Refinement of obverse/reverse twins

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Two examples of structures of obverse/reverse twins are presented. Example (1) is the structure of 2,2,4,4,6,6-hexa-*tert*-butylcyclotrisiloxane. It crystallizes in $R\bar{3}c$. Example (2) is the structure of [{Li(Me$_3$Si)$_3$CAlF$_3$(thf)}$_3$LiF(thf)], tris[lithiuim tetrahydrofuran (trimethylsilyl)methyltrifluoroaluminate]lithium fluoride tetrahydrofuran. It crystallizes in $R3$. Additional to the obverse/reverse twinning this structure shows merohedral twinning. It will be shown how these two structures can be refined with the *SHELXL* program.

1. Introduction

For structures that crystallize in rhombohedral space groups, a twofold axis parallel to the threefold (matrix $-1\ 0\ 0\quad 0\ -1\ 0\quad 0\ 0\ 1$ in the hexagonal setting) or a twofold parallel to **a-b** (matrix $0\ -1\ 0\quad -1\ 0\ 0\quad 0\ 0\ -1$ in the hexagonal setting) as twin law produces a so-called obverse/reverse twin. In the hexagonal setting the reflection condition for the first domain is $-h + k + l = 3n$ (obverse setting), while for the second it is $h - k + l = 3n$ (reverse setting). Therefore, it can be a problem to detect this lattice centring. It can be identified by a comparison of the mean intensity or mean intensity-to-sigma ratio of the reflections with $-h + k + l = 3n$, $h - k + l = 3n$ and all reflections (see, for example, Table 1 produced by the program *XPREP*; Sheldrick, 2001). Also, inspection of reciprocal space plots can help. In layers with $l = 3n$ (see, for example, Fig. 2) only every third reflection should be observed, while in all the other layers one third of the reflections are absent (see, for example, Fig. 3). Version 6.12 of the program *XPREP* gives further help. It checks the mean intensity for the reflections that should be observed

   (i) only in case of the obverse setting,
   (ii) only in case of the reverse setting and
   (iii) for reflections which should be absent in both cases.

Then it estimates the fractional contribution of the second domain.

   With obverse/reverse twinning there are four types of reflections: reflections with $-h + k + l = 3n$ and $h - k + l \neq 3n$ are only observed for the main domain, reflections with $-h + k + l \neq 3n$ and $h - k + l = 3n$ have non-zero intensity only for

Table 1
Systematic absences for lattice centring for structure (1).

N = number of reflections that should be absent for the specified type of lattice centring; N ($I > 3$) = number of reflections that are observed but should be absent; $\langle I \rangle$ = mean intensity; $\langle I/\sigma \rangle$ = mean intensity divided by sigma.

	P	A	B	C	I	F	Obv	Rev	All
N	0	24 007	23 990	24 073	23 965	36 035	31 904	31 933	47 973
N ($I > 3$)	0	6923	6940	7407	6952	10635	4024	6980	13 635
$\langle I \rangle$	0.0	80.7	81.8	84.7	81.2	82.4	16.9	66.5	81.5
$\langle I/\sigma \rangle$	0.0	4.1	4.1	4.3	4.1	4.2	1.6	3.4	4.0

the second domain, reflections with $-h + k + l \neq 3n$ and $h - k + l \neq 3n$ are absent for both domains and reflections with $-h + k + l = 3n$ and $h - k + l = 3n$ have contributions from both domains. Since only one third of the reflections (with $l = 3n$) are affected by the twinning, structure solution is normally not a severe problem, because two thirds of the reflections have contributions from only one domain and are often sufficient for structure solution. *XPREP*6.12 is able to produce a crude untwinned data set, if more data are required for the structure solution.

For the refinement *SHELXL* (Sheldrick, 1997) fits the observed intensity to the combined intensity of the different components as proposed by Pratt *et al.* (1971) and Jameson (1982)

$$(F_c^2)^* = osf^2 \sum_{m=1}^{n} k_m F_{c_m}^2, \qquad (1)$$

where osf 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

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

For an obverse/reverse twin the current version of *SHELXL* needs a special reflection file and the refinement is not possible with a single 'TWIN' command. This restriction is unnecessary and will be removed if and when there is a new release of the program. Detwinned data should not be used for the refinement because of the correlations between twin-related reflections.

After producing the special format for twinned data (*SHELXL HKLF*5 format) further merging of equivalent reflections is not possible, so the reflections should be merged before producing this file. Otherwise all data would be treated as independent, which would lead to mathematically incorrect standard uncertainties.

The twinned data file must be produced in the following way:

Reflections that are absent for both domains are omitted and in practice it may well be expedient to also omit the reflections that have only a contribution from the second domain. Normally the second domain is weaker and is often not as well centred in the beam, when the crystal consists of two physically separate rather than penetrating domains. These additional data are thus of poorer quality and will not improve the model. Secondly they would be treated as independent data, but are of course not independent of reflections of the first domain with the same indices, which would tend to falsify the standard uncertainties. Reflections that have a
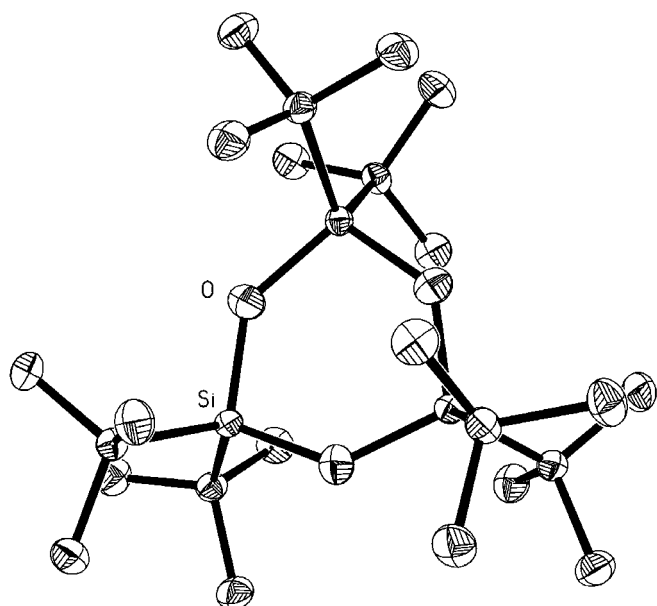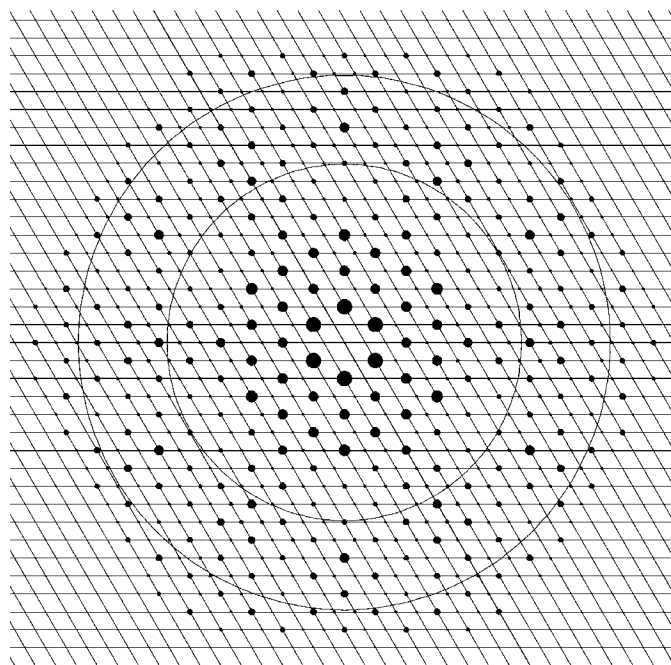

Figure 1
Crystal structure of (1).

Figure 2
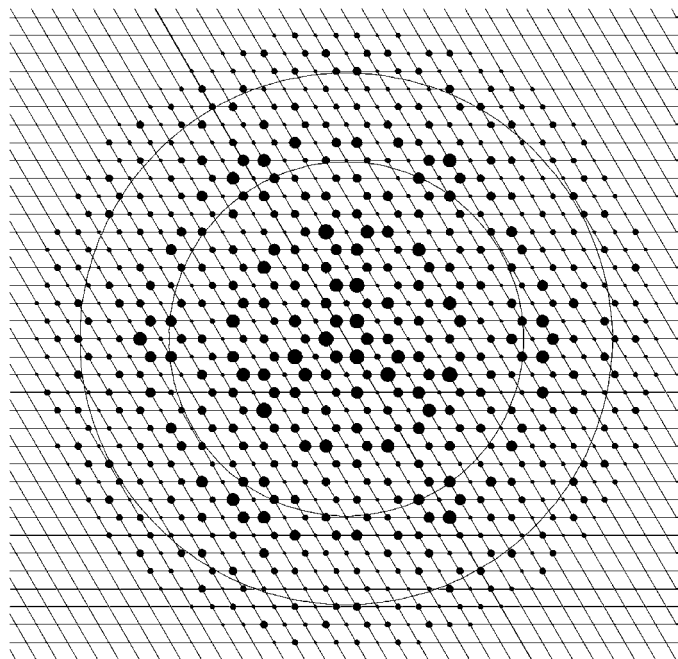Reciprocal space plot of layer $l = 0$ of structure (2).

Table 2
Comparison of different refinement for structure (1).

$K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$.

	Without TWIN	With TWIN
R_1 [$F > 4(F)$]	0.057	0.035
wR_2 (all data)	0.164	0.090
K_2	–	0.151(4)
Res. electron density (e Å^{-3})	0.96	0.39
s.u. (C—C) [Å]	0.0044–0.0046	0.0024–0.0025
K (weakest reflections)	4.498	2.500

contribution only from the main domain are unchanged and are assigned the batch number 1. Reflections with contributions from both domains are split into their two components $\bar{h}\bar{k}l$ and hkl (if the twin axis is parallel to **c**) or $\bar{k}h\bar{l}$ and hkl (if the twin axis is perpendicular to **c**, in the higher-symmetry trigonal Laue group these two twin laws are equivalent). The batch numbers -2 and 1 tell the program that these two reflections of domains 2 and 1 contribute to one observed intensity.

For structures crystallizing in the lower symmetry rhombohedral Laue group, in addition to obverse/reverse twinning the twofold axis parallel to **a** + **b** may act as a further twin law (matrix 0 1 0 1 0 0 0 0 −1). In this case the twinned reflection data file will contain up to four contributions to each observed intensity. Reflections that are only present for the obverse setting are split into the two components $kh\bar{l}$ and hkl with batch numbers -3 and 1, while reflections with $l = 3n$ are split into the four components: $\bar{k}h\bar{l}$, $kh\bar{l}$, $\bar{h}\bar{k}l$ and hkl with the batch numbers assigned as -4, -3, -2 and 1.

Figure 3
Reciprocal space plot of layer $l = 1$ of structure (2).

2. Example (1)

Example (1) is the structure of 2,2,4,4,6,6-hexa-*tert*-butylcyclotrisiloxane. The crystal appears to be trigonal with $a = b = 10.0793\,(7)$ and $c = 48.409\,(4)$ Å. There seemed to be systematic absences for an obverse setting, although some of the reflections with $-h + k + l = 3n$ had small but significant intensity. The systematic absences for a **c** glide plane were quite obvious. Structure solution (Sheldrick, 1990) with direct methods succeeded without problems in $R\bar{3}c$ and also the refinement was straightforward (see Fig. 1).

Although the data seemed to be good, the refinement converged to moderate figures of merit (see Table 2). Perhaps only the residual density, which could not be resolved as disorder or additional solvent, showed clearly that something was wrong. In the list of the 'most disagreeable reflections' it could be noticed that for all of them $l = 3n$ and F_o^2 was always much greater than F_c^2. This could be explained by obverse/reverse twinning. Only the reflections with $l = 3n$ have contributions from the second domain. Therefore, for them the measured intensity is higher than one would calculate for the model. Closer inspection of the systematic absences for the lattice centring (see Table 1) and reciprocal space plots and the new obverse/reverse check in *XPREP*6.12 (mean intensity: obverse only 146.3, reverse only 28.2, neither obverse nor reverse 4.8) confirmed this hypothesis. *XPREP* estimates the fractional contribution of the second domain as 0.162.

Refinement as an obverse/reverse twin leads to a significant improvement (see Table 2). The structure has been previously determined from an untwinned crystal (Clegg, 1982) and the quality of the twin refinement is comparable to that of the original untwinned refinement.

3. Example (2) (Hatop *et al.*, 2001)

The structure determination of the second structure was not as straightforward. The cell constants are $a = b = 14.899\,(2)$, $c = 30.472\,(6)$ Å. Here the space group determination was not as clear. The inspection of the systematic absences for the lattice centring (see Table 3, Figs. 2 and 3) gave a first indication of obverse/reverse twinning, which then was confirmed with the obverse/reverse check (mean intensity: obverse only 9.7, reverse only 5.0, neither obverse nor reverse 0.1). *XPREP* estimates the fractional contribution of the reverse component to be 0.342.

The composition of the compound was not known, but an AlC(SiMe$_3$)$_3$ unit was expected. Direct methods in $R3$ with the original data showed this unit, but the C(SiMe$_3$)$_3$ unit was disordered. Using *SHELXL* with a 'twin reflection file' for obverse/reverse twinning to expand from this unit leads after several steps to the whole structure. Although the whole structure could be found and the disorder could be modelled, the refinement remained unsatisfactory, but was much better than a refinement with the original data without taking the twinning into account (see Fig. 4 and Table 4).

In the refinement with the original data, the $l = 3n$ reflections do not show up as clearly in the list of 'most disagreeable

Table 3
Systematic absences for lattice centring for structure (2).

N = number of reflections that should be absent for the specified type of lattice centring; N ($I > 3$) = number of reflections that are observed but should be absent; $\langle I \rangle$ = mean intensity; $\langle I/\sigma \rangle$ = mean intensity divided by sigma.

	P	A	B	C	I	F	Obv	Rev	All
N	0	62 289	62 289	62 272	62 291	93 425	82 924	82 920	124 456
N ($I > 3$)	0	24 836	24 918	24 978	24 949	37 366	16 134	21 440	49 852
$\langle I \rangle$	0.0	5.5	5.6	5.5	5.5	5.5	1.9	3.5	5.5
$\langle I/\sigma \rangle$	0.0	8.6	8.6	8.6	8.6	8.6	3.5	5.8	8.6

Table 4
Comparison of different refinement for structure (2).

	Without TWIN data set 1	As obverse/reverse twin data set 1	Additional merohedral twin data set 1	Merohedral twin data set 2	Additional obverse/reverse twin data set 2
R_1 [$F > 4(F)$]	0.144	0.110	0.032	0.040	0.032
wR_2 (all data)	0.383	0.304	0.087	0.110	0.087
K_2	–	0.218 (5)	0.004 (2)	0.559 (2)	0.088 (2)
K_3	–	–	0.1345 (11)	–	0.499 (2)
K_4	–	–	0.339 (3)	–	0.007 (2)
Res. electron density (e Å^{-3})	1.14	0.60	0.27	0.30	0.15
s.u. (Al—F) (Å)	0.0064–0.0073	0.0057–0.0062	0.0023–0.0024	0.0028–0.0029	0.0022
Flack x	0.4 (6)	0.3 (5)	0.3 (2)	0.3 (2)	0.3 (2)

reflections' as for the first structure. Further inspection of the data with *XPREP* after applying obverse/reverse 'detwinning' showed warning signs for additional merohedral twinning: The mean $|E^2 - 1|$ value was 0.669 and therefore lower than the expected value of 0.736 for a non-centrosymmetric space group. The R_{int} value for the higher-symmetry Laue group $\bar{3}m$ was 0.237 compared with 0.020 for the correct Laue group. The difference between 0.020 and 0.237 clearly indicated the correct Laue group to be $\bar{3}$, but is small enough for additional twinning with the twin law 0 1 0 1 0 0 0 0 −1. This became much clearer with a second data set. This data set was integrated on an R lattice. No signs of obverse/reverse twinning were noticed at first glance. The mean value for $|E^2 - 1|$ was 0.586, even lower than in the first data set, and the R_{int} values were 0.037 for $\bar{3}$ and 0.070 for $\bar{3}m$. Significantly different R_{int} values for the higher-symmetry Laue group with different crystals of the same compound clearly show that the lower-symmetry Laue group is correct and indicates different extents of twinning.

For the first data set four twin domains were taken into account, as described above. All refinement residuals converged to satisfactory values (see Table 4).

The only remaining unsatisfactory feature is the value of the Flack x parameter (Flack, 1983). It is not possible to determine the absolute structure with certainty. We also tried the feature in *SHELXL* for introducing additional racemic twinning, so that we could be sure that the correct absolute structure of each domain is used. However, this does not improve anything. Of course, Al and Si do not have large anomalous signals with Mo radiation. However, for untwinned data sets better standard uncertainties for the Flack x parameter would be expected in such cases. Therefore, for doubly twinned data sets large anomalous signals would be needed to determine the absolute structure.

4. Conclusions

These two examples clearly show that twin refinement may lead to acceptable results comparable to models derived from single crystals.

Sometimes it is not so easy to detect all possibilities for twinning, but if the twin refinement remains unsatisfactory this is a sign that there may be further problems such as additional twinning.
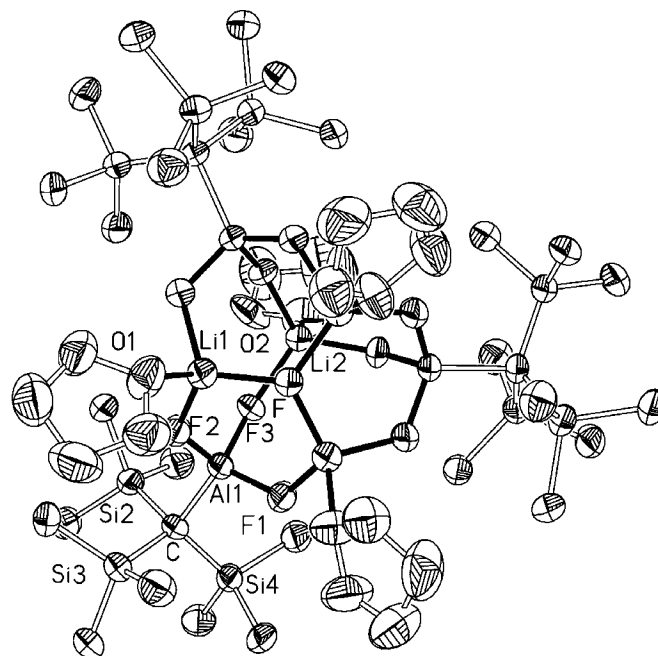

Figure 4
Crystal structure of (2)

For (2) two data sets were collected. With the second data set a refinement taking only the merohedral twinning into account (*i.e.* with a single 'TWIN' command) also leads to satisfactory results. No significant sign of obverse/reverse twinning was apparent for this crystal, but taking this additional obverse/reverse twinning into account in the refinement leads to small but significant improvements, although the fractional contribution is only 8%. The hint that obverse/reverse twinning might be present came only from the other data set. This suggests that obverse/reverse twinning with a small amount of the second domain may be overlooked very easily, especially if the data are integrated on an R lattice. Since a proper twin refinement improves the model, the possibility of obverse/reverse twinning should be checked much more often or even routinely for every structure in a rhombohedral space group.

In a previous paper about twin refinement (Herbst-Irmer & Sheldrick, 1998) we listed some warning signs for twinning:

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

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

(iii) The mean value of $|E^2 - 1|$ is much lower than the expected value (0.736 for the non-centrosymmetric case).

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

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

(vi) Although the data appear to be in order, the structure cannot be solved.

(vii) 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:

(viii) There appear to be one or more unusually long axes.

(ix) There are problems with the cell refinement.

(x) Some reflections are sharp, others split.

(xi) $K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$ is systematically high for the reflections with low intensity.

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

The examples described here show a further typical feature, which should added to the above list:

(xiii) Strange residual density, which could not be resolved as solvent or disorder.

References

Clegg, W. (1982). *Acta Cryst.* B**38**, 1648–1649.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hatop, H., Schiefer, M., Roesky, H. W., Herbst-Irmer, R. & Labahn, T. (2001). *Organometallics*, **20**, 2643–2646.

Herbst-Irmer, R. & Sheldrick, G. M. (1998). *Acta Cryst.* B**54**, 443–449.

Jameson, G. B. (1982). *Acta Cryst.* A**38**, 817–820.

Pratt, C. S., Coyle, B. A. & Ibers, J. A. (1971). *J. Chem. Soc.* pp. 2146–2151.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (2001). *XPREP*6.12, *SHELXTL*. Bruker-AXS, Madison, Wisconsin, USA.