

## Merohedral twin interpretation spreadsheet, including command lines for *SHELXL*

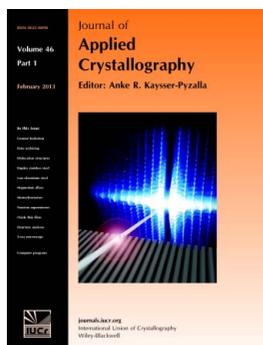
Howard D. Flack and Michael Wörle

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Merohedral twin interpretation spreadsheet,  
including command lines for *SHELXL*Howard D. Flack<sup>a</sup> and Michael Wörle<sup>b\*</sup><sup>a</sup>Chimie minérale, analytique et appliquée, University of Geneva, Geneva, Switzerland, and <sup>b</sup>Laboratorium für Anorganische Chemie, ETH Zürich, HCI H103, Wolfgang-Pauli-Strasse 10, Zürich, CH-8093, Switzerland. Correspondence e-mail: woerle@inorg.chem.ethz.ch

Tables of alphanumeric data concerning crystals twinned by merohedry are presented, assembled into a spreadsheet. The twin table is structured on the 230 space groups and contains the following information: centrosymmetric/chiral indicator, polar axes, twin index, twin operators, some physical property relations, symmetry-related reflections, inversion techniques and a pointer to software use. The software table contains the preceding information translated into command lines for *SHELXL* [Sheldrick (2008). *Acta Cryst. A* **64**, 112–122]. The macromolecular table contains a reduced form of the twin table applicable to enantiomerically pure compounds of known absolute configuration.

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Printed in Singapore – all rights reserved**1. Introduction**

Twinning of a crystal may lead to the exact superposition of the reciprocal lattices of the various twin domains. In the literature, this is commonly referred to as twinning by merohedry. An example is that of twinning by inversion, which arises in the case of the determination of the absolute structure of a noncentrosymmetric crystal structure. If all reflections of any domain superpose exactly all reflections of the other domains, then the only way to treat the diffraction intensities is by including the volume fractions of all domains as variable parameters during the least-squares refinement of the crystal structure. These volume fractions are often called twin fractions and in practice represent the fraction of each twin domain within the total volume of the crystal irradiated during the diffraction experiment. Sometimes even individual crystalline specimens have varying twin fractions within their bulk. Refinement of twins is not a complicated procedure and may be readily and simply achieved. Although information for deriving the twin laws to be applied and for running the least-squares refinement software is available in the literature, it is often in a form that the hard-pressed structure analyst would find difficult and time-consuming to exploit. However, some software is now capable of generating the twin laws, and other products automatically undertake tasks such as inverting a structure. What is lacking is a compilation that gathers all the related information together in an easily accessible form. As a consequence, tables of relevant data have been compiled into a spreadsheet and are presented here. It is most important to note that they provide information both for the implementation of an appropriate least-squares refinement and for the rather neglected area of the interpretation of the twin fractions obtained. In the spreadsheet, the input lines for dealing with twinning are currently only provided for *SHELXL* (Sheldrick, 2008).

Other twinning modes leading to direct-space supercells or split reflections are best treated with entirely different procedures which are not treated here.

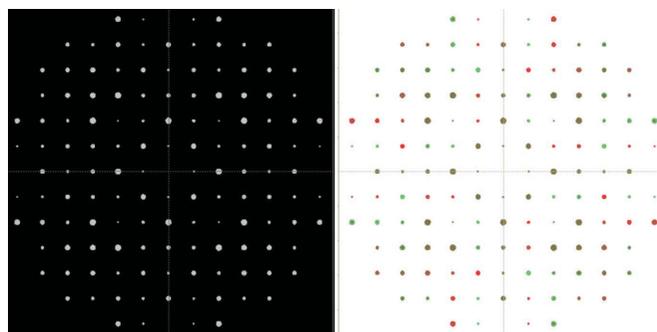
**2. Merohedral twinning – a short tutorial**

A twinned crystal is a composite composed of single-crystal domains. Although these domains all have the same crystal structure they

occur in various orientations in the twinned crystal. In a twin, these orientations are not arbitrary but occur only when the lattices of a pair of domains have certain lines, planes or even the whole lattice in common. Thus, this lattice criterion imposes definite restrictions on the mutual orientations of the domains. An essential element to keep in mind is that twinning always presents some aspect of symmetry reduction between the lattice on which the crystal structure is based and the crystal structure itself, *i.e.* there is always a group–subgroup relationship lurking somewhere in the background of a twinned crystal.

For the treatment of a crystal by X-ray diffraction there are two essential components to be determined: (i) the mutual orientation of the domains and (ii) the relative proportions of each domain in the irradiated macroscopic crystal.

In a twin with exact three-dimensional superposition of the reciprocal lattices of the single-crystal domains, a preliminary examination of reciprocal space may show nothing out of the ordinary. As an example, examine the diffraction pattern of the twin shown in Fig. 1. It looks fine. However, the Laue symmetry  $4/mmm$  of the twin is higher (for a twin ratio  $x_A = x_B = \frac{1}{2}$ ) than the Laue symmetry  $4/m$  of

**Figure 1**

The diffraction pattern with apparent Laue symmetry  $4/mmm$  on the left is composed of two individual diffraction patterns. These are shown on the right, with the individual components in green and red, each showing only a Laue symmetry of  $4/m$  (for which vertical mirror planes are not present in the individual diffraction patterns).

**Table 1**  
Information for space groups  $P4$ ,  $P4_2$ ,  $I4$ ,  $P4_1$ ,  $P4_3$  and  $I4_1$  given in the twin table.

The contents of the twin table are described in §3 of the text.

Space groups	Centro chiral	Polar axes	Twin index	Twin code	Twin operators	Physical properties	Symmetry-related reflections	Space groups	Inversion	<i>SHELXL</i>
$P4$ , $P4_2$ , $I4$	NC	$c$	4	$\alpha$	$1, 2_{[001]}, 4, 4^3$	Flack = $f(\chi) + f(\delta)$	$hkl, \bar{h}\bar{k}l, \bar{k}hl, k\bar{h}l$	$P4, P4_2, I4$	0, 0, 0	<i>SHELXL04</i>
$P4_1, P4_3$				$\beta$	$2_{[100]}, 2_{[010]}, 2_{\bar{1}\bar{1}0}, 2_{[110]}$	$= 1 - f(\alpha) - f(\beta)$	$\bar{h}\bar{k}l, \bar{h}k\bar{l}, \bar{k}h\bar{l}, k\bar{h}\bar{l}$	$P4_1, P4_3$	0, 0, 0	<i>SHELXL05</i>
				$\chi$	$\bar{1}, m_{[001]}, \bar{4}, \bar{4}^3$	$f(\text{chiral}) = f(\chi) + f(\delta)$	$\bar{h}\bar{k}l, h\bar{k}l, \bar{k}h\bar{l}, k\bar{h}\bar{l}$		$P4_1 \leftrightarrow P4_3$	
$I4_1$				$\delta$	$m_{[100]}, m_{[010]}, m_{\bar{1}\bar{1}0}, m_{[110]}$	$f(\text{pyro}) = f(\beta) + f(\chi)$	$\bar{h}kl, h\bar{k}l, khl, \bar{k}h\bar{l}$	$I4_1$	$\frac{1}{2}, 0, 0$	<i>SHELXL06</i>

each of its domains. The intensities of all reflections will have a contribution from both twin domains and this may be written as

$$|G(hkl)|^2 = x_A|F(hkl)|^2 + x_B|F(\bar{h}\bar{k}l)|^2, \quad (1)$$

with  $x_A + x_B = 1$ , where  $x_A$  and  $x_B$  are, respectively, the volume fractions of domains  $A$  and  $B$  in the macroscopic crystal. Notice that the symmetry operation relating  $hkl$  to  $\bar{h}\bar{k}l$  is just one of the vertical mirror planes present in  $4/mmm$  that is not present in  $4/m$ . Indexing to give a tetragonal unit cell and integration of reflection intensities is not problematic, and this type of twinning is therefore very often only detected in the later stages of the structure-determination process. However, it can be quite difficult to determine the correct space group in this case. Firstly, as the apparent Laue group is too high it is difficult to know which of its subgroups to select as the point group of the crystal structure. Secondly, some of the systematic absences may not be visible owing to superposition with reflections of measurable intensity from the other twin domains. A table that gives the correspondence between the apparent Laue classes, the reflection conditions and the apparent space groups of the twin, with possible space groups for the single-crystal domain, is given by Koch (1999). Structure solution may also be difficult, since every reflection from one component is affected by the second component. For the same reason, refinement as a single crystal will not lead to a satisfactory result.

There is a particular case of twinning which falls within the current section and which is of particular and common occurrence in the work of the structure analyst. This is the case of twinning by inversion, which may occur in any noncentrosymmetric crystal. One single-crystal domain is related to the other by the inversion operation. Indeed, such is the importance of twinning by inversion that it is now considered an obligatory requirement in the treatment of any noncentrosymmetric crystal, be it twinned by inversion or not. In a crystal twinned by inversion, even though the centrosymmetric Laue group of the diffraction pattern is the same for the twin and the individual domains, the noncentrosymmetric point group of the single crystal is different. Once again, all reflections of the diffraction pattern have contributions from both twin domains. Twinning by inversion can occur in all crystal systems and may even occur simultaneously with other twinning operations.

### 3. Twin table

To make it easier to understand the content of the twin table, given in full in the supplementary material,<sup>1</sup> Table 1 gives the entry for space groups  $P4$ ,  $P4_2$ ,  $I4$ ,  $P4_1$ ,  $P4_3$  and  $I4_1$ . The columns marked ‘Centro chiral’, ‘Polar axes’, ‘Twin index’, ‘Twin code’, ‘Twin operators’, ‘Physical properties’ and ‘Symmetry-related reflections’ apply to all

those space groups indicated in the space group column. On the other hand, the content of the two columns ‘Inversion’ and ‘*SHELXL*’ applies specifically to the space groups indicated on the same line or its continuation, *i.e.* there are separate entries for the set  $P4$ ,  $P4_2$ ,  $I4$ ; for the set  $P4_1$ ,  $P4_3$ ; and for  $I4_1$ .

The content of the tables is limited in the following ways: (i) indexing the diffraction intensities with integer indices leads to the unit cell of the model or reference structure and not to some supercell, and (ii) cases where twinning depends on a chance metrical relationship between the cell dimensions (metric specialization) are not treated. Consequently, the twin laws treated here apply for any arbitrary cell dimensions, limited only by the point group of the crystal.

#### 3.1. Space groups

This column contains a list of space groups to which the contents of the adjoining columns apply. All standard and alternative settings of the space groups appearing in Part 7 of *International Tables for Crystallography*, Vol. A (Hahn, 2002), are included. Thus, space groups in the monoclinic system are described with both  $b$  and  $c$  as unique axes, space groups in the orthorhombic system appear in two, three or six different orientations according to the case, and space groups with an  $hR$  lattice are described on both hexagonal (labelled HA) and rhombohedral (labelled RA) axes. The alternative orientation ( $Pb\bar{3}$ ) of space group No. 205 is also included, although it does not appear in Hahn (2002). For space groups in the monoclinic system, a short Hermann–Mauguin (H–M) symbol is given only for space groups on axes with  $b$  unique, whereas full H–M symbols are given for all monoclinic space groups. The line following each set of monoclinic space groups states whether the unique axis is  $b$  or  $c$ . For some space groups, Part 7 of *International Tables for Crystallography*, Vol. A (Hahn, 2002), presents alternative choices of origin, but these do not affect the properties described in the current tables.

#### 3.2. Centro chiral

This column contains one of the three codes NC, NA or CA. These were defined by Flack (2003) as follows:

- (a) NC means the crystal structure is noncentrosymmetric and chiral,
  - (b) NA means the crystal structure is noncentrosymmetric and achiral, and
  - (c) CA means the crystal structure is centrosymmetric and achiral.
- Crystal structures in any of the five space groups of Table 1 are noncentrosymmetric and chiral.

#### 3.3. Polar axes

This column indicates both the directions along which the origin of the space group cannot be fixed by reference to the symmetry elements and the limitations on the development of pyroelectricity.

<sup>1</sup> The set of tables discussed in this paper is available from the IUCr electronic archives (Reference: NB5039). Services for accessing these data are described at the back of the journal.

For crystal structures in any of the five space groups of Table 1, the origin of the space groups cannot be fixed by reference to symmetry elements along the  $c$  direction and the crystals may be pyroelectric. The information is taken from Table 10.2.1.2 of Hahn & Klapper (2002).

### 3.4. Twin index

This column indicates the potential maximum number of differently oriented domain states of the same crystal structure that can exist in a macroscopic crystal. In the case of the five space groups of Table 1, the maximum number of potential domain states is four. The twin index is the integer ratio of the order of the holohedry (point group of the crystal lattice) to that of the point group of the crystal structure. The values were calculated using software distributed with *International Tables for Crystallography*, Vol. D (Authier, 2003).

### 3.5. Twin code

This column gives a single Greek character to indicate a subset of symmetry operators of the holohedry, termed twin operators, which are presented adjacent to the 'Twin code' column. In Table 1,  $\alpha$ ,  $\beta$ ,  $\chi$  and  $\delta$  are used for the four sets of twin operators.

### 3.6. Twin operators

Each line of this column comprises a subset of the symmetry operators of the holohedry and is labelled by a single Greek character in the 'Twin code' column. For example, in Table 1 twin code  $\delta$  represents the four symmetry-equivalent twin operations  $m_{[100]}$ ,  $m_{[010]}$ ,  $m_{[\bar{1}10]}$  and  $m_{[110]}$ . The first set of twin operators, always labelled  $\alpha$  ( $1$ ,  $2_{[001]}$ ,  $4$  and  $4^3$  in Table 1), contains the symmetry operations of the point group of the crystal. These map a domain of the reference structure onto itself in the orientation of the structure model. At first view, it may seem that this domain is not twinned, but it is nevertheless convenient and necessary to consider it as one of the potential orientations of the model structure. The second set of twin operators, labelled  $\beta$  if present, gives the list of symmetry-equivalent operators that generate domain  $\beta$  from domain  $\alpha$ . Any of the operators in this second list generates domain  $\beta$  from domain  $\alpha$  and may be used to define the twin in a software application. The twin operators of domains  $\chi$ ,  $\delta$  etc. have similar properties.

For the various twofold axes, the direction of each axis is indicated by directions  $[uvw]$  given in subscript (e.g.  $2_{[100]}$ ). Likewise for the mirror planes, the normal to each mirror plane is indicated in the same manner (e.g.  $m_{[100]}$ ). The number of twin operators for each twin code is always the order of the point group of the crystal structure. The sets of twin operators were determined by coset decomposition of the holohedry with respect to the point group of the crystal structure using software distributed with *International Tables for Crystallography*, Vol. D (Authier, 2003).

### 3.7. Physical properties

In this column, one finds information for determining the effective contribution of the twinned crystal to certain physical properties. These are given in terms of the twin fractions determined by least-squares refinement. For example,  $f(\beta)$  indicates the twin fraction of component  $\beta$  defined in the columns 'Twin code' and 'Twin operators'. In its present form, only the Flack parameter, the crystal chirality and the pyroelectric effect (crystal polarity) are listed. Of course, for some space groups these properties are non-existent. For crystals with more than two domains, such as the example in Table 1, the procedure of Flack & Bernardinelli (1999) has been used to obtain

'Flack' and  $f(\text{chiral})$ . The terms entering into  $f(\text{pyro})$  have been obtained by noting which sets of twin operators conserve or invert the polar axes.

### 3.8. Symmetry-related reflections

This column contains the reciprocal-space equivalent of the twin operators. Each line and its continuation(s) contains a list of symmetry-equivalent reflection indices for the twin domain in the corresponding space groups. For example, in Table 1 twin code  $\beta$  gives rise to the four symmetry-equivalent reflections  $h\bar{k}l$ ,  $\bar{h}kl$ ,  $\bar{k}hl$  and  $kh\bar{l}$ . The set of symmetry-related reflections of the twin operators of twin code  $\alpha$  are those of the untwinned single crystal. The work of Hahn & Klapper (2002) was used extensively in deriving these values.

### 3.9. Inversion

In this column, one finds the relevant information for inverting a crystal structure, for use when the structure refinement indicates an inverted structure. The coordinates of a suitable point of inversion are given, together with an indication of a change of space group if this is necessary. For example, in Table 1 in space groups  $P4$ ,  $P4_2$  and  $I4$ , inversion is achieved by inverting all atomic coordinates at the origin, whereas for space groups  $P4_1$  and  $P4_3$  the origin may still be used as the inversion point, but space group  $P4_1$  must be changed to  $P4_3$  and *vice versa*. The information is taken from Koch *et al.* (2002).

### 3.10. SHELXL

This column contains a pointer to the corresponding entry in the software table in the supplementary material. For example, in Table 1 space groups  $P4$ ,  $P4_2$  and  $I4$  need the *SHELXL* command lines indicated at entry *SHELXL04*, and  $I4_1$  needs those of entry *SHELXL06*.

## 4. Software table

For the production of the software table, the information of the twin table has been used to generate the appropriate command lines for *SHELXL* (Sheldrick, 2008). These command lines apply for least-squares refinement, inverting the crystal structure and the interpretation of the twin fractions. For the latter, the relationship between the batch scale factors, *BASF*, of *SHELXL* and the twin fractions of the domains listed under 'Twin code' and 'Twin operators' of the twin table is given explicitly.

## 5. Macromolecular table

In macromolecular crystallography, it is common practice to assume that the compound is enantiomerically pure and that the absolute configurations of the molecular components of the compound are both known and correctly represented in the model of the crystal structure. If these circumstances are valid then the opportunities for twinning are restricted. This leads to a shortened form of the twin table which is presented under the name of 'Macromolecular table'. Only those space groups composed of translations, pure rotations and screw rotations appear in this table, *i.e.* the 65 Sohncke space groups. There is no 'Centro chiral' column as all structures are noncentrosymmetric and chiral. As the chirality is known in advance, in the 'Physical properties' column one finds only information on the pyroelectric properties. The macromolecular table links into the same software table.

## 6. Spreadsheet application

The most user-friendly presentation of the above information is a spreadsheet application available at <http://crystal.flack.ch/TwinInterpretation.xlsx>. The tables in the supplementary material of this paper were produced directly from this spreadsheet. From sheet 1 of the spreadsheet, one may click on the appropriate symbol for the space group of the structure under study and come in sheet 2 directly to the contents of the twin table for the space group. The link in the *SHELXL* column is also clickable and one is taken to the appropriate entry in the software table in sheet 3. The macromolecular table is in sheet 4, which also allows direct access to the software table.

## 7. Concluding remarks

It is highly advisable to undertake the least-squares refinement of the twin fractions described in the spreadsheet in all circumstances. These twin fractions represent a well defined and well established physical state of the crystal that needs to be modelled during the least-squares refinement of the structure. Moreover, the values of the twin fractions obtained may be interpreted in structural, chemical and physical terms. It is for this reason that the contents of the columns 'Centro chiral', 'Polar axis', 'Twin code', 'Twin operators' and 'Physical operators' have been provided.

Owing to the superposition of reflections, none of the merohedral twinning relationships is of relevance to powder diffraction data.

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