<sup>-3</sup>*  
*Absorption coefficient  $\mu(\text{Mo-K}\alpha)$ = **83.063** mm<sup>-1</sup>*

*By default, CrysAlis uses very small value of  $\mu$  because most measured structures are not strong absorbers. In CrysAlis,  $\mu$  can be edited to proper value and in such case the corrections would be done correctly. **In this example, we have intentionally used small  $\mu$  in CrysAlis in order to simulate the situation of wrongly corrected data.***

File -> structure -> Save as (Create backup copy) **U3Fe2Ge7\_s1**

**NO** (you don't want to continue with the new structure)

## II. Absorption correction

### 1. Correction for a spherical sample + empirical correction + frame scaling

#### Notes

Here we simulate situation when crystal shape is unknown

File -> Reflection file -> **Import/modify the reflection file**

[On the screen: Data repository]

Select **"Modify"**

[On the screen: Define parameters for absorption and scaling procedure]

Select **"correction for spherical sample"** and add radius of the sphere [mm] equal to **0.057**

Check **"Empirical correction and/or frame scaling"; NEXT; (Step 1)**

[On the screen: Define parameters for frame scale and/or empirical absorption correction]

Check **"Scale frame"**, **"Optimize coefficients of spherical harmonics"** using **8** harmonics and

**"Use odd harmonics"** using **7** harmonics (Step 2)

For large absorption, we use maximal number of spherical harmonic functions

**Run optimization;**

This configuration gives a similar  $R(int)$  as the default absorption correction done in CrysAlis.

#### Step 1

#### Step 2

Press **"Accept optimized parameters";**

**OK; Finish; OK;**

#### Notes

Here you can find the evolution of parameter as a function of spherical harmonics parameters

Spherical harmonics	Odd harmonics	R(int)	Rw(int)	T(min)	T(max)
0	0	16.342	21.398	0.0016	0.0105
2	0	13.415	17.718	0.0064	0.0407
4	0	12.275	16.467	0.0065	0.0433
6	0	12.023	15.824	0.0060	0.0407
8	0	11.972	15.597	0.0058	0.0396

	8	1	11.498	14.490	0.0065	0.0481
	8	3	11.190	13.863	0.0063	0.0582
	8	5	10.875	13.511	0.0064	0.0652
	8	7	10.598	13.448	0.0063	0.0859

**NEXT** to confirm threshold  $3\sigma$ ; **OK**; **OK**

*[On the screen: settings for merging of reflections]*

**NEXT**; **OK**;

Select "Accept the new DatBlock and calculate coverage"; **FINISH**; **OK**

**Run Refinement**

Notes

*The resulting R value is similar like before but there are no warnings about ADP*

File -> structure -> Save as (Create backup copy) **U3Fe2Ge7\_s2**

**NO** (you don't want to continue with the new structure)

Correction for an indexed shape + empirical correction + frame scaling

Notes

*Here we simulate situation when crystal shape is known. Unfortunately, the shape of this sample is not far of a sphere so the advantage of using the indexed shape is not convincing. For more anisotropic shape using of the indexed shape would bring a real benefit.*

File -> Reflection file -> **Import/modify the reflection file**

*[On the screen: Data repository]*

Select "**Modify**"

*[On the screen: Define parameters for absorption and scaling procedure]*

Select "**Gaussian integration method.**"

**Check** "Empirical correction and/or frame scaling" (Step 3)

Notes

*You can observe the crystal shape if you click on Edit Face -> Show the shape*

**NEXT**;

*[On the screen: Define parameters for frame scale and/or empirical absorption correction*

Check "Scale frame", "Optimize coefficients of spherical harmonics" using **8** harmonics and "Use odd harmonics" using **7** harmonics (Step 4)

**Run optimization**

*This configuration gives a better  $R(int)$  than the previous method.*

### Step 3

Define parameters for absorption and scaling procedure

None or done before importing

Correction for spherical sample  radius of the sphere [mm]

Gaussian integration method:  integration grid

Empirical correction and/or frame scaling Crystal shape enclosed by 17 faces

Define absorption coefficient =>

Define formula =>    
Number of formula units

### Step 4

Define parameters for frame scale and/or empirical absorption correction

Apply cutoff for weak reflections => Reflections with  $I \leq$   % of  $I(\max)$  will be skipped

Apply cutoff for strong reflections => Reflections with  $I \geq$   % of  $I(\max)$  will be skipped

Apply culling => Reflections  $|I-I(\text{ave})| >$   % of  $I(\text{ave})$  will be culled

Limit maximal number of unique reflections =>

Scale frames Set  frames= scale    
 Use step-like correction  Use linear approximation

Optimize coefficients of spherical harmonics Number of even harmonics:   
 Use odd harmonics Number of odd harmonics:

Use the point group from m50: mmm  
 Define point group

Press “Accept optimized parameters”;

OK; Finish; OK;

NEXT to confirm threshold 3sigma; OK; OK

NEXT; OK;

Select "Accept the new DatBlock and calculate coverage"; FINISH; OK

Run Refinement

#### Notes

*Refinement results are better than before*

*R factors [371=350+21/27]*

*GoF(obs)  $\approx$  4.40; R(obs)  $\approx$  5.35; wR(obs)  $\approx$  8.17; R(all)  $\approx$  5.54; wR(all)  $\approx$  8.19*

File -> structure -> Save as (Create backup copy) **U3Fe2Ge7\_s3**

**NO** (you don't want to continue with the new structure)

Correction for refined indexed shape + empirical correction + frame scaling

File -> Reflection file -> **Import/modify the reflection file**

[On the screen: Data repository]

Select “**Modify**”

[On the screen: Define parameters for absorption and scaling procedure]

Select “**Gaussian integration method.**”

**Check** “Empirical correction and/or frame scaling” (Step 5)

Press “Edit faces”

[On the screen: Face specification]

## Notes

The form allows for running the X-shape program. This is very practical software for refinement of the crystal shape to get a shape minimizing differences between intensities of symmetrically equivalent reflections. Unfortunately, X-Shape is a part of Stoe diffractometer software and cannot be freely distributed. For this reason, we provide result of the shape refinement as a crs file, which will be imported in the following step.

Press “Read from file” and import **U2Fe3Ge7.crs** file (Step 6)

OK; OK; OK

**NEXT;**

**Step 5**

Define parameters for absorption and scaling procedure

None or done before importing

Correction for spherical sample  radius of the sphere [mm]

Gaussian integration method:  integration grid

Empirical correction and/or frame scaling Crystal shape enclosed by 17 faces

Define absorption coefficient =>

Define formula =>

Number of formula units

**Step 6**

Face specification

	Indices	d [mm]
1st face	-6 -2 0	0.0502
2nd face	5 -14 -3	0.0614
3rd face	0 30 -3	0.041
4th face	-1 -18 -5	0.0696
5th face	4 -21 2	0.0669
6th face		
7th face		
8th face		
9th face		
10th face		

[On the screen: Define parameters for frame scale and/or empirical absorption correction  
Check “Scale frame”, “Optimize coefficients of spherical harmonics” using **8** harmonics and  
“Use odd harmonics” using **7** harmonics

### Run optimization

Resulting  $R(int)$  is slightly better compared with the original unrefined shape.

Press “Accept optimized parameters”;

OK; Finish; OK;

NEXT to confirm threshold 3sigma; **OK; OK**  
**NEXT; OK;**  
Select "Accept the new DatBlock and calculate coverage"; **FINISH; OK**  
**Run Refinement**

#### Notes

*Refinement gives almost identical results like with the unrefined shape. Again, with more anisotropic shape the benefit of the shape refinement would be more convincing.*

File -> structure -> Save as (Create backup copy) **U3Fe2Ge7\_s4**  
**NO** (you don't want to continue with the new structure)

#### Conclusion

*Because the real shape is close to a sphere, the three methods for data correction yield very similar results. Also difference Fourier maps are similar.*

## References

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**Revised: 10 May 2015**

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*Taking a closer look for a broader view: combining powder diffraction with electron crystallography for a better understanding of modulated structures*



## Header

kType	2	for Jana2006
KADoublet	0	data for data measured with wave length
	1	for $K\alpha_1$ and $K\alpha_2$
DataType	0	X-ray/neutron CW data
	1	TOF data as a function of time
	2	TOF data in d values
	3	energy dispersive data
NPhases		number of phases
(NDim(i),i=1,NPhases)		number of indices used for each phases

## Bragg positions

h,k,l,...	n diffraction indices, where $n = \max(\text{NDim}(1), \dots, \text{NDim}(\text{NPhases}))$ . For phases having the dimension smaller than n the indices are completed by zeros.
Multiplicity	multiplicity of the reflection following from the symmetry
KPhase	defines the phase the reflection belongs to
<i>The following four items are repeated twice if KADoublet=1. The first block corresponds to <math>K\alpha_1</math></i>	
TwoTheta/Time/d/energy	angular position/time (or for TOF d value/energy) of the peak as calculated from cell parameters and modulation vectors
Shift	the angular shift of the peak position due to a zero shift, sycos and sysin parameters (it need not be constant for all reflections). The actual of reflections with respected to the profile should be calculated as: [TwoTheta/Time/d/energy] -Shift
FWHM	in the same units are previous values
Icalc(h,k,l)	intensity as calculated from Rietveld (corrected for multiplicity and preference orientation) or as extracted from the profile by le Bail fit.
<i>The list of Bragg peaks ends with the integer 999 at the position of the h index.</i>	

## Profile points

TwoTheta/Time/d/energy	diffraction angle/time for TOF/d value/energy of the profile point
Iobs	observed intensity
Icalc	calculated intensity
sig(Iobs)	standard uncertainty of Iobs
TwoTheta-corr/Time-corr/d-corr/energy-corr	diffraction angle/time for TOF/d value/energy of the profile point corrected for zero shift, sysin and sycos
Icalc	calculated intensity
Skip flag	0 if the profile point was used in the refinement
	1 if the profile point belongs to one of excluded region
Icalc(1)	calculated intensity of the first phase
	...
Icalc(NPhases)	calculated intensity of the first phase
Ib	background intensity
<i>The list of peak points ends with the real number "999".</i>	