

Refinement of Twinned Structures with *SHELXL97*

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Abstract

Four examples of the refinement of twinned structures are discussed. These structures illustrate three different types of twins: twinning by merohedry, pseudo-merohedry and non-merohedral twins. How the twinning was detected, how the structures were solved and how they were refined are shown in this paper. The difference between a refinement as a disordered model and a twinned model is illustrated. Sometimes the twin law was necessary to solve the structure, while in the other examples the twinning was first recognized during refinement of the structures. Finally, a list of ‘characteristic warning signs’ is presented which are indicative of possible twinning.

1. Introduction

A typical definition of a twinned crystal is the following: ‘Twins are regular aggregates consisting of crystals of the same species joined together in some definite mutual orientation’ (Giacovazzo, 1992). Therefore, for the description of a twin two things are necessary: a description of the orientation of the different species relative to each other (the twin law) and the fractional contribution of each component. The twin law can be expressed as a matrix which transforms the *hkl* indices of one species into the other.

In *SHELXL* (Sheldrick, 1998) the twin refinement method of Pratt *et al.* (1971) and Jameson (1982) has been implemented. F_c^2 values are calculated by

$$(F_c^2)^* = (\text{o.s.f.})^2 \sum_{m=1}^n k_m F_{c_m}^2 \quad (1)$$

where o.s.f. is the overall scale factor, k_m is the fractional contribution of twin domain m , F_{c_m} is the calculated structure factor of twin domain m and n is the number of twin domains. The sum of the fractional contributions k_m must be unity, so $(n - 1)$ of them can be refined and k_1 is calculated by

$$k_1 = 1 - \sum_{m=2}^n k_m. \quad (2)$$

Four types of twins may be distinguished:

(a) Twins by merohedry: The twin law is a symmetry operator of the crystal system, but not of the point group of the crystal. This means that the reciprocal lattices of the different twin domains superimpose exactly and the twinning is not directly detectable from the reflection pattern. Two types are possible:

(i) The twin operator belongs to the Laue group, but not to the point group of the crystal. These crystals are racemic twins. There are no special problems in solving and refining such structures. The only question to be resolved is the determination of the absolute structure. Even if the determination of the absolute configuration is not one of the aims of the structure determination, it is important to refine any non-centrosymmetric structure as the correct absolute structure in order to avoid introducing systematic errors into the bond lengths *etc.* (Cruickshank & McDonald, 1967). In some cases the absolute structure will be known with certainty (*e.g.* proteins), but in others it has to be deduced from the X-ray data. Generally speaking, a single phosphorus or heavier atom suffices to determine an absolute structure using Cu $K\alpha$ radiation and with accurate high-resolution low-temperature data, including Friedel opposites, such an atom may even suffice for Mo $K\alpha$.

The definition of the Flack parameter (Flack, 1983; Bernardinelli & Flack, 1985) is a special case of (1)

$$(F_c^2)^* = (1 - x)F_c^2(hkl) + xF_c^2(\overline{hkl}) \quad (3)$$

where x is the fractional contribution of the inverted component of a ‘racemic twin’; it should be zero if the absolute structure is correct, unity if it has to be inverted and somewhere in-between if racemic twinning is really present. Thus, the above formulae apply with $n = 2$ and the twin law $\mathbf{R} = (\overline{1}00, 0\overline{1}0, 00\overline{1})$.

(ii) The twin operator is part of the symmetry of a lattice point (holohedry). It does not belong to the Laue group of the crystal. This type is possible in the trigonal, tetragonal, hexagonal and cubic crystal systems. If the different twin domains have similar contributions, the reflection intensities appear to possess a higher symmetry than the true structure. The determination of the correct space group and solving the structure can be difficult. Patterson or molecular replacement methods may solve the problem. This type of merohedral twin-

ning may, at least in theory, occur simultaneously with racemic twinning (i).

(b) Twinning by pseudo-merohedry: The twin operator belongs to a higher crystal system than the structure. This may happen if the metric symmetry is higher than the symmetry of the structure; typical examples are monoclinic structures with either β very close to 90° or a and c almost equal. The problems are the same as in the case of type (ii). Depending on how well the higher metric symmetry is fulfilled it may happen that the reciprocal lattices overlap exactly and the twinning is not detectable from the diffraction pattern. The structure appears to have a higher symmetry than it in fact possesses. Solving and refining such twins requires essentially the same procedures as for merohedral twins.

In contrast to the two first types of twinning, in the remaining two types not every reflection is affected by the twinning. This means that the twinning may be detectable from the diffraction pattern. Structure solution may be possible by identifying and using only those reflections that are contributed to by a single twin domain alone.

(c) Twinning by reticular merohedry: A typical example is obverse/reverse twinning of a rhombohedral structure. This means that the reciprocal lattices of the different twin domains again superimpose exactly, but that systematic absent reflections for one domain are present for the others and *vice versa*. If enough reflections are only present for one twin domain, structure solution should be possible using these reflection intensities alone, possibly augmented by the intensities of the common reflections divided by the number of contributors.

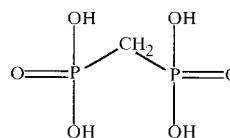
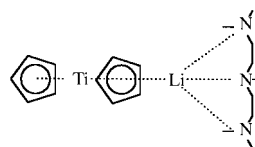
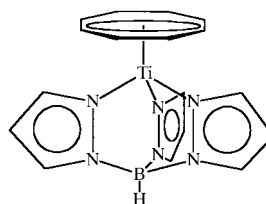
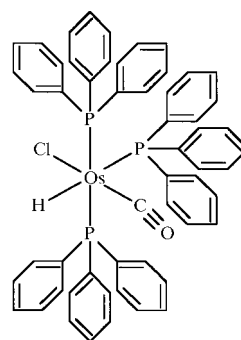
(d) Non-merohedral twins: The twin operator is an arbitrary operator. The reciprocal lattices do not exactly overlap. There are some reflections which overlap or cannot be distinguished from each other, while the majority of the reflections are not affected by the twinning. The diffraction pattern should normally reveal the twinning. Cell determination using automated diffractometer software may be a problem. Space-group determination may be a little complicated, because some systematically absent reflections may be affected by the other twin domains. With the correct unit cell and a subset of the data, structure solution should normally be possible, but the refinement may well be unsatisfactory unless overlap of some reflections caused by the twinning is taken into account.

If the reciprocal lattices of the twin domains do not exactly overlap, even a refinement taking the twinning into account often still remains unsatisfactory. Different reciprocal lattices have different orientation matrices. If the data are measured on a normal four-circle diffractometer without any kind of area detector and only the orientation matrix of one domain is used, the reflections of the other domains are of poor quality. The reflections

that have contributions from several domains may have bad shapes and macroscopic domains may well not be centred on the goniometer. Sometimes it is easier to look for better crystals than to collect such data and try a refinement taking twinning into account (see Example 4). Otherwise, special programs for data collection should be used (Henke, 1995). Area detectors are much better suited than point detectors for the collection of data from twinned crystals, but special software is required to analyse the data (Hahn, 1997). Sparks (1997) has presented programs for area detectors and discussed examples of their use.

2. Examples

Twinned crystals tend to have a poor effective data-to-parameter ratio, so they often require restraints



to obtain a satisfactory refinement (Watkin, 1994). In these examples, except where otherwise stated, the following restraints were employed: distance restraints

for chemically equivalent 1,2- and 1,3-distances, planarity restraints for groups such as phenyl rings, rigid-bond anisotropic displacement parameter (ADP) restraints (Hirshfeld, 1976; Rollett, 1970; Trueblood & Dunitz, 1983) and 'similar ADP restraints' (Sheldrick, 1998). Even when restraints are employed the distribution of the displacement parameters (*ORTEP* plot; Johnson, 1965) and residual features in a difference electron density map are often less satisfactory than for a normal structure determination.

3. Example 1

Structure (1) is an example of twinning by merohedry. It could not be solved by routine methods. The composition of the compound was not known with certainty, but some triphenylphosphine ligands were anticipated. The first problem was to determine the space group. The crystals appear to be trigonal with $a = b = 12.623$ (2) and $c = 26.325$ (5) Å. There were systematic absences for a 3_1 or a 3_2 axis. The R_{int} value ($R_{\text{int}} = \Sigma|F_o^2 - F_o^2(\text{mean})| / \Sigma[F_o^2]$) for the Laue group $\bar{3}$ was quite acceptable (0.067), but the value for the Laue group $\bar{3}m$ was only slightly higher (0.120). It was possible to obtain the coordinates of the osmium and four P atoms from the Patterson (Sheldrick, 1992) in the space group $P3_2$, but the resulting difference electron density map was not very satisfactory. In spite of the relatively low R values [$wR_2(\text{all data}) = 0.57$, $R_1 [I > 2\sigma(I)] = 0.24$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$] only a small part of the structure could be identified.

However, there were some typical warning signs of twinning. The mean value of $|E^2 - 1|$ was very low

(0.510) and the R_{int} value for the higher symmetric Laue group was significantly, but only slightly, higher than for the lower symmetric one. This could mean that the twofold axis was not a true crystallographic one, but the twin law. This axis interchanges h and k and reverses l , so the matrix is $010, 100, 00\bar{1}$. Taking this twinning into account substantially improved the refinement. The R values dropped to 0.13 (R_1) and 0.35 (wR_2). Several phenyl rings could now be located and after a few cycles of refinement the whole structure could be found. The refinement of k_2 converged to 0.404 (5). Fig. 1 shows the final structure. The structure will be discussed more fully elsewhere.

In non-centrosymmetric space groups and with heavy atoms such as osmium it should be possible to determine the absolute structure. The Flack parameter x (Flack, 1983) refined to 0.61 (6). This could mean that the absolute structure is wrong and the space group $P3_1$ is correct rather than $P3_2$ and/or that there is some additional racemic twinning. Changing to the space group $P3_1$ and refining as a four-component twin so as to take racemic twinning into account showed that $P3_1$ is indeed the correct space group and that there is no racemic twinning, but that the twin law should be changed to $0\bar{1}0, \bar{1}00, 001$. This could be recognized by the refined k values: $k_2 = 0.064$ (13) for matrix $010, 100, 00\bar{1}$, $k_3 = 0.038$ (17) for matrix $\bar{1}00, 0\bar{1}0, 00\bar{1}$ and $k_4 = 0.329$ (13) for matrix $0\bar{1}0, \bar{1}00, 001$. It was necessary to introduce some restraints. There are nine chemically equivalent phenyl rings, so all chemically equivalent 1,2- and 1,3-distances in the nine rings were restrained to be the same. For every phenyl ring a planarity restraint was employed. For the anisotropic displacement parameters of the C atoms it was necessary to use the rigid bond and simi-

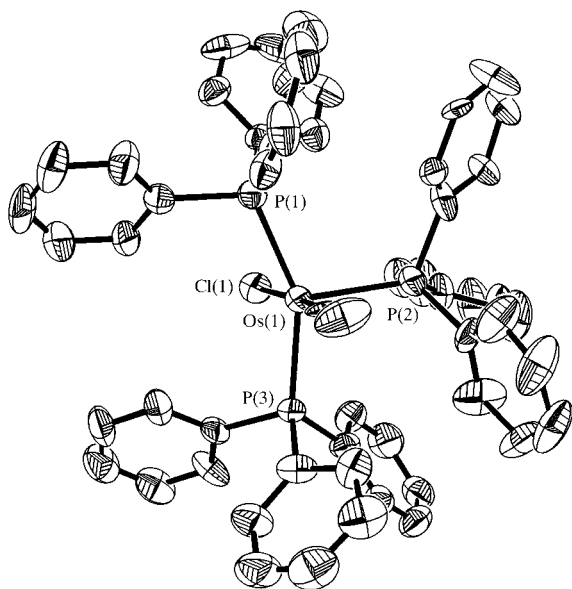


Fig. 1. Structure of (1), hydrido-chloro-carbonyl-tris(triphenylphosphine)osmium(II).

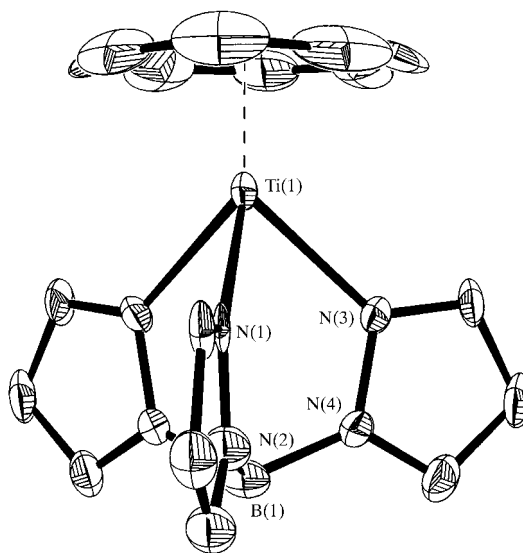


Fig. 2. Structure of (2), (η^8 -cyclooctatetraenyl)[hydrotris(pyrazol-1-yl)borato]titan(III).

Table 1. Comparison of the refinements of (2) in *Cm* and

	<i>R3m</i>	
	<i>Cm</i>	<i>R3m</i>
$R_1 [I > 2\sigma(I)]$	0.025	0.020
wR_2 (all data)	0.069	0.050
k_2, k_3	0.341 (5), 0.327 (5)	—
Flack x	-0.06 (3)	-0.01 (3)
Number of data	1064	437
Parameters	131	111
Restraints	165	168
Data/parameter ratio	8.1	3.9
S.u. (C—C) in C_8H_8	0.004–0.006	0.012–0.014
S.u. (C—C) in pyrazole	0.005–0.008	0.004

larity restraints. There is also one disordered ethanol molecule in the cell; distance and ADP restraints were employed to refine it. The refinement of 606 parameters with 4384 data and 1354 restraints converges to $R_1 = 0.046$ [for $I > 2\sigma(I)$], $wR_2 = 0.102$ (all data) and an absolute structure parameter of 0.026 (13).†

4. Example 2

The second structure (Kilimann *et al.*, 1994) is an example of twinning by pseudo-merohedry. Fig. 2 shows the final structure. The structure appeared to be rhombohedral [$a = b = 11.083$ (2), $c = 11.953$ (2) Å]. Again the mean value of $|E^2 - 1|$ (0.647) was lower than expected. There were no additional systematic absences. The R_{int} values for the Laue groups $R\bar{3}$ and $R\bar{3}m$ were identical (0.042) and the structure was initially solved by direct methods (Sheldrick, 1990) in the space group $R3m$. The pyrazole ring system was quite normal, but rather than the eight-membered cyclooctatetraene ring a six-membered ring with very long carbon–carbon bonds appeared in the electron density map. This was caused by the assumption of a threefold axis; there was only one sixth of a molecule in the asymmetric unit, so the eight-membered ring should be disordered. With distance restraints for the equivalent 1,2- and 1,3-C—C distances, a planarity restraint for the ring, rigid-bond restraints and hard similarity restraints (standard uncertainty, s.u., of 0.005), even an anisotropic refinement of the disordered model was possible, but the data-to-parameter ratio was awful.

Since part of the structure does not fulfil the threefold symmetry, the correct space group may be *Cm* rather than $R3m$, with the apparent threefold axis as the twin law. The low value for R_{int} in $R3m$ would then be caused by twinning. With the matrix $\begin{pmatrix} -0.3333 & 0.3333 & -0.6667 \\ 110 & 0.3333 & -0.3333 \\ -0.3333 & -0.3333 & 110 \end{pmatrix}$, the hexagonal cell is transformed into a monoclinic *C*-centred cell with $a =$

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: JZ0004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Systematic absence exceptions for example (3)

	2_1	a	c	n
Number of reflections	22	225	225	232
Number of reflections with $I > 3\sigma$	0	84	83	167
Mean intensity	0.6	32.6	27.6	57.3
Mean intensity-to-sigma ratio	0.5	8.7	8.3	16

10.220 (2), $b = 11.083$ (3), $c = 7.538$ (3) Å, $\beta = 96.85$ (3)°. The structure was solved again by direct methods in the new space group. Now there is one half of the molecule in the asymmetric unit. The structure fulfils the mirror symmetry and there is no longer any disorder. To derive the matrix notation of the threefold axis in the monoclinic cell it is necessary to multiply three matrices. The first matrix is the one above that transforms the hexagonal cell into the monoclinic one, the second describes the threefold axis in the hexagonal cell (010, $\bar{1}\bar{1}0$, 001) and the last is the transformation from monoclinic to hexagonal, which is the inverse of the first matrix. The result is the matrix $\begin{pmatrix} 0.5 & -0.5 & 1 \\ 0.5 & -0.5 & -1 \\ 0.5 & 0.5 & 0 \end{pmatrix}$. For the refinement of this model again several restraints were helpful. All chemically equivalent 1,2- and 1,3-distances were restrained to be equal. For the anisotropic displacement parameters of the N and C atoms relatively hard rigid-bond (s.u. 0.002) and softer similarity restraints (s.u. 0.01) were used. For the eight-membered ring a planarity restraint was imposed. It was necessary to employ damping, otherwise the refinement did not converge. Since this leads to slightly lower s.u.'s than the correct ones, the final refinement cycle was performed with zero 'shift multipliers' and without damping in order to obtain unbiased standard uncertainties. Table 1 compares the two refinements. Primarily because of the better data-to-parameter ratio, we preferred the twinned refinement to the disordered refinement and the structure was published in *Cm*. The almost identical k values show that the crystal was an ideal 'drilling' (a German word), which explains the low R_{int} value in the rhombohedral space group.

5. Example 3

The third example is the structure of the thallium compound $C_{19}H_{33}LiN_3Tl$ (Armstrong *et al.*, 1993). It is again an example of twinning by pseudo-merohedry. The data were collected with the following monoclinic primitive cell: $a = 13.390$ (3), $b = 25.604$ (6), $c = 13.390$ (3) Å, $\beta = 112.39$ (3)°. a and c have equal lengths and therefore the matrix $\begin{pmatrix} 101 & \bar{1}01 & 0\bar{1}0 \end{pmatrix}$ transforms this cell into an orthorhombic *C*-centred one with $a = 14.900$, $b = 22.252$, $c = 25.604$ Å (LePage, 1982). The R_{int} values are similar: 0.097 for the orthorhombic case and 0.081 for monoclinic, so the orthorhombic system was tried first. The mean value for $|E^2 - 1|$ was 1.074, but the systematic absences were strange and the Siemens *SHELXTL-Plus* program *XPREP* (Sheldrick, 1991)

Table 3. Comparison of different refinements of (4)

	(A) original data	(B) without $\Delta F^2/\text{s.u.} > 6$	(C) without $ h = 0, 1, 5, 6$	(D) $ h = 0$ or 6 split	(E) $ h = 0, 1, 5$ or 6 split	(F) E less $\Delta F^2/\text{s.u.} > 6$
Unique data	1667	1654	991	2977	2992	2974
$R_1 [I > 2\sigma(I)]$	0.101	0.091	0.040	0.083	0.057	0.050
wR_2 (all data)	0.300	0.251	0.104	0.252	0.221	0.146
K^\dagger	13.225	8.490	0.023	4.436	0.388	0.413
$\Delta\rho_{\text{max}}$ (e \AA^{-3})	1.97	1.70	0.33	1.47	0.80	0.56
k_2	—	—	—	0.206 (6)	0.170 (3)	0.205 (2)
S.u. (P–O, P–C)	0.006–0.008	0.005–0.007	0.002–0.004	0.004–0.006	0.003	0.002–0.003

$\dagger K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$ for $0 < F_c/F_{c_{\text{max}}} < 0.016$.

could not find any acceptable space group. In the monoclinic crystal system the mean value of $|E^2 - 1|$ was 1.119. Again the systematic absences were strange, as shown in the following reciprocal space plot of the $h0l$ layer (Fig. 3) and in Table 2.

The distributions for an a or a c glide plane were quite similar. In the reciprocal space plane $h0l$ there are many very strong and also many very weak reflections (this is the reason for the anomalously high value for the mean of $|E^2 - 1|$). All reflections with h and l even are very strong and all reflections with both h and l odd are nearly absent. Taking into account that a and c have equal lengths, there is a simple explanation. The crystal is twinned and the twin law is $001, 0\bar{1}0, 100$. Therefore, a and c are interchanged and the correct space group is $P2_1/c$. The absences are caused by the overlap of the two twin domains with effective space groups $P2_1/c$ and $P2_1/a$. Again the relatively low R_{int} value for the higher symmetric (*i.e.* orthorhombic) description is caused by twinning. It was possible to obtain the coordinates of two Ti atoms from a Patterson map in $P2_1/c$. With these coordinates the whole structure could be found in a difference electron density map. There are two independent and almost identical molecules in the asymmetric unit. The structure refined to $R_1 [I > 2\sigma(I)] =$

0.043, wR_2 (all data) = 0.112, $k_2 = 0.474$ (1). Fig. 4 shows one of the cation–anion pairs.

6. Example 4

The last structure is methylene diphosphonic acid, $\text{CH}_6\text{O}_6\text{P}_2$ (DeLaMatter *et al.*, 1973; Peterson *et al.*, 1977), and is an example of a non-merohedral twin. The space group is $P2_1/c$ with $a = 7.820$ (4), $b = 5.468$ (3), $c = 13.693$ (6) Å, $\beta = 103.57$ (4)°. Direct methods solved the structure with no problems. There were several reflections that violate the systematic absences. For most of them $|h|$ was 6 or 1. There were also no problems with the refinement, but the R values were very high (see refinement A in Table 3). Many reflections disagreed substantially with the model. For all of them $|h|$ was 0, 1, 5 or 6, and F_o was greater than F_c . The factor $K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$ was very high for the reflections with low intensity. There were also many high residual peaks with densities of more than 1 e \AA^{-3} . Omission of the 'most disagreeable' reflections with $F^2/\text{s.u.} > 6$ (refinement B) lowers the R values and also the residual density, but the result was not yet satisfactory. Disorder or solvent molecules were not detectable.

Again interpretation of the twinning solved the problem. To derive the twin law we had to find a matrix that transforms the cell into an equivalent cell, see Fig. 5. We knew that a factor of $1/6$ or $5/6$ in a was involved. After several trials we found the matrix $100, 0\bar{1}0, -0.8217$ ($\sim 5/6$) $0\bar{1}$. The reciprocal lattices coincide

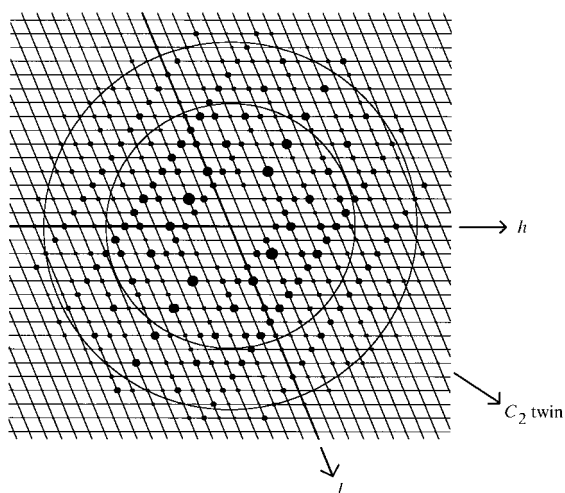


Fig. 3. $h0l$ layer of reciprocal space for example (3).

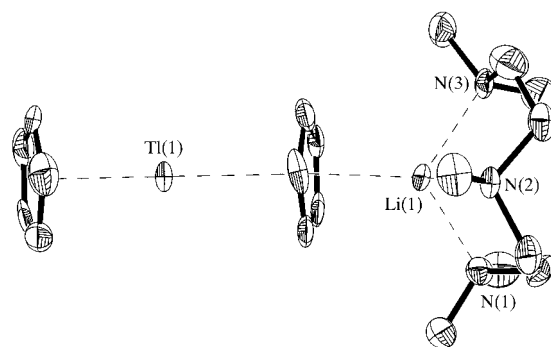


Fig. 4. Structure of (3), showing one of the two independent cation–anion pairs $[\text{PMDETA.Li}]^+[\text{CpTi}^-\text{Cp}]^-$.

almost exactly when $|h| = 0$ or 6. When $|h| = 1$ or 5, the reflections are so close that in most cases they cannot be resolved from one another.

In test *C* all reflections with $|h| = 0, 1, 5$ or 6 were omitted. The *R* values dropped substantially and the residual density was now in the normal range. The *K* value [$\text{mean}(F_o^2)/\text{mean}(F_c^2)$] for the reflections with $0 < F_c/F_{c_{\text{max}}} < 0.016$ is now very low. The most disagreeable reflection has $\Delta F^2/\text{s.u.} = 6.96$. In a second step we took twinning for the reflections with $|h| = 0$ or 6 into account. The *R* values dropped, but there were still many reflections with $|h| = 1$ or 5 which were inconsistent. Therefore, we also split the reflections with $|h| = 1$ and 5 (refinement *E*). This refinement was better, but now the intensities of some reflections with $|h| = 1$ were underestimated. For these reflections, both reciprocal lattices were distinguishable and only one reflection had been measured. Therefore, for our final refinement (*F*) we omitted all the reflections with $F^2/\text{s.u.} > 6$.

This structure is known and in the literature there is no indication of twinning. Refinement *F* results in similar s.u.'s to the published untwinned structure, although the *R* value is higher, probably because of the problem handling partial overlap; we also suspect that one twin component was better centred in the beam than the other.

7. Conclusions

Twinning usually arises for good structural reasons. When the heavy atom positions correspond to a higher symmetry space group it may be difficult or impossible to distinguish between the twinning and disorder of light atoms (Hoenle & von Schnering, 1988). Since refinement as a twin usually requires only two extra instructions and one extra parameter, in such cases it should be attempted first before investing many hours in a detailed interpretation of the 'disorder'! Refinement of twinned crystals often requires the full arsenal of constraints and restraints, since the refinements tend to be less stable, and the effective data-to-parameter ratio may well be low. In the last analysis chemical and crystallographic

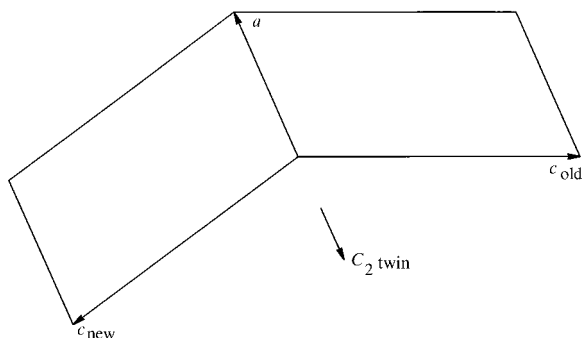


Fig. 5. Scheme of the twin law of (5); twin axes $[100]$ with $c_{\text{new}} = (2c \cos \beta/a) \cdot a - c_{\text{old}}$, where $(2c \cos \beta/a) = -0.8217$.

intuition may be required to distinguish between the various twinned and disordered models, and it is not easy to be sure that all possible interpretations of the data have been considered.

Experience shows that there are a number of characteristic warning signs for twinning given in the following list. Of course not all of them can be present in any particular example, but if one finds several of them, the possibility of twinning should be given serious consideration.

(a) The metric symmetry is higher than the Laue symmetry.

(b) The R_{int} value for the higher-symmetry Laue group is only slightly higher than for the lower-symmetry Laue group.

(c) The mean value for $|E^2 - 1|$ is much lower than the expected value of 0.736 for the non-centrosymmetric case. If we have two twin domains and every reflection has contributions from both, it is unlikely that both contributions will have very high or very low intensities, so the intensities are distributed so that there are fewer extreme values. Other tests based on intensity statistics have been proposed (Rees, 1980). However, the use of the mean $|E^2 - 1|$ value is particularly simple, because it is a single number and often calculated by data reduction and direct methods programs.

(d) The space group appears to be trigonal or hexagonal.

(e) The apparent systematic absences are not consistent with any known space group.

(f) Although the data appear to be in order, the structure cannot be solved. This may also happen if the cell is incorrect, e.g. with a halved axis.

(g) The Patterson function is physically impossible. The following points are typical for non-merohedral twins, where the reciprocal lattices do not overlap exactly and only some of the reflections are affected by the twinning.

(h) There appear to be one or more unusually long axis.

(i) There are problems with the cell refinement.

(j) Some reflections are sharp, others split.

(k) $K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$ is systematically high for the reflections with low intensity. This may also indicate a wrong choice of space group in the absence of twinning.

(l) For all of the 'most disagreeable' reflections, F_o is much greater than F_c .

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