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The derivation of non-merohedral twin laws during refinement by analysis of poorly fitting intensity data and the refinement of non-merohedrally twinned crystal structures in the program *CRYSTALS*

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Although non-merohedrally twinned crystal structures can normally be solved without difficulty, problems usually arise during refinement. Careful analysis of poorly fitting data reveals that they belong predominantly to certain distinct zones in which $|F_o|^2$ is systematically larger than $|F_c|^2$. In the computer program *ROTAX*, a set of data with the largest values of $(|F_o|^2 - |F_c|^2)/u(|F_o|^2)$ is identified and their indices transformed by rotations or roto-inversions about possible direct- and reciprocal-lattice directions. Matrices that transform the indices of the poorly fitting data to integers are identified as possible twin laws.

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1. Introduction

A twinned crystal is an aggregate in which different domains are joined together according to a specific symmetry operation, *i.e.* the twin law (Giacovazzo, 1992; van der Sluis, 1989). The diffraction patterns derived from different domains are rotated, reflected or inverted with respect to one another, depending on the nature of the relationship between the different domains, and weighted according to the quantity of a particular domain present in the crystal (Pratt *et al.*, 1971; Jameson, 1982). The diffraction pattern measured during data collection is a superposition of all of these. Reflections from different domains may overlap and twinned crystals fall broadly into two categories in which either all reflections or only certain zones of reflections are affected by overlap. The former occurs when a crystal lattice belongs to a higher point group than the crystal structure itself. Examples of this type are merohedral twins in the low-symmetry tetragonal, trigonal, hexagonal and cubic systems, and pseudo-merohedral twins which may form when, say, a monoclinic crystal structure happens to have a value of β close to 90° (Herbst-Irmer & Sheldrick, 1998). In the case of a monoclinic crystal where $\beta \simeq 90^\circ$, the lattice possesses twofold symmetry about the **a** direction (and the **c** direction) which is not present in the point group of the crystal structure. This operation may therefore act as a twin law, defining which reflections are affected by overlap:

$$\mathbf{R}\mathbf{h} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix} = \begin{pmatrix} h \\ -k \\ -l \end{pmatrix} = \mathbf{h}'.$$

Reflections with indices hkl from one domain overlap with reflections $h\bar{k}\bar{l}$ from the other, and what is measured as the **h**

reflection actually contains a contribution from the **h'** reflection. In merohedral and pseudo-merohedral twinning, the nature of the twin-law matrix means that all integer triples are converted into other integer triples, so that all reciprocal-lattice points overlap.

Twins in which only certain zones of data are affected by overlap are classified as being non-merohedral. Here the twin law is commonly a symmetry operation belonging to a higher-symmetry supercell. A simple example which might be susceptible to this form of twinning is an orthorhombic crystal structure where $a \simeq 2b$. A metrically tetragonal supercell can be formed by doubling the length of b so that there is a pseudo-fourfold axis about **c**. If two domains of the crystal are related by this operation, then the true orthorhombic unit cells in the different domains of the twin are related by the matrix

$$\mathbf{R} = \begin{pmatrix} 0 & 2 & 0 \\ -0.5 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

This matrix expresses the twin law, but only data with $h = 2n$ are affected by overlap.

Diffraction patterns from non-merohedrally twinned crystals contain many more spots than would be observed for an untwinned sample. Since individual spots may come from different domains of the twin, such diffraction patterns are frequently difficult to index. Excellent programs such as *DIRAX* (Duisenberg, 1992) and *GEMINI* (Sparks, 1999) have been developed to index such diffraction patterns. In many cases a pattern can be completely indexed with two orientation matrices, and both these programs offer procedures by which the relationship between these alternative matrices is analysed to suggest a twin law. It is usually the case that

twinning can be described by a twofold rotation about a direct- or reciprocal-lattice direction. Indeed, if two such directions are parallel and the vectors describing them have a dot product of greater than two, then a higher-symmetry supercell can be derived. An undocumented option in the software *CREDUC* implementing the procedure of Le Page (1982) for searching unit-cell symmetry makes it clear that Le Page was well aware of the above possibility. The option was activated in a rewrite of *CREDUC* for the *Xtal3.2* system (Hall *et al.*, 1992) incorporating an explicit evaluation of the twin laws by coset decomposition (Flack, 1987). Le Page (1999) briefly reported algorithmic developments of his technique and recently gave full details of the program *OBLIQUE* (Le Page, 2002).

It is sometimes the case, though, that if a diffraction pattern has been indexed in default mode, then twinning will not have been noticed by the diffractometer operator. In the case of four-circle data, there may not have been a sufficient number of reflections located in a random search to enable two matrices to be defined; this is especially the case if the twin-component scale factor is small. Furthermore, it may be the case that powerful indexing programs like *DIRAX* and *GEMINI* are not used to their full capability, and that data are collected once the first plausible unit cell has been derived.

Since data sets from non-merohedral twins contain large numbers of reflections that are unaffected by twinning, it is our experience that their structures can be solved without difficulty, and in the cases described above the first intimation that a crystal is twinned is during refinement. Symptoms such as large inexplicable difference peaks and a high *R* factor may indicate that twinning is a problem, while careful analysis of poorly fitting data reveals that they belong predominantly to certain distinct zones in which $|F_o|$ is systematically larger than $|F_c|$. If twinning is not taken into account it is likely that these zones are being poorly modelled and that trends in their indices may provide a clue as to a possible twin law.

We have written a computer program, called *ROTAX*, that makes use of this idea to identify possible twin laws. A set of data with the largest values of $(|F_o|^2 - |F_c|^2)/u(|F_o|^2)$ (where *u* is the standard uncertainty of $|F_c|^2$; in the past the symbol σ was used for this quantity) is identified and the indices transformed by twofold rotations or other symmetry operations about possible direct- and reciprocal-lattice directions. Matrices that transform the indices of the poorly fitting data to integers are identified as possible twin laws. The analyst then has a set of matrices that might explain the source of the refinement problems described above.

In the following sections we outline the formulae used to generate the symmetry-operation matrices, define the figure of merit and discuss its interpretation, and finally give some examples of where this procedure has proved to be helpful.

2. Algorithm

The matrix describing a rotation of coordinates through an angle φ about any direct- ($s^i \mathbf{a}_i$) or reciprocal- ($s_j \mathbf{a}^j$) lattice direction has been given by Sands (1982) and Shmueli (1993):

$$R_j^i = s^i s_j + (\delta_j^i - s^i s_j) \cos \varphi + g^{ik} \varepsilon_{klj} s^l \sin \varphi,$$

where $\delta_j^i = 1$ if $i = j$, but 0 otherwise; g^{ik} and ε_{klj} are respectively elements of the reciprocal metric tensor and permutation tensor. For application to anticlockwise rotations of axes, this matrix is transposed. A matrix for a roto-inversion through φ can be generated by making each term in the rotation matrix negative. The user is prompted for which type of operation is of interest.

The 30 data with the largest values of $(|F_o|^2 - |F_c|^2)/u(|F_o|^2)$ are identified, and their indices (**h**) stored. Matrices, **R**, for the selected operation about all distinct direct- and reciprocal-lattice vectors with $-12 < h < 12$, $-12 < k < 12$, $0 < l < 12$, are generated as described above. During this procedure, thousands of matrices are generated, any of which could act as a twinning operation, and it is necessary to define a figure of merit so that the most likely potential twin laws can be spotted easily.

The indices of the poorly fitting data are transformed with each matrix:

$$\mathbf{R}\mathbf{h} = \mathbf{R} \begin{pmatrix} h \\ k \\ l \end{pmatrix} = \begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = \mathbf{h}'.$$

The figure of merit is based on the average distance from **h'** to the nearest reciprocal-lattice point. Usually the nearest point will be the one with rounded indices, but this might not be the case for a crystal structure with a skew cell and a long axis. If the average deviation from reciprocal-lattice points is 0.002 \AA^{-1} or less, **R** is accepted as a possible twin law. Otherwise largest deviations are omitted from the calculation of the average until either the average drops below 0.002 or 15 reflections have been omitted.

In order to put it on a convenient scale, the figure of merit printed in the output is 1000 times the average deviation in \AA^{-1} after omissions. The figure of merit calculated with no omissions is also printed, as is the number of omitted reflections. In most cases, matrices that produce a figure of merit of over 5 (*i.e.* the average deviation of transformed indices from reciprocal-lattice points is 0.005 \AA^{-1}) can be disregarded, although this cut-off can be controlled by the user. A list of transformed indices is printed with their deviation from reciprocal-lattice points; omitted reflections are indicated with a message. The program takes six seconds to run on a 1 GHz PC under Microsoft Windows NT.

The process of omitting a set of the largest deviations has been found to be necessary because there is a possibility that some of the 30 largest $(|F_o|^2 - |F_c|^2)/u(|F_o|^2)$ values are due to the model being incorrect or incomplete ($|F_c|^2$ too small) rather than the presence of overlapping reflections ($|F_o|^2$ too large). Estimates of $|F_c|^2$ are sensitive to the structural model; it is important that this is complete before attempting to invoke the *ROTAX* procedure. High figures of merit might also be obtained for crystals containing more than two domains. This is exemplified in the structure determination of Me_3SnH (see below); one twin law affected all the $h = 2n$ data; a second twin law affected only the $h = 0$ and ± 1 layers. Prior to modelling of

twinning, 26 of the 30 most poorly fitting data were of the class $h = 2n$. The remainder had $h = 1$, but though they were few in number, their transformed indices were far enough away from reciprocal-lattice points that their inclusion increased the figure of merit for the rotation matrix corresponding to the first twin law from 0.36 to 8.67.

The maximum direct- or reciprocal-lattice index tested in this procedure is 12. This value was chosen arbitrarily, although it is usually the case that twinning occurs about axes with much lower indices than this. No account is taken of symmetry and all lattices are treated as though they are triclinic. We considered examining only symmetry-independent indices and excluding symmetry directions (*e.g.* [010] for monoclinic crystals), but this would have made the input to the program slightly more complicated and may have caused users to miss certain merohedral or pseudo-merohedral twin laws, which are also printed. The matrices corresponding to these directions are therefore output in the version presented here, but can usually be readily identified as they have a figure of merit of exactly zero.

Any rotation or roto-inversion axis may be tested, although in our experience by far the majority of non-merohedral twins are affected by twofold rotations. There are some exceptions to this, especially in low-symmetry phases of 'inorganic' compounds which have high-symmetry polymorphs, as recently described, for example, by Petříček and coworkers (Gaudin *et al.*, 2000; Güelylah *et al.*, 2001).

3. Implementation

The program *ROTAX* is available as a stand-alone program compiled under Windows. It requires a *SHELXL97* (Sheldrick, 1997) .fcf file containing observed and calculated structure factors in CIF format for input. As presently written, the program is quite specific to this format. The unit-cell dimensions and the poorly fitting data are obtained from this file. The program may be called from the DOS prompt with the command *rotax*, the user being prompted for the compound code (the suffix .fcf is assumed), the symmetry operation to be tested and the maximum figure of merit for a matrix to be printed. The output is written to a file called *rotax.out*, and consists of a set of possible twin laws and their associated figures of merit. Methods by which this information may be incorporated into the refinement model have been described by Herbst-Irmer & Sheldrick (1998); a suitable .hkl file can be generated with the program *ROTWIN* (Young, 2001) or the 'Make HKLF5 File' procedure in *WinGX* (Farrugia, 1999). The *ROTAX* procedure has also been incorporated into *CRYSTALS* (Watkin *et al.*, 2000). For maximum convenience, the parameters referred to above are input and possible twin matrices applied *via* a graphical user interface.

For a two-component non-merohedral twin, some observations will contain a contribution from only one component and some from both; each observation is given an 'element' tag to indicate which twin components are contributing to the total observed value. In twins where overlap between reflec-

tions is only partial, refinement statistics are quite sensitive to the model used for tagging reflections. The ideal model for any given crystal will depend on the integration method, the mosaicity and the lengths of the cell edges, and it therefore depends upon exact experimental conditions. The most efficient procedure should be to compute the splitting of each reflection during data collection or integration; this facility is currently under development by some instrument manufacturers and is already available in other packages. In every case, it is good practice to go back to the experimental data and check whether previously unindexed reflections can be indexed on an alternative lattice generated using the putative twin law. However, *CRYSTALS* can compute a good guess at the tag from the twin laws. A reflection **h** is overlapped with **h'** if they are within a certain distance of one another in reciprocal space. This distance (referred to in the program as the 'twintolerance') is a variable that is input by the user. This implementation greatly facilitates rapid comparison of several tagging models; full details are given in the *CRYSTALS* manual.

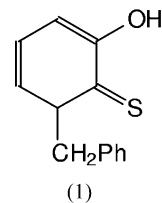
Young and coworkers (Choe *et al.*, 2000; Colombo *et al.*, 2000; Reger *et al.*, 2001; Schweitzer *et al.*, 2000) have shown that data sets where partial overlap leads to problems in developing a suitable tagging model can be treated by refining different twin scale factors for separate degrees of overlap. *CRYSTALS* can handle up to nine twin components.

4. Examples

In the examples below, all refinements were performed against $|F_o|$ excluding data for which $|F_o| < 4u$ because it is useful to be able to compare unweighted and weighted *R* factors directly. The unweighted *R* factor under these refinement conditions is quite insensitive to the weighting scheme. For the most part, we have chosen examples where the twin law could be evaluated by several methods; this demonstrates that *ROTAX* does indeed give correct twin law matrices, but also illustrates our experience that twin laws can usually be evaluated by several routes. Both the following examples were analysed using *CRYSTALS*.

4.1. Example 1: compound (1)

Crystals of (1)



grew as coaxially aligned aggregates of needles (Smith, 2000). A random reflection search on a four-circle diffractometer located 50 reflections. This pattern was indexed using *DIRAX* on the basis of two orientation matrices. Some reflections in the search list gave integral indices with only one of these matrices; others could be satisfactorily indexed with both. The

crystal system was monoclinic P , $a = 7.28$, $b = 9.74$, $c = 15.23$ Å, $\beta = 94.39^\circ$, space group $P2_1/n$. We describe below how the program *ROTAX* can be used to evaluate the twin law; however, the same matrix could also be obtained with the program *2VIEW*, which is part of the *DIRAX* system. Data were collected using one of the matrices derived by *DIRAX*. The structure was solved by Patterson methods (*DIRDIF*; Beurskens *et al.*, 1996) and refinement converged to $R_1 = 14.8\%$ and $R_w = 18.5\%$ with unit weights, anisotropic displacement parameters and all hydrogen atoms except that attached to the hydroxyl group placed in calculated positions. The difference synthesis maximum of $1 \text{ e } \text{\AA}^{-3}$ was close to the S atom, but in a chemically implausible position.

Prior to modelling of twinning, it is interesting to examine the effect of the weighting scheme on the refinement statistics. Most weighting schemes are based in some way on experimentally derived values of $u(|F_o|)$. These are obtained from the same observation as $|F_o|$ and so if this is substantially in error the values for u may be in error also. This situation may arise in data collected using non-merohedral twins because the overlap of reflections derived from different twin domains may be imperfect. A weighting strategy available in *CRYSTALS* assumes that once a model is reasonably complete the values of F_c are likely to be quite reliable. The average residual as a function of $|F_c|$ can be obtained by fitting the variation of Δ^2 against $|F_c|$ to a mathematical function, which in *CRYSTALS* is a Chebychev polynomial (Carruthers & Watkin, 1979). Reflections with residuals deviating significantly from this estimate are either in error or they contain important information on structural features which are as yet unmodelled. In principle, therefore, a Chebychev weighting scheme can be an important diagnostic tool during structure analysis of twinned crystals. In the case of compound (1), introduction of such weights gave a value of $R = 13.5\%$ and $R_w = 2.7\%$! All reflections being given low weights had $h = 3n$.

A similar conclusion can be drawn by use of *ROTAX*, by which the most poorly fitting data were analysed against a set of twofold rotation matrices. An edited output listing is given in Fig. 1. The matrix having the lowest figure of merit (except for twofold axes about **b** and **b***) is

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0.33 & 0 & 1 \end{pmatrix},$$

which corresponds to a twofold axis about the [106] direct-lattice direction. This acts to overlap reflections hkl with $h = 3n$ from one domain with reflections $-h, -k, (h/3 + 1)$ from the other domain. Incorporation of this twin law into the refinement cleaned-up the difference map considerably, allowing the hydroxyl hydrogen atom to be located. The final R factors were $R = 5.16\%$ and $R_w = 4.11\%$, with twin scale factors of 0.562 and 0.437 (3). Notice that R_w is still less than R ; this means that outliers are being down-weighted because they have high residuals. The most likely cause for this is inadequate modelling of partially overlapped data, although as Herbst-Irmer & Sheldrick (1998) have pointed out, it is also possible that one twin domain was better centred in the X-ray

beam than the other. A weight histogram (Fig. 2) shows that the number of such reflections is quite low and that they are recognizable as outliers. If these 17 data are omitted from the refinement, R drops to 4.78%.

Inspection of Fig. 1 shows that twofold axes about the direct-lattice directions [100] and [106] and the reciprocal-lattice directions [001] and $[\bar{6}01]$ are all clearly related. Parallel direct and reciprocal directions are suggestive of a metrically higher-symmetry supercell if the dot product of their vectors is greater than 2. In this case the dot product is 6, and this information is helpful as input to the program *CREDOC*, which is extremely useful for the identification of supercell symmetry. In the case of this crystal, a supercell can be obtained by application of the matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 1 & 0 & 6 \end{pmatrix},$$

which transforms the true monoclinic cell to a metrically orthorhombic cell with dimensions $a = 7.29$, $b = 9.74$ and $c = 91.12$ Å. It is important to attempt to identify the metric

```
Symmetry element tested: 180.0 degree rotation
Max figure of merit printed = 5.00
Largest index tested = 12
Cell dimensions: 7.2847 9.7400 15.2310 90.0000 94.3860
90.0000
The following thirty data are used to test possible twin laws.
These have the largest values of [F2obs-F2calc]/sigma.
-3 3 3 86.07 -3 4 5 55.69 0 2 3 54.24
0 1 3 48.98 0 1 2 48.89 -3 2 7 45.57
-3 5 3 39.25 0 0 8 37.78 0 2 7 37.41
[... and so on]

180.0 degree rotation about 1. 0. 0. direct lattice direction:
[ 1.000 0.000 0.000]
[ 0.000 -1.000 0.000]
[ -0.320 0.000 -1.000]
Figure of merit = 1.60
No reflections omitted
Distances in Ang**1 of transformed indices from integral r.l. points:
d1 = distance of transformed indices to nearest r.l. point
d2 = d1 - distance to r.l. point with rounded transformed indices
In a well-behaved system d2 should be zero, but it could deviate from this
value in the case of a highly skew unit cell.
Orig. Trans. d1 d2
-3. 3. 3. -3. -3. -2. 0.00267 0.00000
-3. 4. 5. -3. -4. -4. 0.00267 0.00000
0. 2. 3. 0. -2. -3. 0.00000 0.00000
0. 1. 3. 0. -1. -3. 0.00000 0.00000
[... and so on]

180.0 degree rotation about -6. 0. 1. reciprocal lattice direction:
[ 0.999 0.000 -0.003]
[ 0.000 -1.000 0.000]
[ -0.333 0.000 -0.999]
Figure of merit = 1.54
No reflections omitted

180.0 degree rotation about 0. 0. 1. reciprocal lattice direction:
[ -1.000 0.000 0.000]
[ 0.000 -1.000 0.000]
[ 0.320 0.000 1.000]
Figure of merit = 1.60
No reflections omitted

180.0 degree rotation about -11. 0. 2. reciprocal lattice direction:
[ 0.998 0.000 -0.010]
[ 0.000 -1.000 0.000]
[ -0.363 0.000 -0.998]
Figure of merit = 4.65
15 reflections omitted
Figure of merit with no omissions = 6.93

180.0 degree rotation about 1. 0. 6. direct lattice direction:
[ -0.999 0.000 0.003]
[ 0.000 -1.000 0.000]
[ 0.333 0.000 0.999]
Figure of merit = 1.54
No reflections omitted

180.0 degree rotation about 2. 0. 11. direct lattice direction:
[ -0.998 0.000 0.010]
[ 0.000 -1.000 0.000]
[ 0.363 0.000 0.998]
Figure of merit = 4.65
15 reflections omitted
```

Figure 1

Abbreviated *ROTAX* output for compound (1); an unedited version has been deposited.

symmetry of the supercell because the fact that this cell is orthorhombic, and no higher, implies that there is no need to search for further twin laws. Decomposition of *mmm* into cosets with subgroup *2/m* yields the identity operator and a twofold axis about **a** or **c** of the supercell, which has, of course, already been identified (Flack, 1987; Schlessman & Litvin, 1995).

Indexing programs may suggest large high-symmetry supercells, which much assists the determination of twin laws, assuming that the correct sub-cell can be recognized. In favourable circumstances this can be achieved by inspecting the data set for unusual systematic absences or weaknesses.

4.2. Example 2: trimethyltin hydride (Me₃SnH), (2)

Trimethyltin hydride, (2), is a gas under ambient conditions and its melting point is *ca* 160 K (Brown, 1996). Crystals of compounds which are not solid at room temperature may be grown in a capillary mounted on a diffractometer; such *in situ* crystallization methods have been reviewed by Boese & Nussbaumer (1994). Some compounds crystallize as needles, and in these cases it can be exceptionally difficult to grow a single crystal rather than a clump of coaxially aligned needles. Trimethyltin hydride was just such a case. After some considerable effort, a crystal grown at the slightly tapered tip of the capillary gave a diffraction pattern that could be indexed with *DIRAX*, but it was clear from a rotation photograph that the sample was far from single. The unit cell chosen for data collection was a metrically monoclinic *C*-centred cell with dimensions *a* = 6.255 (2), *b* = 12.113 (4), *c* = 15.963 (6) Å, β = 91.66 (6)°, although it was noted that γ was significantly different from 90° at 90.10 (3)°. It was clear from the Laue symmetry of the data set that the crystal system was triclinic. In addition, the data set showed strong pseudo-translational symmetry of the form (*h* + *k* + 2*l*) = 4*n*, this information being readily available in the output of *SIR97* (Altomare *et al.*, 1999), but also in the Patterson map which

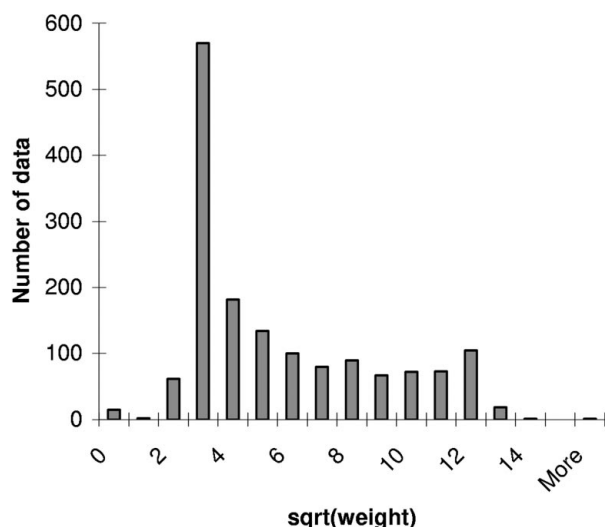


Figure 2
Weight histogram for compound (1). The 17 data in the two far-left bins were omitted in the final refinement.

showed a very large peak at (1/4, 1/4, 1/2). The unit cell was transformed with the matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0.5 & 0.5 & 0 \\ 0.25 & 0.25 & 0.5 \end{pmatrix}$$

and re-refined to give the triclinic setting *a* = 6.262, *b* = 6.822, *c* = 8.640 Å, α = 67.41, β = 80.92, γ = 62.62°. The structure was solved easily by Patterson methods and the carbon atoms were located in a subsequent difference map. Isotropic refinement converged to *R* = 6.81%, *R_w* = 8.11% with unit weights; anisotropic refinement led one carbon atom to develop a non-positive-definite displacement factor. The difference map showed a very large peak (6.42 e Å⁻³) in a chemically unreasonable position. Application of *ROTAX* identified twofold axes about the $[\bar{1}20]$ direct-lattice direction (or alternatively the $[021]$ reciprocal-lattice direction) as a potential twin law. This is described by the matrix

$$\begin{pmatrix} -1 & 0 & 0 \\ -1 & -1 & 0 \\ -0.5 & 1 & -1 \end{pmatrix}.$$

This matrix can also be derived by recognizing that twinning may occur by a twofold rotation about the *b* axis of the monoclinic supercell. In terms of the triclinic axis system, this symmetry operation is given by a triple matrix product consisting of the transformation of the triclinic to the monoclinic cell, its inverse and the twofold about the monoclinic *b* axis:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0.5 & 0.5 & 0 \\ 0.25 & 0.25 & 0.5 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ -1 & 2 & 0 \\ 0 & -1 & 2 \end{pmatrix}.$$

Incorporation of the twin law into the model gave an *R* factor of 3.14% and even allowed hydrogen atoms to be located in a difference map. *R_w* with a Chebychev four-term polynomial as a weighting scheme was 1.21%, so that there were still significant disagreements in certain data. An agreement analysis identified the offending data as belonging to the zones where $|h| = 1$ or 0 (see Table 1, model *A*). Reapplication of *ROTAX* suggested that twinning *via* a twofold axis about the $[100]$ reciprocal-axis direction, described by the matrix

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0.066 & -1 & 1 \end{pmatrix},$$

was also affecting the refinement. Splitting the $|h| = 1$ and further splitting the *h* = 0 layers with this matrix reduced *R* slightly to 3.01%, but an agreement analysis still showed that the $|h| = 1$ data were being poorly modelled, probably because the 0.066 term in this second twin law causes only partial overlap in these layers (Table 1, model *B*). Leaving the $|h| = 1$ layers unsplit gave *R* = 2.80% and cured the poor agreement in the *h* = 0 layer (Table 1, model *C*). Omitting the $|h| = 1$ layers, which appear to be systematically poorly measured, gave *R* = 2.27% (Table 1, model *D*). Optimization of the Chebychev

Table 1

Agreement analyses for different twinning models for structure (2).

The models A–D are described in the text. The *R* factor is based on $|F|$ with $|F| > 4u(|F|)$.

<i>h</i>	No. of data	<i>R</i> (%)			
		Model A	Model B	Model C	Model D
–7	2	2.41	2.89	2.14	1.87
–6	21	2.25	3.3	2.17	1.98
–5	39	1.92	1.87	1.85	1.91
–4	59	1.81	2.05	1.69	1.62
–3	71	2.35	2.54	2.29	2.24
–2	86	3.73	3.64	3.51	3.48
–1	91	6.12	5.11	6.05	
0	101	3.92	2.98	1.99	2.01
1	95	3.82	4.39	3.67	
2	96	2.89	2.95	2.53	2.44
3	88	1.74	2.04	1.76	1.83
4	78	1.66	1.71	1.75	1.98
5	65	2.11	2.15	1.97	1.89
6	46	2.07	2.2	2.12	2.14
7	17	6.38	6.49	6.88	6.8
Scale factors		0.813 (2)	0.788 (3)	0.760 (3)	0.759 (2)
		0.187 (2)	0.180 (3)	0.153 (3)	0.151 (2)
			0.031 (3)	0.087 (4)	0.090 (2)
Total	955	3.14	3.06	2.80	2.27

weighting scheme gave a final $R_w = 0.86\%$, from which it is clear that systematic errors are still present in the data. In view of the rotation photographs taken during data collection, this was far from surprising.

Partial overlap is a significant problem when analysing diffraction data from non-merohedrally twinned crystals. Several schemes for splitting reflections usually need to be tested to find the best model, and it is often necessary to omit certain zones of data that are badly affected. Young's method (see above) can help to minimize the number of data it is necessary to reject. Other procedures include down-weighting affected data and careful selection of integration parameters (e.g. box size).

Problems of this sort occur when non-rational terms appear in the twin-law matrix as a result of supercell metrics deviating from ideal values. The second of the two twin laws described above for Me_3SnH can be considered to fall into this category: the β angle of the monoclinic supercell is close enough to 90° that it appears, from the point of view of the twin domains present in the crystal, to be behaving as though it were an orthorhombic supercell. Under these conditions, coset decomposition suggests that there may be a fourth domain, related to the first by a twofold rotation about the *c* axis of the supercell. However, when this was incorporated into the model, the scale factor for this domain fell to just 0.01, with negligible improvement in the refinement statistics.

5. Conclusion

We have found *ROTAX* to be useful as a diagnostic tool in the analysis of crystal structures suffering from non-merohedral twinning. Its incorporation into *CRYSTALS*, together with a new procedure for handling reflections which need to be split over different twin domains has been shown greatly to facil-

itate structure determination, particularly when used in conjunction with established crystallographic tools such as optimized weighting schemes and agreement analyses. In particular, the Carruthers & Watkin (1979) weighting scheme based on Chebychev polynomials appears to be very efficient for identifying and down-weighting data which may be affected by partial overlap, and which can cause frustrating problems in this area.

In some ways this paper addresses a problem that should never arise with modern X-ray diffraction equipment. Programs such as *DIRAX* and *GEMINI* enable the twin laws to be determined from a diffraction pattern, and if they are used to their full capacity it is unlikely that *ROTAX* will yield any further information. On occasion, however, problems that might have been spotted during data collection need to be diagnosed during data analysis. Whether *ROTAX* is used or not, it is always necessary to check that any proposed twin law is consistent with the experimental diffraction data. It is also important to derive supercell symmetry, as coset decomposition can then be used to derive the number of potential twin domains which may need to be modelled. If this information is not available from indexing software, supercell transformations may be derived from the axes identified by *ROTAX* or by use of the invaluable program *CREDUC*.

A version of *CRYSTALS* incorporating the *ROTAX* routine can be downloaded from the *CRYSTALS* Web site at <http://www.xtl.ox.ac.uk/>. The program also appears in the *WIN/GX* program suite (Farrugia, 1999) available from <http://www.chem.gla.ac.uk/~louis/software/>, while a stand-alone version is available from the authors by e-mail (s.parsons@ed.ac.uk), or via the CCP14 web site (<http://www.ccp14.ac.uk/>).

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References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Beurskens, P. T., Beurskens, G., Bosman, W. P., de Gelder, R., Garcia-Granda, S., Gould, R. O., Israel, R. & Smits, J. M. M. (1996). *The DIRDIF96 Program System*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Boese, R. & Nussbaumer, M. (1994). In *Correlations, Transformations and Interactions in Organic Crystal Chemistry*, edited by D. W. Jones & A. Katrusiak. Oxford University Press.
- Brown, D. (1996). PhD thesis, University of Edinburgh.
- Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* **A35**, 698–699.
- Choe, W. V., Pecharsky, K., Pecharsky, A. O., Gschneidner, K. A., Young, V. G. & Miller, G. J. (2000). *Phys. Rev. Lett.* **84**, 4617–4620.
- Colombo, D. G., Young, V. G. & Gladfelter, W. L. (2000). *Inorg. Chem.* **39**, 4621–4624.
- Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1987). *Acta Cryst.* **A43**, 564–568.

- Gaudin, E., Petříček, V., Boucher, F., Taulelle, F. & Evain, M. (2000). *Acta Cryst.* **B56**, 972–979.
- Giacovazzo, C. (1992). Editor. *Fundamentals of Crystallography*. Oxford University Press.
- Guelylah, A., Madariaga, G., Petříček, V., Brezowski, T., Aroyo, M. I. & Bocanegra, E. H. (2001). *Acta Cryst.* **B57**, 221–230.
- Hall, S. R., Flack, H. & Stewart, R. F. (1992). *Xtal3.2*. University of Western Australia.
- Herbst-Irmer, R. & Sheldrick, G. M. (1998). *Acta Cryst.* **B54**, 443–449.
- Jameson, G. B. (1982). *Acta Cryst.* **A38**, 817–820.
- Le Page, Y. (1982). *J. Appl. Cryst.* **15**, 255–259.
- Le Page, Y. (1999). *Acta Cryst.* **A55**, Supplement, Abstract M12.CC.001 (this refers to a lecture given by Le Page at the IUCr Conference in Glasgow, 1999).
- Le Page, Y. (2002). *J. Appl. Cryst.* **35**, 175–181.
- Pratt, C. S., Coyle, B. A. & Ibers, J. A. (1971). *J. Chem. Soc.* pp. 2146–2151.
- Reger, D. L., Little, C. A., Young, V. G. & Pink, M. (2001). *Inorg. Chem.* **40**, 2870–2874.
- Sands, D. E. (1982). *Vectors and Tensors in Crystallography*, p. 102, Equation 4-42. New York: Dover.
- Schlessman, J. & Litvin, D. B. (1995). *Acta Cryst.* **A51**, 947–949.
- Schweitzer, J. W., Martinson, L. S., Baenziger, N. C., Swenson, D. C., Young, V. G. & Guzei, I. (2000). *Phys. Rev. B*, **62**, 12792–12799.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Shmueli, U. (1993). *International Tables for Crystallography*, Vol. B, p. 7. Dordrecht: Kluwer Academic Publishers.
- Sluis, P. van der (1989). Thesis, University of Utrecht.
- Smith, A. (2000). PhD thesis, University of Edinburgh.
- Sparks, R. A. (1999). *GEMINI*. Bruker AXS, Madison, Wisconsin, USA.
- Watkin, D. J., Prout, C. K., Carruthers, J. R., Betteridge, P. W. & Cooper, R. I. (2000). *CRYSTALS*, Issue 11. Chemical Crystallography Laboratory, University of Oxford.
- Young, V. G. (2001). *ROTWIN*. University of Minnesota, Minneapolis, USA.