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Crystallographic computing system Jana2006: solution and refinement of twinned structures

DOI 10.1515/zkri-2016-1956
Received May 4, 2016; accepted August 25, 2016

Abstract: Twinning is a phenomenon complicating structure analysis of single crystals of standard as well as modulated structures. Jana2006 as a software for advanced structure analysis contains tools for recognition and refinement of twins including most complicated cases of modulated and magnetic structures. In order to efficiently use the tools of Jana2006 related to twinning, we explain the basic terminology and the underlying theory, especially the symmetry of the diffraction patterns affected by twinning. We present typical diffraction patterns of twins and show how twinning can be recognized or detected by various tools and described with twinning matrices. Data processing of twins and ways of how they can be imported to Jana2006 are also discussed. Two examples demonstrate the solution of typical twins: twinning by metric merohedry and twinning by reticular merohedry, followed by the third example demonstrating twinning in a commensurately modulated structure. The relationship between the dimensionality of the structure and twinning is discussed, too.

Keywords: crystal structure analysis; Jana2006; twinning.

Introduction

The phenomenon of twinning can occur in various samples of dissimilar origin. Many natural minerals are affected by twinning with macroscopic implications for their morphology and this is why a classification of twins was introduced into science a long time before Max von Laue's discovery of X-ray diffraction [1, 2]. Diffraction theory latter proved that the diffraction pattern of a twin is composed of several superimposed diffraction patterns.

Twinning in the crystal can considerably affect the process of solution and refinement of the particular crystal structure. The occurrence of several independently diffracting domains in a twinned sample can generally lead to considerable or even complete overlaps of diffraction spots. The more overlaps that are present in the diffraction pattern the more difficult it is to solve the crystal structure. On the other hand, as soon as some reasonable structure model is known, the structure finalization by subsequent refinements and difference Fourier syntheses is more or less routine work.

In many cases presence of twin domains in the sample can be influenced by the crystallization method used and conditions of the crystal growth such as temperature, pressure, magnetic or electric field, etc. Very often, twinned and single crystal specimens are present within the same batch and careful sample selection may help to avoid troubles with twinning. Experienced crystallographers can recognize promising samples in a mostly twinned batch by their habitus, often leading to selection of very small single crystals measurable only with microfocus sources. Thus, we have some chance to reduce or even eliminate twinning, but it is certainly not possible in every case.

Generally, the process of twin elimination becomes difficult for twins resulting both from sygnonic merohedry and metric merohedry (pseudo-merohedry with experimentally negligible oblique) [3–5]. Practical issues further complicate the selection: with natural samples available in a very limited number of crystals we simply do not have enough trials, while with unstable samples the limiting factor is the time available for the selection. Finally, there is a special class of experiments investigating phase transitions in a crystal, especially the magnetic ones, where the lowering of symmetry leads naturally to the unavoidable presence of twin domains.

Let us consider that the sample is composed from n twin domains related by the twinning operations expressed by the 3×3 twinning matrices $\mathbf{T}_i$ ($i=1, \dots n$). Without loss of generality we can define that the twinning matrix for the first domain is a unit matrix and thus remaining twinning matrices relate each domain to the first domain. Thus the diffraction indices $\mathbf{h}_i=(h_i, k_i, l_i)$ of the i^{th} domain with respect to the first domain can be expressed as:

$$\mathbf{h}_i=\mathbf{h}_1\mathbf{T}_i \tag{1}$$

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The detected intensity from a twin is expressed as a sum of *n* contributions:

$$\mathscr{F}^2(\mathbf{h}) = \sum_{i=1}^{n} v_i F^2(\mathbf{h}\mathbf{T}_i) \tag{2}$$

$$\sum_{i=1}^{n} v_i = 1 \tag{3}$$

where F is the structure factor, v_i is the volume fraction of the i^{th} twin domain and $\mathscr{F}^2$ is a square of the resulting structure factor related to the measured intensities. For practical reasons, the first domain should be the one with the largest v_i because it has the strongest intensities.

The relatively simple equation (2) is valid only if the main and critical assumption for twinning is fulfilled: twin domains diffract independently and the diffracting domains are randomly distributed within the investigated sample. Then the probability that i^{th} domain contributes to the combined intensity at any diffraction geometry is equal to v_i. Violation of this basic assumption occurs, e.g. in case of large domains in a sample with not negligible absorption (see Figure 1). In such a case the effective volume fractions depend on diffraction indices, actual setting of the crystal for a selected diffraction spot, shape of the crystal and distribution of domains in the sample, and usually they cannot be evaluated, causing failure of structure analysis. Surprisingly, in spite of these very strong limitations the equation (2) describes the resulting intensities for the majority of twinned crystals reasonably well.

The equation (2) can also be used in cases when systematically absent reflections are combined (due to twinning operations) with those fulfilling reflection conditions and also in cases when some of the products $\mathbf{h}\mathbf{T}_i$ lead to non-integer components (the twinning matrices are generally composed from both integers and real numbers). For the latter case we suppose that the structure factor for a non-integer diffraction vector is identically equal to zero.

The main aim of this paper is to explain and present how the twinning affects the various steps of the structure analysis and how demanding task twinning may represent. For this purpose, we shall divide twins into three types in a close analogy with the classification of Nespolo and Ferraris [5]. Each of these types (see Figure 2) requires a different way of handling diffraction patterns and choice of methods used for the structure solution:

Type I: Twins by sygnonic merohedry and metric merohedry (i.e. Class I, IIA and IIB from [5]): The diffraction pattern is composed from diffraction spots having generally non-zero contributions from all *n* twin domains. Such diffraction pattern does not have split reflections and looks like from a regular (non-twinned) crystal. Twinning operations can be derived from the lattice and structure point group. The twinning matrices related to the lattice metrics are built from integers. Individual reflection overlaps

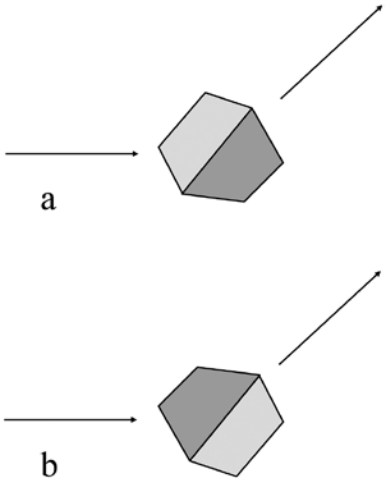


Fig. 1: Example of a sample with not randomly distributed twin domains. Sample orientations (a) and (b) are such that the obtained diffractions are symmetry equivalent. Nevertheless, absorption effects can considerably reduce diffracted intensity from the obscured domain, resulting in different intensities uncorrectable with usual data reduction methods due to unknown geometry of the domains.

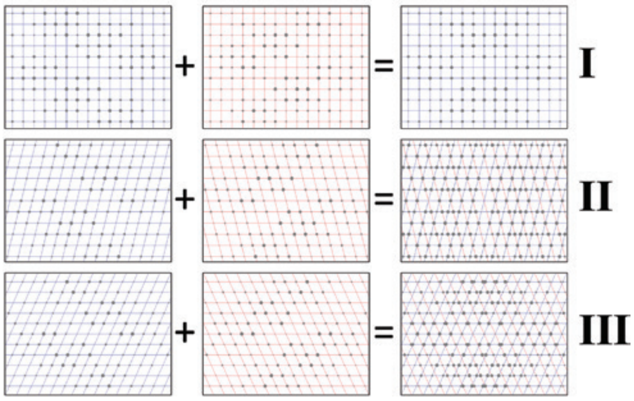


Fig. 2: Examples of three basic types of twins. Type I: two pseudo-orthorhombic lattices of a monoclinic structure related by 180° rotation around a* give rise to the Type I twin diffraction pattern with orthorhombic diffraction symmetry. Type II: Reticular merohedry: two domains of a monoclinic structure related by 180° rotation around a* give rise to a pseudo-orthorhombic reticular lattice – twin index = 2. Type III: Reticular pseudo-merohedry: two domains of a monoclinic structure related by 180° rotation around a* gives rise – twin index = 2.

are completely determined by the twinning matrices.

Type II: Twins by reticular merohedry: The diffraction pattern is composed from diffraction spots having generally different number of contributions from twin domains depending on actual reflections. The twinning matrices are built from rational numbers and they allow predicting all overlaps without any additional information from experiment. There is always some sub-lattice allowing indexing of all diffraction spots from all domains, but some of these points can have systematically zero-contribution from twin domains.

Type III: Pseudo-merohedry with apparent oblique: Twinning matrices contain non-rational numbers. For prediction of overlaps we need to know not only the twinning matrices but also the actual setting of a measured reflection on the diffractometer.

Refinement of twinned structures has been done since the 1980s. In 1982 it was already possible to refine modulated twins by REMOS of Yamamoto [6] who realized an importance of twinning for studies of phase-transitions. The first version of program Jana [7] from 1985, developed for the refinement of regular and modulated structures, was written on the basis of two older programs, LINUX77 and SDS, which already allowed refinement of twins by sygnonic and metric merohedry (Type I), dating refinement of twins to the beginning of the 1980s, too [8, 9]. Also the most widely used program for structure determination SHELX allows refinement of twinned structures [10, 11].

Nevertheless, despite the fact that almost everything about twinning was devised 30 or more years ago, we witnessed a boom of articles about twinning only in the last years. It seems that many older matters have been rediscovered due to a boom of twinned structures measured by area detectors where twinning, especially of the Type II and III, can scarcely be overlooked. Also the quantity of measured structures grows significantly, increasing the probability of encountering all kinds of twinning even within the service crystallography. The diffractometer software like CrysAlis [12] or Apex [13] of the main producers supports automatic detection of twins, which is of great importance for routine structure determinations.

While the overview paper by Parsons [14] makes very nice introduction to twinning, our article focuses on twin tools available in the Jana2006 program and it can be understood as a continuation of our paper [15] about the general features of Jana2006. With developing new procedures for structure analysis of regular, modulated, composite and magnetic structures the twinning option has been considerably improved but till now no review paper reporting this option has been published. This article fills the gap and presents all procedures in Jana2006, which can be used for the study of twinned structures.

Data collection and reduction

Recognition of twins and data collection

The first question is how we can recognize that the crystal is affected by twinning, and how we can get a set of twinning matrices for application of the equation (2) in the subsequent crystal structure analysis. In this section, we will focus on the cases where twinning can be recognized from the diffraction pattern. In many cases, however, the twinning need not be recognized directly either due to complete overlaps of diffractions or week intensities of minor domains. Then, at any stage of the structure analysis, when some problems occur, it is worthwhile to use some testing tools for finding possible twinning. Namely the program Geminography [16] can predict most probable twin laws just on the basis of the known unit cell and assumed point symmetry of the structure. Another possibility is to recognize an overlooked twin problem from a refined structure model, using, e.g. TwinRotMat [17] or ROTAX [18], which are based on comparison of calculated and observed structure factors. Twinning can also be detected by statistical methods – see the section "Type I: twinning matrices from the cosets decomposition".

Type I: twinning matrices from the cosets decomposition

Twins of the diffraction Type I yield a diffraction pattern which looks the same as for a regular crystal (see Figure 2), and data collection process for such twin is the same as for a regular non-twinned structure. There are some special cases of higher symmetrical lattices (tetragonal, trigonal, hexagonal and cubic) for which some specific extinctions can indirectly prove that twinning is present. As an example see Figure 3, in which the orthorhombic extinctions for $(h,k,0)$ $h=2n+1$ induce non-standard extinctions in a tetragonal lattice, $h=2n+1 \wedge k=2n+1$, by the twinning operation 2_{x-y}.

Nevertheless, in most cases the Type I twinning cannot be recognized visually from the diffraction pattern.

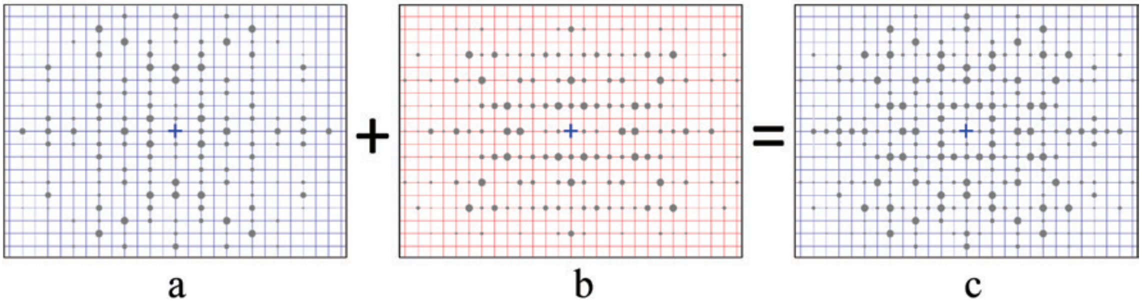


Fig. 3: Non-standard extinction rules indicating the Type I twinning by the four-fold axis along ***c*** in a pseudo-tetragonal lattice of an orthorhombic structure *Pmma*. (a), (b) The reciprocal plane (hk0) for the first and second domain shows the reflection condition $h=2n$. (c) The combined diffraction pattern of a twin with equal volume fractions shows that reflections (hk0) are systematically extinct only if both *h* and *k* indices are odd. The origin is indicated with a blue cross.

We can then distinguish two cases based on the equality or non-equality of the twin volume fractions.

1. If the twin volume fractions are equal, the diffraction pattern simulates exactly a higher Laue symmetry with perfect R_{int} value. In such a case, the twin is recognized indirectly due to difficulties with structure solution or refinement.
2. For unequal twin volume fractions, the higher symmetry is fulfilled only approximately (e.g. with R_{int} 0.1–0.2), which alerts us that twinning would be possible.

In both cases, in order to find a better solution or better merging R value, we can try to lower symmetry from the holohedral point group to a sub-group by using a group–subgroup relationship. The twinning matrices can be deduced from the relationship between the point symmetry *H* of the lattice and the point symmetry of the crystal structure *G*. The twin operations can be selected as arbitrary chosen representatives from each coset [19]. Again, without loss of generality we can select the first twinning operation as an identity operator. Correct twinning matrices are recognized indirectly from the fact that the structure model refinement converges with a reasonably low R value or that geometry of the structure model has improved, e.g. incorrect distances or disorder.

Other ways to indicate possible Type I twinning are based on statistical methods [20–23]. While the first one can be used even for equal volume fractions, the second and third ones cannot. These methods were tested on a group of inorganic crystal structures by Kahlenberg [24], who concluded that “they represent useful tools in the early stages of a structure analysis and should be applied routinely in the preliminary stage of a structure determination whenever a twinning by merohedry is possible.”

Type II and III: twinning matrices from orientation matrices

For twins of diffraction Type II and III the determination of the twinning matrix is very straightforward because data collections are made almost exclusively on diffractometers equipped by area detectors. The experiment planning is usually done based on an orientation matrix of one domain (Type III) or an orientation matrix of the common supercell (Type II). Such a matrix is usually determined automatically followed by some alerting marks, like double points in the single area detector frames indicating unreasonably large unit cell parameters (both Type II and III) or low percentage of the indexed reflections (Type III). After making the full data collection, a twin can be immediately discovered visually either in a projection of peak positions or in a reconstructions of different sections throughout the reciprocal space. Here we show two examples of how twinning can be recognized from the diffraction pattern. The examples are based on the Rigaku Oxford diffraction equipment but there should be no difference with other instruments.

Figure 4 shows the simplest case of the Type II twinning found in a structure of an iodine salt of agomelatine [25]. The structure of this salt is triclinic and the sample is twinned by 180° rotation around **b**:

$$\mathbf{T}=\begin{pmatrix} -1 & 0 & 0 \\ 0.5005 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Due to special metrics of this triclinic unit cell the diffraction spots can also be indexed in a common fourfold monoclinic supercell, which is preferred by the automatic indexing procedure of CrysAlis. Single diffraction frames contain some alerting features like double-points

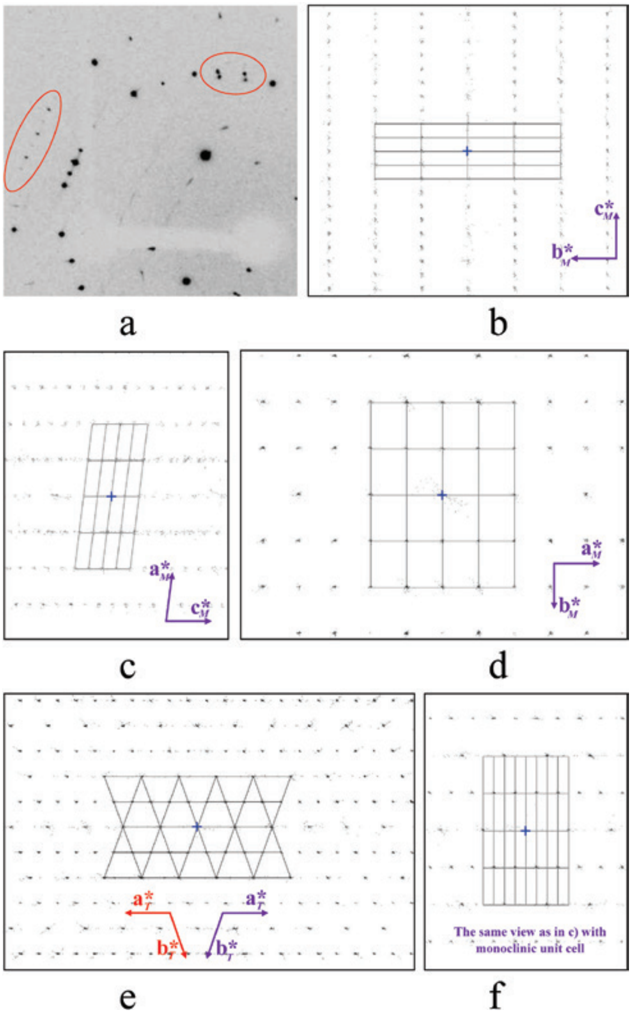


Fig. 4: Example of a Type II twin determined from the diffraction pattern [25]. *T* and *M* stand for the triclinic and monoclinic system, respectively. (a) A part of the single CCD frame with double-points and with rows of alternating strong and weak reflections indicating possible twinning; (b, c, d) peak positions from peak hunting projected along $\mathbf{a}_M$*, $\mathbf{b}_M$* and $\mathbf{c}_M$* of the monoclinic four-fold supercell as found from the automatic indexing procedure of CrysAlis. Unit cell parameters: $a_M=18.7211(5)$ Å, $b_M=14.6044(4)$ Å, $c_M=49.4784(9)$ Å, $\alpha_M=89.9447(18)°$, $\beta_M=96.8701(18)°$, $\gamma_M=90.009(2)°$, $V_M=13430.8(5)$ Å^3; (e) peak positions from peak hunting projected along $\mathbf{c}_T^*\equiv\mathbf{c}_M^*$. The triclinic unit cell was found by the automatic indexing procedure of CrysAlis when a user constraint on the unit cell size was applied. The c_T* is the common axis of both the first (blue) and second (red) twin domains. Unit cell parameters: $a_T=13.2071(3)$ Å, $b_T=14.6069(4)$ Å, $c_T=18.7205(5)$ Å, $\alpha_T=89.997(2)°$, $\beta_T=75.953(2)°$, $\gamma_T=73.882(2)°$, $V_T=3356.94(15)$ Å^3; (f) peaks from (e) overlaid with the four-fold supercell oriented along $\mathbf{c}_T$* of the triclinic unit cell. Origin is indicated with a blue cross.

meaning either twinning or very large unit cell, and rows of diffractions with alternating strong and weak intensity, which could occur due to the co-existence of stronger and weaker twin domains. However, the most striking is an unrealistically large unit cell. Its incorrectness can be discovered after taking a closer look into the diffraction pattern. It contains many systematical absences, caused by twinning of Type II, and also shows a typical alternation of the dense and sparse rows of spots, but not necessarily in a view along the three basic reciprocal axes. The triclinic unit cell and the corresponding twining matrix can be found automatically in CrysAlis when we constrain the maximal dimension of the unit cell to 30 Å. How such twinning could be discovered with Jana2006 using a data set processed in the monoclinic supercell is shown in the section Examples.

Figure 5 shows a typical Type III twin [26]. Experimental frames exhibit very close spots unequivocally indicating twinning because their distances correspond to extremely large unit cell parameters in the direct space. The automatic indexing procedure can index only about 60% of reflections and projections of peak positions along reciprocal axes clearly show that another rotated unit cell would describe the unindexed reflections. The twinning matrix automatically determined by CrysAlis corresponds to the 180° rotation around c:

$$\mathbf{T}=\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.733 & 0 & 1 \end{pmatrix}$$

With the help of these tools we can determine and refine orientation matrices of twin domains. Once we know the orientation matrices of each domain we can calculate twinning matrices:

$$\mathbf{T}_i=(\mathbf{U}_1\mathbf{U}_i^{-1})^T \tag{4}$$

where $\mathbf{U}_1$ and $\mathbf{U}_i$ are orientation matrices of the first and i^{th} twin domains, respectively. The symbol T represents the transpose matrix and it is used here as in the commonly accepted definition of the orientation matrix diffraction vectors **h** are used in a non-standard way as a column 3×1.

Manual determination of the twin component orientation matrices is laborious but straightforward: one has to recognize and discard spots of the other domains, index the remaining reflections, and repeat the process for all domains. Because of this simplicity, the most used data collection programs allow automatic detection of twin domains: CrysAlis [12] offers this possibility in its common user interface while in Apex [13] users achieve similar results by combining CELL NOW, SAINT and TWINABS. Both programs create a crude hklf4 file with reflections suitable for solution of the phase problem, and hklf5 file for refinement of the structure model. Also, both programs allow to index twins in a manual graphical mode

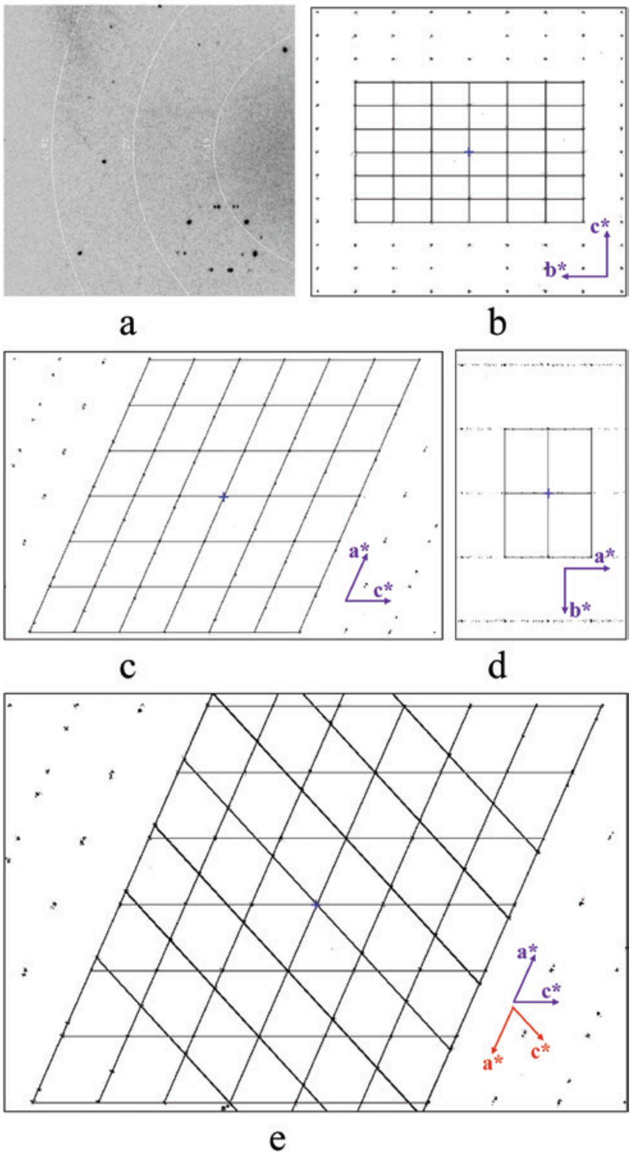


Fig. 5: Example of a Type III twin determined from the diffraction pattern [17]. (a) A single CCD frame with double-points indicating twinning or split sample; (b, c, d) peak positions from peak hunting projected along **a***, **b*** and **c*** of the monoclinic unit cell found from the automatic indexing procedure of CrysAlis. Unit cell parameters: a = 14.5961(12) Å, b = 9.8524(5) Å, c = 16.0470(10) Å, $\alpha = 90.001(4)^\circ$, $\beta = 113.830(7)^\circ$, $\gamma = 90.040(5)^\circ$, V = 2110.9(2) Å^3; (e) the same view like in (c) with two monoclinic unit cells as found from the automatic twin indexing procedure of CrysAlis. The **b*** is the common axis of both the first (blue) and second (red) twin domains; (f) part of the experimental frame from (a) with indicated peaks of the first (red) and second (green) domain (square, cross and rotated square indicate incoming, diffracting and leaving spots). The origin is indicated with a blue cross.

using the displayed peak positions. Automatic twin recognition works the best for the Type III twins. For the Type II twins it is less reliable, because the possibility to index all reflections with a common supercell may confuse the automatic procedure. Here, the visual inspection and manual indexing is often necessary.

While twin recognitions are relatively easy for Type II and III twins, the data input to the structure determination software is a more complicated topic because there are several options available, each of them having their pros and cons.

1. One approach is to make a separate data processing for each twin domain and import to the structure determination software reflection files of these domains and corresponding twinning matrices. The twinning matrix is then used by the structure determination software to detect overlaps of diffraction spots from different twin domains. This approach works very reliably for the Type II where the twinning matrix predicts the overlaps unequivocally, while it is less reliable for the Type III where additional experimental information would be necessary for absolutely correct overlap prediction. However, for many cases of the Type III twins the overlaps prediction works sufficiently well.
2. A modified approach is preferred for cases with a dominating first domain. For such samples diffraction intensities of additional domains are considerably weaker and their introduction to the structure determination may considerably increase an R value. Therefore in this modified approach we import only a reflection file of the first (strong) twin domain and twinning matrices without further data for detection of overlaps.
3. For the Type II data processing can be also done using the common reciprocal sub-lattice (supercell) to integrate all diffraction spots in one run. Then we import only one data set, the twinning matrices and a transformation matrix from the supercell to the actual unit cell of one twin domain.
4. In order to overcome the difficulties with overlaps prediction for the Type III, the so-called hklf5 format introduced by Sheldrick [11] has been widely accepted. In this file the overlaps are defined during the data reduction process when the necessary geometric information is available. The structure determination software only needs the hklf5 file but not twinning matrices, because they are not needed for predicting the overlaps. The hklf5 format is the proper way to treat the Type III twins with considerable overlaps. However, in practice, its usability strongly depends on the way how it is implemented in the diffractometer software and which user parameters were applied during the process of the overlap recognition.

Thus, the old way of using separately processed twin domains and twinning matrices is still worth of trying in cases when refinement based on the hklf5 file provides unsatisfactory results.

Symmetry of the diffraction pattern of twins

Overlaps of reflections from different twin-domains change the symmetry of the diffraction pattern considerably. Thus the lattice point group symmetry G (the holohedral point group) may differ from the structure point group symmetry. Let us start with the twin diffraction Type I and say that the set of symmetry operations of the structure point group is $H=\{\mathbf{S}_1=\mathbf{E}, \mathbf{S}_2, \ldots, \mathbf{S}_m\}$. Then applying any symmetry operation to the observed intensities (2) gives:

$$\mathcal{F}^2(\mathbf{hS}_j)=\sum_{i=1}^{n} v_i F^2(\mathbf{hS}_j\mathbf{T}_i) \tag{5}$$

The fact that the volume fractions come from the experimental data does not allow making any assumption about their particular values. This leads to the conclusion that the symmetry element $\mathbf{S}_j$ is present in the diffraction pattern of the twinned sample only if the equation (5) holds for each twinning operation [27]:

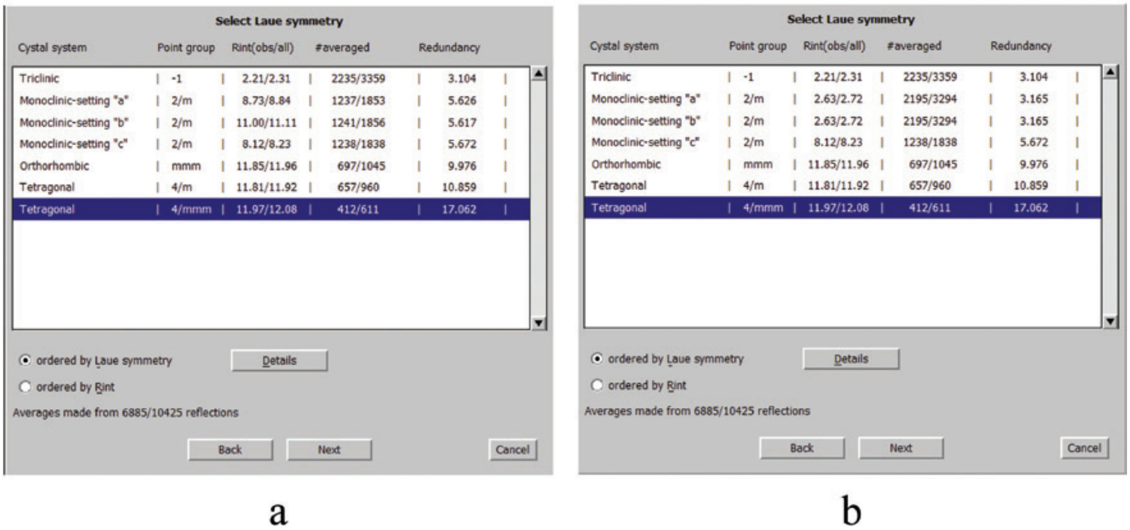
$$\begin{gathered}\mathcal{F}^2(\mathbf{hS}_j)=\mathcal{F}^2(\mathbf{h}) \Rightarrow \\ \forall i \in \{1,\ldots n\}: \exists \mathbf{S}_k \in H: \mathbf{S}_j\mathbf{T}_i=\mathbf{T}_i\mathbf{S}_k \Rightarrow \mathbf{T}_i^{-1}\mathbf{S}_j\mathbf{T}_i=\mathbf{S}_k\end{gathered} \tag{6}$$

This means that for each twinning operation $\mathbf{T}_i$ there exists a symmetry operation $\mathbf{S}_k$ that fulfills the equation. In other words, the symmetry of the diffraction pattern of the twinned sample will follow the structure symmetry only if the H is a normal subgroup of G. The minimal symmetry of the diffraction pattern is then $H' \subset H \subset G$ which is the maximal subgroup of H being normal with respect to the group G. Note that the subgroup H of order 2 in G is always normal and therefore, for most common twinned structures the minimal symmetry of the diffraction pattern is G.

On the other hand, in the idealized case $v_1=v_2=\ldots=v_n$ any permutation of individual terms in (5) is allowed without changing $\mathcal{F}^2(\mathbf{h})$, thus the maximal symmetry of the diffraction pattern is the lattice point group G. As for most of the twins generated by phase transitions the twin domains are almost equally occupied, symmetry of the diffraction pattern does not allow for making any definitive conclusions about the crystal structure symmetry.

For the twin diffraction Type II the number of overlapped domains can be different for different reflections and then the equation (6) is required to be used selectively. Even more complicated situations arise for the diffraction Type III, where we have to take into account not only diffraction indices and twinning matrices but also information about actual overlaps as presented in the hklf5 file.

Figure 6 demonstrates consequences of these rules for analysis of a reticular Type I twin (an unpublished data set) with a tetragonal unit cell. One of the screens of the Jana2006 wizard shows merging R values (R_{int}) for Laue symmetries possible for the given lattice. In case of a Laue symmetry lower than the symmetry of the lattice (here 4/*mmm*), the user can choose whether the twinning



a

Select Laue symmetry

Cystal system	Point group	Rint(obs/all)	#averaged	Redundancy
Triclinic	-1	2.21/2.31	2235/3359	3.104
Monoclinic-setting "a"	2/m	8.73/8.84	1237/1853	5.626
Monoclinic-setting "b"	2/m	11.00/11.11	1241/1856	5.617
Monoclinic-setting "c"	2/m	8.12/8.23	1238/1838	5.672
Orthorhombic	mmm	11.85/11.96	697/1045	9.976
Tetragonal	4/m	11.81/11.92	657/960	10.859
Tetragonal	4/mmm	11.97/12.08	412/611	17.062

● ordered by Laue symmetry
○ ordered by Rint

Averages made from 6885/10425 reflections

b

Select Laue symmetry

Cystal system	Point group	Rint(obs/all)	#averaged	Redundancy
Triclinic	-1	2.21/2.31	2235/3359	3.104
Monoclinic-setting "a"	2/m	2.63/2.72	2195/3294	3.165
Monoclinic-setting "b"	2/m	2.63/2.72	2195/3294	3.165
Monoclinic-setting "c"	2/m	8.12/8.23	1238/1838	5.672
Orthorhombic	mmm	11.85/11.96	697/1045	9.976
Tetragonal	4/m	11.81/11.92	657/960	10.859
Tetragonal	4/mmm	11.97/12.08	412/611	17.062

● ordered by Laue symmetry
○ ordered by Rint

Averages made from 6885/10425 reflections

Fig. 6: A screen of the Jana2006 symmetry wizard with merging R values (R_{int}) for Laue symmetries possible for the tetragonal lattice of a Type I reticular twin (an unpublished data set) with unequal twin fractions. In the merging procedure, the twinning operation following from the symmetry lowering is either ignored (a) or taken into the account (b).

operations following from the symmetry lowering should be considered in the merging procedure. The screen on the left (Figure 6a) shows the situation without considering the twinning operations. The “almost good” R_{int} for the tetragonal symmetry signals possible twinning, and the very good R_{int} for the triclinic symmetry suggests that the structure could be an eight-fold triclinic twin. On the other hand, when we consider the twinning, some symmetry operations cannot be used for the merging because $2_x/m_x$ is not the normal subgroup of $4/mmm$, and the tools (Figure 6b) reveals the structure could be a monoclinic four-fold twin. We can immediately suppose that such a twin would have unequal twin fractions, otherwise the differences in Laue symmetry would not be present and the diffraction pattern would mimic a tetragonal symmetry.

For the twin diffraction Type II the number of overlapped domains can be different for different reflections, and the equation (6) must be used selectively. The situation is even more complicated for the diffraction Type III, where we have to take into account not only diffraction indices and twinning matrices but also information about actual overlaps as presented in the hklf5 file. On the other hand, for symmetry merging of the Type III twin the situation demonstrated in Figure 6 cannot occur because there is no common supercell of a higher symmetry.

Solution and refinement of twinned structures

Structure solution of a twinned crystal can be a difficult task, especially for the diffraction Type I, where the contributions of the volume fractions to the diffraction spots are equal or almost equal and cannot therefore be reliably detected from the diffraction pattern. The crystal symmetry used at the first steps of the structure solution is usually based on the holohedral point group G. Omitted twinning is manifested by problems during the structure solution, because solution methods like direct methods do not account for twinning. Recently developed charge flipping methods [28] give a better chance for solution but these methods can be biased by twinning as well. The structure model resulting from solution, based on data from a twinned crystal, may yield a partial structure model or a structure model with some strange disorder, which cannot be properly described by the model without taking account of twinning. Therefore, twinning for the diffraction Type I is introduced and tested in cases when a structure solution is not satisfactory.

In the case that the structure contains one or a small number of heavy atoms a generalized heavy atoms method can be used. The Patterson map, as follows from the equation (2), is a weighted sum of n individual Patterson maps from each twin domain. In some specific cases it allows both recognizing twins and finding positions of heavy atoms from Patterson peaks [9].

In cases when the volume fractions of the Type I twin are not equal a “de-twinning procedure” can be used. Thus for the case $n=2$ the following formula can be applied:

$$v = v_2 \quad \mathbf{T}_1 = \mathbf{E} \quad \mathbf{T}_2 = \mathbf{T} \Rightarrow F^2(\mathbf{h}) = \frac{[(1-v)\mathfrak{F}^2(\mathbf{h}) - v\mathfrak{F}^2(\mathbf{hT})]}{(1-2v)} \tag{7}$$

However, this formula can be used only if the volume fraction v is already known, or if it can be estimated as proposed by Murray-Rust [29]. Moreover, this method is applicable only if the volume fraction is significantly different from the ½. For the twins induced by phase transitions, where the volume fractions are usually close to ½, we can start the refinement from the structural model of the high symmetry.

For diffraction Type II and III twinning is introduced based on the knowledge of the diffraction pattern, which reveals the twinning operation. Structure solution can be based on separated reflections from the first domain and the remaining ones treated by the de-twinning method according the equation (7). In the case of the equal volume fractions we can just divide them by the twin multiplicity. Then we can try traditional methods of structure solution. For the Type III, partial overlaps of diffraction spots complicate the situation even more. The data reduction software often creates, along with the hklf5 file, also the hklf4 file, which contains de-convoluted and de-twinned intensities (based on the estimated volume fractions) that can be used for the structure solution. Like with the hklf5 format, using hklf4 is the proper way how to solve structures of twins, and again its usefulness depends on the how the particular diffractometer software analyses partially overlapped reflections. In the case of troubles there is always the possibility to try the structure solution from data of one twin domain. We can conclude that for twins of the Type II and III the structure solution also yields only a partial structure model but, unlike the Type I, we know the twinning matrix beforehand and we can easily complete the structure from the refinement and Fourier syntheses.

Once we have the starting model for the refinement, we can continue with a more or less straightforward process of completion and refinement of the structure. In the refinement the only new parameters are $(n-1)$ volume fractions. For completion of the structure the Fourier and difference Fourier maps can be used as for regular structures, but with properly corrected amplitudes of observed structure factors (intensities):

$$F^2_{\text{obs}}(\mathbf{h}) = \frac{\mathfrak{F}^2_{\text{obs}}(\mathbf{h}) - \sum_{i=2}^{n} v_i F^2_{\text{calc}}(\mathbf{h}\mathbf{T}_i)}{v_1}$$
$$F^2_{\text{obs}}(\mathbf{h}) = \mathfrak{F}^2_{\text{obs}}(\mathbf{h}) \frac{F^2_{\text{calc}}(\mathbf{h})}{\mathfrak{F}^2_{\text{calc}}(\mathbf{h})} \qquad (8)$$

where the index obs and calc stand for observed and calculated values, respectively.

While the first method cumulates differences between observed and calculated overall intensities into the term describing the intensity of the first domain, the second method distributes these differences into all domains according to the ratio $\frac{F^2_{\text{calc}}(\mathbf{h})}{\mathfrak{F}^2_{\text{calc}}(\mathbf{h})}$.

Generalization of twin approach to modulated and multiphase systems

Modulated structures can be affected by twinning as well. The equation (2) is still valid there, but now indices are described as a row of three generally non-rational numbers $\mathbf{H}$:

$$\mathbf{H} = \mathbf{h} + m\mathbf{q} \qquad (9)$$

where $\mathbf{q}$ is a modulation vector. In the following part we shall concentrate only on (3+1)d cases, but a generalization to higher dimensional modulation would be straightforward. For predicting overlaps of diffraction spots we can use exactly the same procedure as for non-modulated structures, because the twinning matrices transform indices of main reflections as well as of satellites. A crucial point for a correct description of the modulated structure is to find the smallest number of modulation vectors which can fully index the diffraction pattern. The presence of twinning by merohedry can generate additional satellite reflections which can mimic a higher-dimensional case with two or more q-vectors. The crucial point for distinguishing a twinned (3+1)d structure from a higher-dimensional (3+2)d or (3+3)d case is the verification whether the satellites $\mathbf{q}$, $\mathbf{q}\mathbf{T}_2$, …, $\mathbf{q}\mathbf{T}_n$ are accompanied by their combinations such as $\mathbf{q} \pm \mathbf{q}\mathbf{T}_2$, …. When the combinations are present then this is a higher-dimensional case and not a twin. On the other hand, when these combinations are not observed, the crystal is either a twinned (3+1)d sample or a higher-dimensional case with very weak (unobserved) spots arising from the combinations. For such cases it is good to reconstruct the relevant sections through the reciprocal space using (if possible) an increased scaling factor because this procedure is more sensitive than a standard peak hunting and may help to discover very weak combined satellites. Another powerful method consists in projecting all peak positions into one unit cell (Figure 7).

As mentioned above, diffraction pattern of reticular twins can be indexed in a supercell and only non-standard systematic absent reflections can help to recognize that the sample is a twin. However, similar absences can be present in commensurately modulated structures due to the fact that satellites of higher order are unobserved. Figure 8 shows an example of the high-pressure

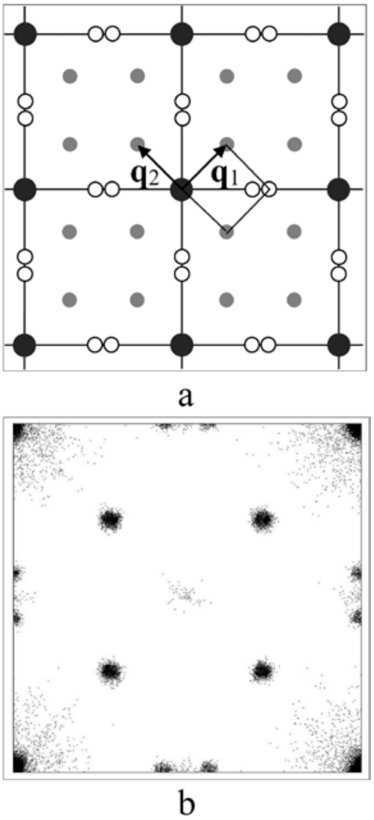


Fig. 7: (3+2)d modulated structure of melilite [30] with satellites arisen from combination of two q vectors. The presence of the combined satellites prove that the structure is not a twin of two (3+1)d modulated domains rotated by 90°, but a true two-dimensionally modulated structure. (a) Idealized diffraction patterns in four unit cells viewed along c*: main reflection are black, satellites of $\mathbf{q}_1$ or $\mathbf{q}_2$ are gray, combined satellites are white. (b) Diffraction spots (one pixel representation) from peak hunting projected to one unit cell by the indexing tool of Jana2006. The cumulating of some spots in the middle of the plot and in the halves of unit cell axes is caused by the $\lambda/2$ effect of the classical sealed Mo tube with graphite monochromator.

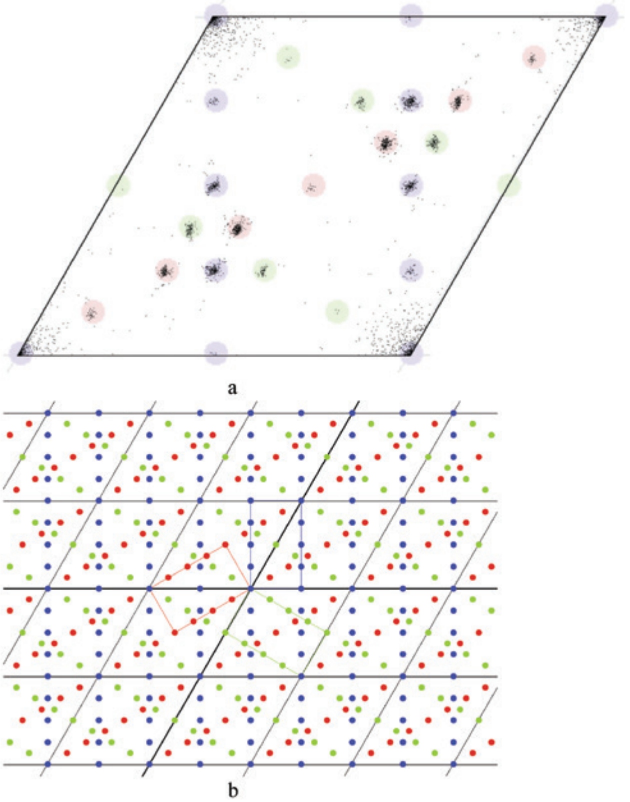


Fig. 8: Diffraction pattern of a (3+1)d commensurately modulated three-fold reticular twin [31] viewed along c* of the average structure. (a) Diffraction spots (one pixel representation) from peak hunting projected to one unit cell of the average structure by the indexing tool of Jana2006, and overlaid with the simulated diffraction pattern. (b) Diffraction pattern simulated by the Reciprocal space viewer of Jana2006 with twin domains distinguished like blue, red and green spots.

silicate Intermediate Phase-X $K_{1.5}Mg_2Si_2O_7H_{0.5}$ [31]. Diffraction pattern of this compound (Figure 8a) reveals the main spots conforming with the hexagonal space group $P6_3/mcm$, and satellite reflections, which can be described with two modulation vectors (α,α,0) and (−2α,α,0), α = 3/8, i.e. like the (3+2)d commensurately modulated structure [32]. However, the space group tests revealed that the hexagonal symmetry is systematically violated by the satellite reflections and that lowering of symmetry and introducing corresponding twinning is necessary. Finally, it was proven that the structure is orthorhombic, (3+1)d commensurately modulated, with a twinning by reticular merohedry defined as a rotation around the three-fold axis of the average structure (Figure 8b).

Another generalization of the twin approach can be made for multiphase crystals in which two or more phases with the closely related cell parameters are present in the same sample. Overlaps can exist between the diffraction patterns of the individual phases, and such patterns can be also twinned. The formula (2) can be rewritten to the form:

$$\mathfrak{F}^2(\mathbf{h}) = \sum_{i=1}^{n} v_i F_j^2(\mathbf{h}\mathbf{T}_i) \qquad (10)$$

where i is the twin domain. It differs from the equation (2) by the index $j = 1, \ldots, p$ (where p is the number of phases) which defines the phase connected with the i^{th} domain. The twinning matrices define the relation between the cell parameters of both domains and their mutual orientations. In all cases studied by this method until now, the number p was equal 2 and the cell parameters were either identical or related by simple relationship such as $\mathbf{c}' = 3\mathbf{c}$. Most of the applications were found either for mineral samples [33, 34] or for the results of not fully completed phase transition [35].

Implementation into Jana2006

Jana2006, in fact, can handle a general number of twin domains. However, a large number of twin domains is usually reserved for the Type I, where the number of corresponding twinning matrices can be very large, especially for the group–subgroup transformation. On the other hand, working with a large number of twin domains is usually not feasible for the Type II and III twins because of the problems with diffraction overlaps that might be very severe. For this reason the diffractometer software usually does not tend to work with more than four twin domains during the twin data reduction.

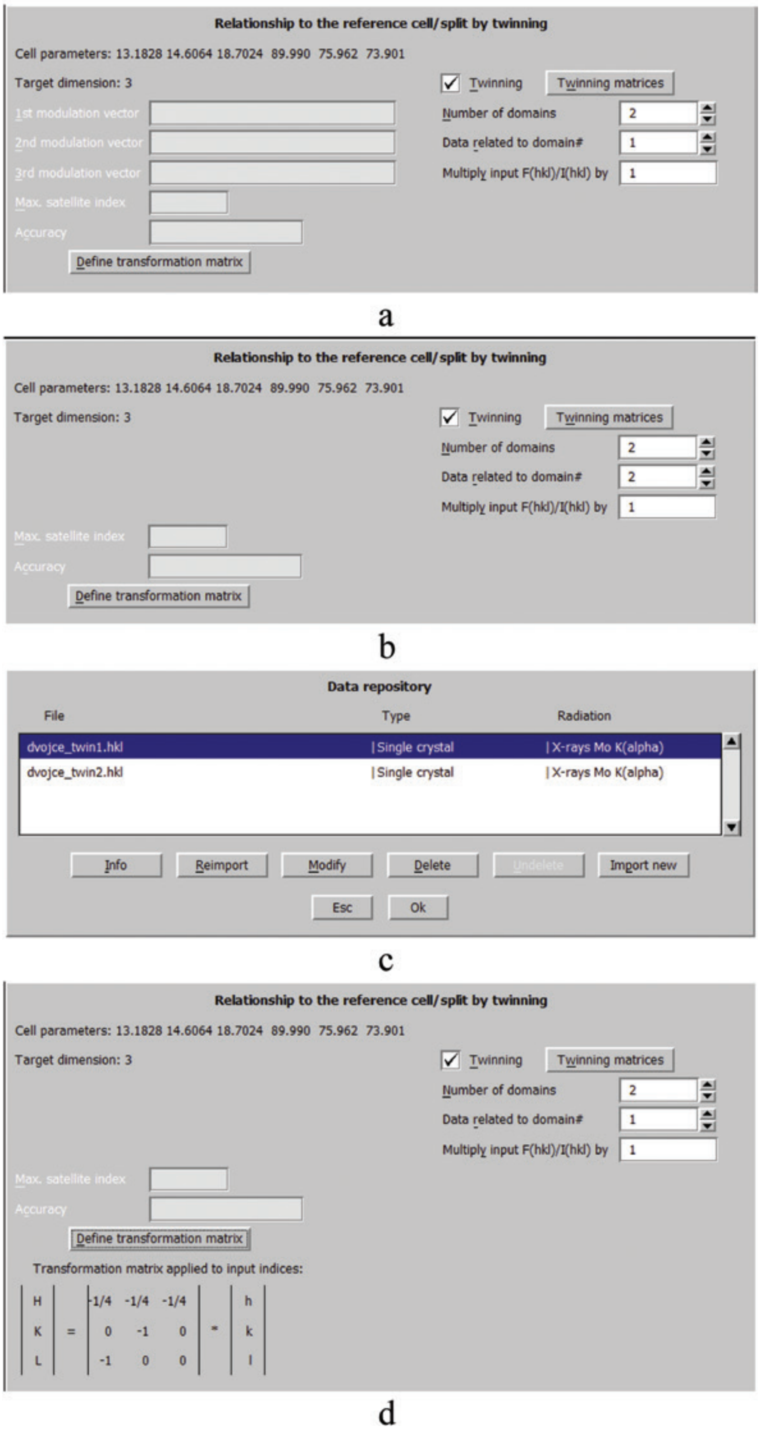
Import of reflection files into Jana2006

For twins of the Type I, there is usually no indication of twinning at this point and we start the work exactly like in case of a non-twinned structure. All reflections from the input file are imported as for a regular non-twinned structure and there is no need to introduce twinning matrices during the data import.

On the other hand, reflection files of the Type II twins can be supplied either in one file using a common supercell or as a set of files individually processed for each twin domain. For both possibilities twinning matrices must be supplied during the import procedure. Moreover, for the supercell input the transformation matrix from the supercell to the first twin domain is required.

For the twin diffraction Type III Jana can import either an individual reflection file for each twin domain as in the previous case or (preferably) the hklf5 format which contains unique information about overlaps of individual reflection. These overlaps cannot be completely predicted only on the basis of the cell parameters and twin matrices. In fact, the hklf5 format can be used for all types of twins. With the hklf5 format, twinning matrices are only needed for the data processing while in later stages of structure analysis the information about overlaps is known from the overlap keys.

Figure 9 illustrates possibilities for the import of the Type II twin data known from Figure 4. In case that the



Relationship to the reference cell/split by twinning (a)

Cell parameters: 13.1828 14.6064 18.7024 89.990 75.962 73.901

Target dimension: 3

☑ Twinning

Number of domains: 2

Data related to domain#: 1

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

Relationship to the reference cell/split by twinning (b)

Cell parameters: 13.1828 14.6064 18.7024 89.990 75.962 73.901

Target dimension: 3

☑ Twinning

Number of domains: 2

Data related to domain#: 2

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

Data repository (c)

File	Type	Radiation
dvojce_twin1.hkl	Single crystal	X-rays Mo K(alpha)
dvojce_twin2.hkl	Single crystal	X-rays Mo K(alpha)

Relationship to the reference cell/split by twinning (d)

Cell parameters: 13.1828 14.6064 18.7024 89.990 75.962 73.901

Target dimension: 3

☑ Twinning

Number of domains: 2

Data related to domain#: 1

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

Transformation matrix applied to input indices:

$$\begin{vmatrix} H \\ K \\ L \end{vmatrix} = \begin{vmatrix} -1/4 & -1/4 & -1/4 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{vmatrix} * \begin{vmatrix} h \\ k \\ l \end{vmatrix}$$

Fig. 9: Importing the Type II twin to Jana2006. (a) Importing of the first separately processed domain; (b) importing of the second separately processed domain; (c) two separately processed domains in the data repository of Jana2006; (d) an alternative way – importing of data processed in the common supercell.

data reduction was done separately for both twin domains, the two datasets can also be separately imported to the program (Figure 8a,b) and they finally appear as two lines in the data repository of Jana2006 (Figure 9c). A twinning matrix is required for this kind of the data import as well as an indication of which unit cell was used for the data reduction ("Data related to domain #"). During the import, the program offers discarding of the multiply imported reflections common to both domains because the data reduction of both domains is based on the same experimental frames, and multiple import of identical reflections would bias the weighting scheme. Figure 9d shows the import wizard for the case when data were processed in the common supercell. In such a case only one dataset is imported and the required information is not only the twinning matrix but also the transformation matrix from the supercell to the final unit cell (in our case the transformation from the four-fold monoclinic unit cell to the triclinic unit cell). The advantage of this second approach consists in the simplicity of the data reduction, where, e.g. the question of the data scale does not occur. On the other hand, the large supercell with many extinct reflections which cannot be described with standard extinction rules might generate too dense diffraction pattern which is unsuitable for data reduction.

Space group test

The program Jana2006 includes the procedure for performing a symmetry test, which allows not only finding possible space groups but also allows recognizing the twinning for the twin diffraction Type I.

It starts by checking supercells of the higher lattice symmetry than the symmetry which can be associated with the input cell parameters, using a procedure analogical to [36]. For instance, it can find an orthorhombic supercell related to a monoclinic unit cell used for the data processing. This is the first hint, which can help to find a hidden twinning not detected during data processing, because twinning of the Type II may occur in the supercell while the crystal structure may be described in the original unit cell. In the next step, the program tests internal R factors for all Laue point groups being compatible with the point symmetry of the selected cell. During this procedure the averaging can be made (on request) according to the symmetry consideration described above in the section "Symmetry of the diffraction pattern of twins." In the final step, we can select the symmetry to be either as high as the point symmetry of the lattice, or lower. In the case where the selected symmetry is lower than the point symmetry of the lattice, we can either introduce twinning following from the lowering of the point symmetry, or continue to work in a lower space group without twinning being applied.

Group–subgroup transformations

Jana2006 contains a procedure for transformation of the actual space group used for the description of the studied structure into a subgroup. Not only symmetry but also atomic positions and the refinement reflection files are transformed so that the resulting structure can be immediately refined. The set of subgroup generators can be chosen either interactively or by predefined maximal isomorphic subgroups as listed in the International Tables vol. A [37]. The procedure works in the following steps:

a) It generates new atom positions from the original atom, using the symmetry elements removed by lowering symmetry. All structural parameters are transformed including those describing anharmonic ADPs, population parameters used for charge density studies and modulation parameters. For atoms located on the former (now removed) symmetry elements site occupancies are modified accordingly. Such a transformed structure model still contains the symmetry of the higher symmetrical parent-structure but the explicitly defined symmetry is lower.

b) It starts an automatic procedure that processes reflections according to the new (lower) symmetry and prepares the reflection file for a future refinement. Details are given in the general description of Jana2016 [15], where we have explained the difference between the reflection repository file and the file used in the refinement procedure.

c) In the case that the selected subgroup is in a non-standard setting, the program offers an additional optional transformation to the standard setting. However, Jana2006 will work for any setting of the space group.

d) In the next step, the program offers an introduction of twinning. With *G* and *H* being the original and the target (lower) symmetry, twinning matrices can be selected as arbitrarily chosen representatives from each coset. The resulting structure model is a Type I twin, and this procedure is the main tool for testing various twinned models to get a satisfactory structure solution.

e) Optionally, the representative of each coset can be saved as a "local symmetry operation." Users can use these operations to restrict any pair of atoms with symmetry, which is not present in the current space group symbol. Moreover, the program can automatically generate the corresponding "local symmetry operation" one for each pair generated at the paragraph a) so that the resulting structural parameters still obey the higher space group even during the refinement. Then we can remove such restrictions only for atoms really breaking the higher symmetry, which usually improve the convergence during the structure refinement.

Refinement of twinned structure

Introduction of twinning does not lead to special or serious problems during the refinement procedure. The only new parameters are the volume fractions as defined in the formula (2). This formula is also used to calculate twin intensities and their derivatives as needed for the refinement. Overlaps in the formula (2) for each reflection are either calculated from twinning matrices or read from the hklf5 file. Both methods work properly, but the first method is more flexible, especially when different models of twinning are tested. On the other hand, without the information provided by the file hklf5 overlaps for the diffraction Type III cannot be reliably predicted.

To meet this contradiction, Jana2006 also contains an alternative method to predict overlaps, which is based on distances between reflections from different domain. Let the distance between two reflections, one from the i^{th} and the second from the j^{th} domain, be expressed as a difference in diffraction angles:

$$\Delta\theta = \arcsin\left(\frac{\left|\mathbf{h}_1\mathbf{T}_i - \mathbf{h}_2\mathbf{T}_j\right|\lambda}{2}\right)$$

then we can define two constants, $\Delta\theta_{\min}$, $\Delta\theta_{\max}$ and we can suppose that pairs of reflections laying in the interval (0, $\Delta\theta_{\min}$) are fully overlapped and the pair of reflections laying in the interval ($\Delta\theta_{\max}$, ∞) are fully separated. The reflections from the interval ($\Delta\theta_{\min}$, $\Delta\theta_{\max}$) are discarded from the refinement. The constants $\Delta\theta_{\min}$, $\Delta\theta_{\max}$ must be determined by trial and error, considering that the discarding of large number of reflections is not good for refinement. The aim is to discard reflections biased by partial overlaps only. The advantage of the hklf5 format over this method is obvious because there are no reflections discarded and also no trial and error is further needed. On the other hand, this rather primitive method has been working surprisingly well for many cases. Moreover, the hklf5 format may be incorrectly generated in some cases because even the diffractometer software can be incapable of treating some kinds of overlaps.

In the paragraph a), section "Group–subgroup transformations," we have mentioned that the transformed structure model still contains the symmetry of the higher symmetrical parent structure. Refinement of such a model in the lower symmetry would be singular. In order to overcome this problem, we can use the option to randomize the starting atomic positions using a small random displacement. This randomized procedure can be used selectively by keeping or deleting specific restrictions as generated during the group–subgroup transformation.

Examples

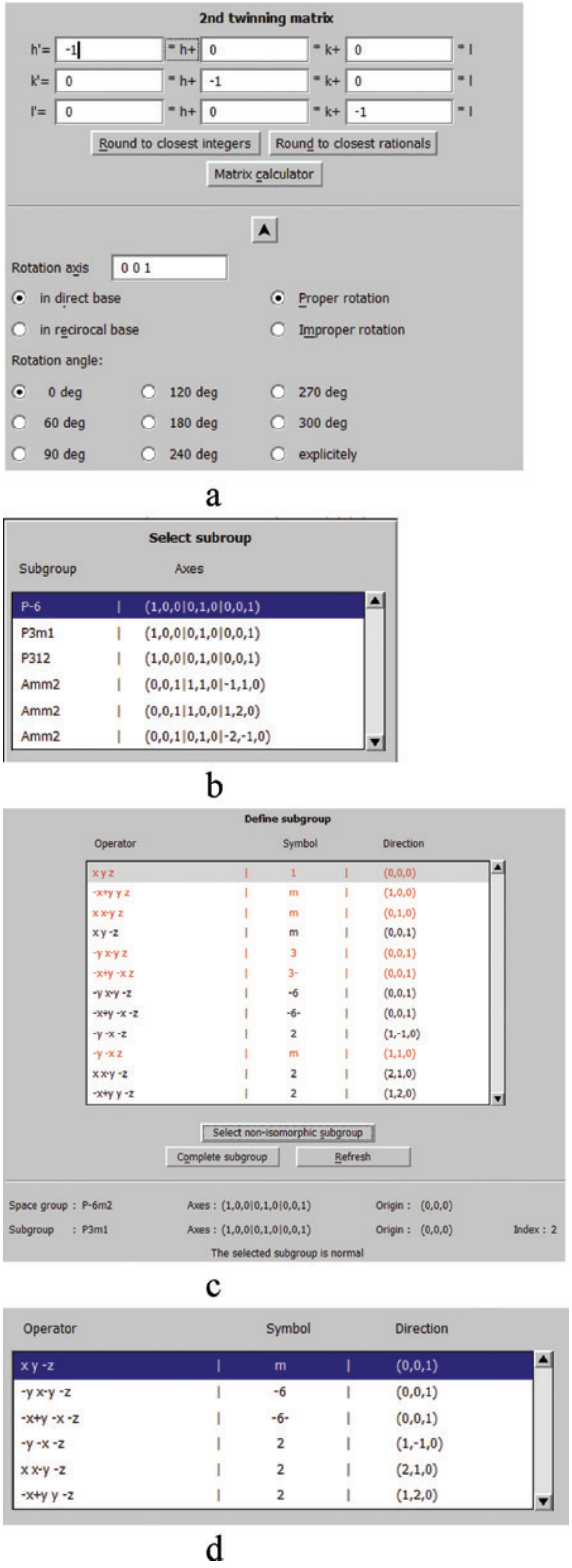
Recognition and refinement of a merohedric twin

Data: Pd_3HgTe_3, the synthetic analogue of temagamite [38] measured with a home lab X-ray diffractometer.

Unit cell: a = 7.8311(6) Å, b = 7.8311(6) Å, c = 17.2813(11) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, V = 917.81(12) Å^3.

Steps of solution:

1. Data of this compound were processed in the above given hexagonal unit cell and imported into Jana2006. Superflip [28] indicated the non-centrosymmetric space group $P\bar{6}m2$. The structure could be solved in this space group with the R(obs) value of 0.0766, however, some interatomic distances were too short. For this reason, merohedric twinning was considered.
2. Because the space group was non-centrosymmetric, inversion twinning was added manually using the interface shown in Figure 10a. Refinement of the inversion twin slightly decreased the R(obs) value to 0.0713 and the twin volume fraction refined close to 0.5 indicating a racemic mixture.
3. Jana2006 contains a tool for transformation of the complete structure to a subgroup. Figure 10b shows the list of possible non-isomorphic subgroups offered by the tool for the symmetry $P\bar{6}m2$. From this list, the subgroup $P\bar{6}$ led to the same troubles so that the next possibility, i.e. $P3m1$ was tested.
4. Figure 10c shows the tool after selecting the subgroup $P3m1$. The index of this subgroup is 2. Next page Figure 10d shows the symmetry operations contained in the coset decomposition; each of them could be selected as a twinning operation. In our case, "x y −z" was selected. Finally, Jana2006 transformed the structure model to the selected subgroup and inserted the twinning matrices. The structure model in $P\bar{6}m2$ was an inversion twin. Therefore, the structure model



2nd twinning matrix

h'=	-1	*h+	0	*k+	0	*l
k'=	0	*h+	-1	*k+	0	*l
l'=	0	*h+	0	*k+	-1	*l

Rotation axis: 0 0 1

● in direct base
○ in recirocal base
● Proper rotation
○ Improper rotation

Rotation angle:

● 0 deg ○ 60 deg ○ 90 deg ○ 120 deg ○ 180 deg ○ 240 deg ○ 270 deg ○ 300 deg ○ explicitely

Select subroup

Subgroup	Axes
P-6	(1,0,0|0,1,0|0,0,1)
P3m1	(1,0,0|0,1,0|0,0,1)
P312	(1,0,0|0,1,0|0,0,1)
Amm2	(0,0,1|1,1,0|-1,1,0)
Amm2	(0,0,1|1,0,0|1,2,0)
Amm2	(0,0,1|0,1,0|-2,-1,0)

Define subgroup

Operator	Symbol	Direction
x y z	1	(0,0,0)
-x+y y z	m	(1,0,0)
x x-y z	m	(0,1,0)
x y -z	m	(0,0,1)
-y x-y z	3	(0,0,1)
-x+y -x z	3-	(0,0,1)
-y x-y -z	-6	(0,0,1)
-x+y -x -z	-6-	(0,0,1)
-y -x -z	2	(1,-1,0)
-y -x z	m	(1,1,0)
x x-y -z	2	(2,1,0)
-x+y y -z	2	(1,2,0)

Space group : P-6m2 Axes : (1,0,0|0,1,0|0,0,1) Origin : (0,0,0)
Subgroup : P3m1 Axes : (1,0,0|0,1,0|0,0,1) Origin : (0,0,0) Index : 2
The selected subgroup is normal

Operator	Symbol	Direction
x y -z	m	(0,0,1)
-y x-y -z	-6	(0,0,1)
-x+y -x -z	-6-	(0,0,1)
-y -x -z	2	(1,-1,0)
x x-y -z	2	(2,1,0)
-x+y y -z	2	(1,2,0)

Fig. 10: Steps of solution of the merohedric twin of temagamite [35]. (a) Tools for manual definition of a twinning matrix; (b–d) tools for transformation of the structure model to a subgroup; (b) list of non-isomorphic subgroups of $P\bar{6}m2$; (c) the transformation tool with selected $P3m1$; (d) the coset decomposition.

in $P3m1$ was a four-fold merohedric twin because each of the two original twinning matrices was expanded by the new twinning operation:

$$\mathbf{T}_1=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix},\ \mathbf{T}_2=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix},\ \mathbf{T}_3=\begin{pmatrix}1&0&0\\0&1&0\\0&0&-1\end{pmatrix},$$

$$\mathbf{T}_4=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}$$

5. The resulting structure model in $P3m1$ still kept the original higher symmetry which was used for expanding the atomic positions. The refinement option “Randomize atomic coordinates” was used to break this former symmetry to enable structure refinement. Refinement converged with $R = 0.0522$ and twin domains refined close to ¼. The structure model was now correct without unrealistically short distances.

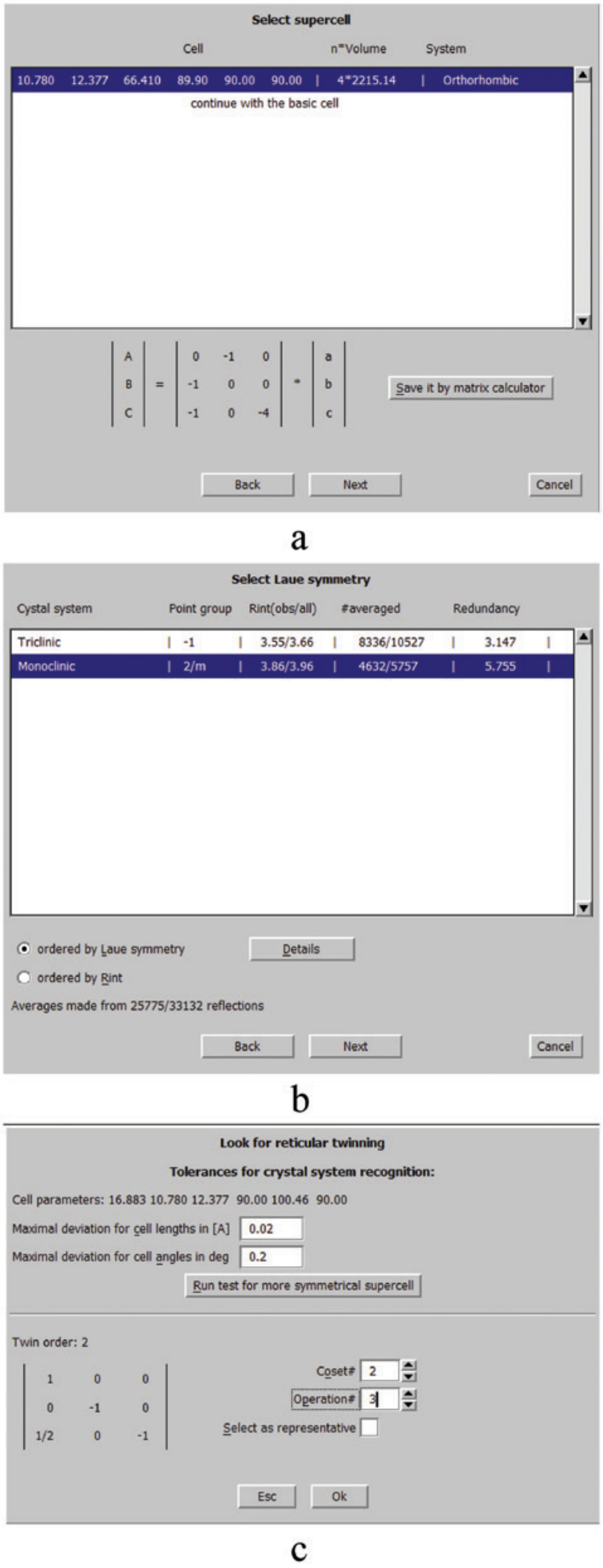
Recognition and refinement of a simple reticular twin

Data: unpublished data set of $Cu_2Cl_8(C_8N_4H_{20})\cdot 2H_2O$ measured with a home lab X-ray diffractometer.

Unit cell: $a = 12.3767(8)$ Å, $b = 10.7802(5)$ Å, $c = 16.8827(3)$ Å, $\beta = 100.456(4)°$, $V = 2215.14(18)$ Å^3.

Steps of the solution:

1. Data of this compound were processed in the above given monoclinic unit cell and imported to Jana2006.
2. The symmetry wizard of Jana2006 showed the possibility to transform the monoclinic unit cell to a four-fold orthorhombic supercell (Figure 11a) but there was no reason at this point to use it. In the next screen (Figure 11b), a very good R_{int} indicated the monoclinic symmetry (Figure 11b).
3. The structure was solved and refined. The resulting structure model was looking correct, however, refinement was unstable and R(obs) value of the refinement was above 0.16.
4. The existence of the four-fold monoclinic supercell (Figure 11a) indicates that the sample could be a reticular twin. The latest versions of Jana2006 (since May 2016) has a tool “Search for reticular twinning,” which lists possible supercells (as in the symmetry wizard) and finds possible twinning in these supercells. The found twinning matrices are transformed to the current unit cell and introduced to the structure. Using this tool (Figure 11c), the following twinning matrix was found for our structure:



Select supercell

Cell	n*Volume	System
10.780 12.377 66.410 89.90 90.00 90.00	4*2215.14	Orthorhombic

continue with the basic cell

$$\begin{vmatrix} A \\ B \\ C \end{vmatrix} = \begin{vmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ -1 & 0 & -4 \end{vmatrix} * \begin{vmatrix} a \\ b \\ c \end{vmatrix}$$

a

Select Laue symmetry

Cystal system	Point group	Rint(obs/all)	#averaged	Redundancy
Triclinic	-1	3.55/3.66	8336/10527	3.147
Monoclinic	2/m	3.86/3.96	4632/5757	5.755

● ordered by Laue symmetry

○ ordered by Rint

Averages made from 25775/33132 reflections

b

Look for reticular twinning

Tolerances for crystal system recognition:

Cell parameters: 16.883 10.780 12.377 90.00 100.46 90.00

Maximal deviation for cell lengths in [A]: 0.02

Maximal deviation for cell angles in deg: 0.2

Twin order: 2

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 1/2 & 0 & -1 \end{vmatrix}$$

Coset# 2

Operation# 3

Select as representative ☐

c

Fig. 11: Jana2006 screenshots illustrating steps of solution of the Type II twin in the section "Recognition and refinement of a simple reticular twin." (a) Symmetry wizard indicating a four-fold supercell; (b) possible Laue symmetries for the monoclinic unit cell; (c) a tool for discovering a twinning by reticular merohedry.

$$\mathbf{T} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0.5 & 0 & -1 \end{pmatrix}$$

This twinning matrix would take a simple form in the orthorhombic supercell, where it defines a 180° rotation around a.

5. Using the twinning matrix for a monoclinic unit cell, refinement if $P2_1/a$ converged with an excellent R(obs) 0.0359, and twin volume fractions refined as 0.6964(12) and 0.3036(12).

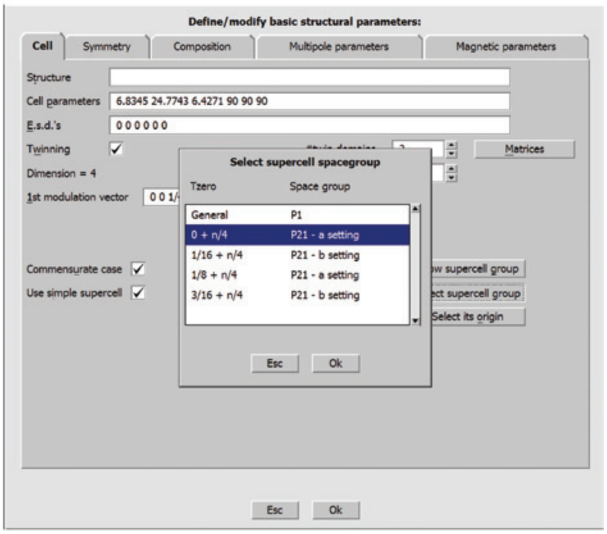
We should note that the described process reveals the twinning matrix but the reflections belonging only to the second domain are missing because they were not present in the original data set. Although using the first domain together with the twinning matrix is sufficient for the structure solution, a purist's approach would require going back to the experimental frames and making the data reduction in the supercell in order to obtain all available data.

The twinning matrix used for this refinement can also be obtained from Geminography [16], which can be called directly from Jana2006 as an external program.

Twinning in a commensurate structure

For commensurately modulated structures, a careful symmetry analysis is very important as the symmetry used in the superspace need not be fully reproduced in the 3d supercell [39]. A useful example is the structure of ephedrine originally described as a regular structure [40] with cell parameters a = 25.358 Å, b = 6.428 Å, c = 6.901 Å, space group $P2_12_12_1$. Ephedrine is modulated below room temperature [41], with superspace group $P2_12_12_1(00\gamma)000$ and modulation vector (0,0,1/4). The structure could also be described in the supercell 1×1×4 but the superspace approach is preferable because of very weak satellites. From the superspace theory [39] it follows that there are several possibilities how the superspace symmetry is "projected" into the 3d supercell, depending on selection of so-called t-section through the superspace. Jana2006 contains a tool (Figure 12) showing (for the given superspace symmetry and q vector) possible t-sections and corresponding symmetry in the supercell.

For ephedrine, three non-equivalent supercell space groups are possible, two of them monoclinic and one triclinic. By the subsequent refinement it was found the most reasonable description is for the t-section t = 0 with corresponding supercell symmetry $P2_1$. Refinement with



Structure
Cell parameters 6.8345 24.7743 6.4271 90 90 90
E.s.d.'s 0 0 0 0 0 0
Twinning ☑
Dimension = 4
1st modulation vector 0 0 1/
Commensurate case ☑
Use simple supercell ☑

Select supercell spacegroup

Tzero	Space group
General	P1
0 + n/4	P21 - a setting
1/16 + n/4	P21 - b setting
1/8 + n/4	P21 - a setting
3/16 + n/4	P21 - b setting

Fig. 12: Tool of Jana2006 for selection of the t-section for refinement of a commensurately modulated structure.

this t-section converged with R(obs) 0.0626, 0.0281, 0.055 and 0.3351 for all, main, 1st order satellite and 2nd order satellite reflections, respectively. The fit for the second order satellites was very poor.

The supercell corresponding to the selected t-section is within experimental accuracy orthorhombic. For more complicated cases, we could verify metrics of the supercell by transforming the structure to the supercell with a tool available in Jana. With orthorhombic supercell and monoclinic space group, there was a chance for twinning by metric merohedry, using the twinning matrix

$$\mathbf{T} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Indeed, the final refinement with two domains related by two-fold axis along the **c** axis converged with a significantly better fit, especially for the second order satellites: R(obs) 0.0362, 0.0270, 0.0394 and 0.0797 for all, main, 1st order satellite and 2nd order satellite reflections, respectively.

So for commensurately modulated structures we have to always take into account the difference between superspace and supercell symmetry as follows from different t-sections.

Examples on twinning in the Jana2006 Cookbook

The Jana2006 Cookbook is available in http://jana.fzu.cz and contains step-by-step examples how to solve typical crystallographic problems. Data for the examples can also be downloaded. Several examples in the cookbook are devoted to twinning:

- Example “3.1 AD3” explains solution and refinement of a simple pseudo-merohedric twin (Type I) with unequal twin volume fractions.
- Example “3.2 PyNinit” explains solution and refinement of a Type III twin and application of hklf5 file.
- Example “3.3 $CsLiSO_4$” shows solution of complicated Type II three-fold twin solved with help of the “Go to subgroup” tool.
- Example “7.1 Ephedrine” shows in detail the solution of Ephedrine from the previous section.
- Example “20.2 HfPdGHe” shows import of hklf5 file for a six-fold twin.

Conclusions

In this article we presented the knowledge necessary for efficient usage of the tools available in Jana2006 software for twinned structures. The terminology (Type I, II and III twins) is based on the much more detailed works of Nespolo and Ferraris [5], and it was intentionally simplified to keep it on the level necessary for practical structure determination of twins. We focused on the ways of how to recognize twins from the diffraction pattern, and how to work with typical twinned structures in Jana2006. We would like to draw attention to the part about symmetry of the diffraction pattern of twins, because the rules for merging symmetry equivalent reflections (see Figure 6) do not belong to the general knowledge of practical crystallographers. We showed that twins are also an important topic in the fascinating field of modulated structures.

Acknowledgments: We acknowledge support of the Czech Science Foundation project 15-12653S and 14-03276S. We thank to Mathias Meyer for explanations concerning the hklf5 format in Crysalis, Pascal Roussel, Ivana Císařová and Olivier Perez for information about possibilities of APEX and related software, Michael Ruf and Charles Campana for supplying data of modulated Pseudoephedrine Hydrochloride. We also acknowledge Brahim El Bali for providing us with a sample necessary, for example, on reticular twinning.

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