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Twinning by Merohedry and X-ray Crystal Structure Determination

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Twins by merohedry can be usefully divided in two classes. Class I: the twin operation is contained in the Laue symmetry of the crystal and twin-related reflexions have equal intensities; in this case the set of intensities collected from a twin is indistinguishable from that collected on a single crystal. Class II: at least one of the independent twin operations is contained in the lattice symmetry but not in the Laue symmetry of the crystal (twin-related reflexions differ in intensity); a knowledge of fractional volumes of crystals is necessary to solve the structure. The solution and refinement of a structure from measurements performed on a twin of class I are discussed.

Introduction

According to a recent classification (Donnay & Donnay, 1974), TLQS (twin-lattice quasi-symmetry) twins show two or more reciprocal lattices differently oriented, giving rise to double or multiple diffraction spots, while TLS (twin-lattice symmetry) twins show a single orientation of the reciprocal lattice with single diffraction spots. TLQS twins are generally recognizable simply by optical observations; TLS twins, however, are optically indistinguishable, except those that unite a right-handed crystal with a left-handed one (without submicroscopic intergrowth), which can be detected by determination of the optical activity. It should be added, however, that the exact orientations of the crystals in a TLS twin may sometimes be altered by macroscopic deformations [*cf.* a case in Catti & Ferraris (1976)], so that some or all of the reflexions are multiple even though corresponding spots always have the same θ value, but different ω values (Weissenberg photographs); care should be taken in this instance, since some particular sections of the reciprocal lattice of a TLQS twin can also show multiple reflexions with the same θ value and different ω, and confusion could arise between the two cases.

The case of twinning which gives more trouble in X-ray structural studies, and which we analyze here, is that of TLS twins with twin index = 1, where the twin lattice and the crystal lattice are one and the same. After Friedel (1926), these are called twins by merohedry, since the crystal symmetry is a merohedry of order n (subgroup of index n) of the symmetry of its lattice: therefore, the twin by merohedry has one or more symmetry operations which are not present in the crystal, but which are present in the crystal lattice.

Twins by merohedry and Laue symmetry of the crystal

Twins by merohedry can be usefully grouped in two classes, in order to explain their diffraction behaviour. Twins of class I show the same crystal Laue symmetry as the lattice symmetry, and therefore the twin operation belongs to the Laue symmetry of the crystal. All these twins are twins by hemihedry, and therefore contain only two crystals; the centre of inversion can always be chosen as a twin operation: for instance, a crystal of class 2 could give a twin with $2/m'$ symmetry, and either m' or $\bar{1}'$ can be considered to be the twin operation [for the symbolism see Curien & Donnay (1959)]. In a twin of unit volume the intensity I_t of a reflexion is actually contributed by two reflexions, one from each crystal, which are equivalent by Laue symmetry; let their intensities per unit volume be I_1 and I_2 respectively. As long as Friedel's law is valid (the anomalous scattering is not taken into account), we have:

$$I_t = I_1 = I_2 \,. \qquad (1)$$

It can be inferred that, on an absolute scale, the set of intensities measured on the twin is identical with one that would be measured on a single crystal (absorption is neglected).

Class II comprises twins with the Laue symmetry of the crystal lower than the crystal lattice symmetry, so that at least one of the independent twin operations is contained in the lattice symmetry but not in the Laue symmetry of the crystal. Twins by hemihedry, tetartohedry and ogdohedry (these are possible only for crystals of class 311) can be observed; they contain two, four and eight crystals respectively. In twins by hemihedry, the only independent twin operation does not belong to the crystal Laue symmetry (and it is never a centre of inversion). In twins by tetartohedry and ogdohedry there are always also independent twin operations which belong to the crystal Laue symmetry, except for twins $6'''/m''' \; 2'/m' \; 2''/m''$ made up of four crystals of class $\bar{3}11$,* where both twin operations are not contained in the Laue symmetry. The intensity of a reflexion of a twin by hemihedry (unit volume) is contributed by two reflexions which are not equivalent by

* The lattice must be hexagonal primitive, in order to have a true twinning by merohedry; with a rhombohedral lattice, a twinning by reticular merohedry would actually be present.

Laue symmetry, so that $I_1 \neq I_2$ and, if v is the volume of crystal 1,

$$I_t = vI_1 + (1-v)I_2 \,. \qquad (2)$$

This equation has already been discussed (*e.g.*, Britton, 1972), but without being related to the problem of the crystal Laue symmetry. An example of this kind could be a twin with $4/m\ 2'/m'\ 2'/m'$ symmetry formed by two crystals of class $4/m$. As for twins by tetartohedry, let us consider the case of a crystal of class 4 which gives a twin with $4/m'\ 2''/m'''\ 2''/m'''$ symmetry made up of four individuals: then a reflexion of the twin is contributed by four reflexions, one from each individual; we have that $I_1 = I_2 \neq I_3 = I_4$, where reflexions 1 and 2 and reflexions 3 and 4 are related by the twin operation contained in the crystal Laue symmetry, and reflexions 1 and 3 and reflexions 2 and 4 are related by the other twin operation, which does not belong to the crystal Laue symmetry. If v is the sum of volumes of crystals 1 and 2, then:

$$I_t = vI_1 + (1-v)I_3 \,. \qquad (3)$$

Clearly the set of intensities measured on this twin could not be distinguished from one given by the twin of the previous example. A different case would be that of a twin $6'''/m'''\ 2'/m'\ 2''/m''$ formed by four crystals of class $\bar{3}11$, since then the twin reflexion would be contributed by four inequivalent reflexions:

$$I_t = v_1I_1 + v_2I_2 + v_3I_3 + (1-v_1-v_2-v_3)I_4 \,. \qquad (4)$$

In order to solve the crystal structure, a knowledge of the fractional volume of one or more of the crystals forming the twin is necessary for twins of class II, but not for twins of class I. It should be added that twins of class I cannot be distinguished from single crystals in all physical properties which depend on volume; the diffraction intensity is a particular example.

If the anomalous scattering is to be taken into account, then equation (2) holds instead of (1) for twins of class I also. The knowledge of v would in principle allow a determination of the polarity, but it would be a hopeless task in most cases, owing to the small difference between I_1 and I_2; the best case is for $v \simeq 0$, and the worst one for $v \simeq 0.5$.

Table 1 shows the occurrence of the two classes of twins by merohedry in the 32 crystal point groups. The diffraction symmetry of twins of class II is generally given by the Laue point group of the crystal; however, if the parts related by the twin operation not contained in the crystal Laue symmetry have the same volumes, then a diffraction symmetry equal to the lattice symmetry is simulated, as can be easily seen by inspection of (2), (3) and (4).

Table 1. *Occurrence of the two classes of twins by merohedry in the* 32 *crystal point groups.*

Crystals belonging to a vertical series of point groups can give twins with the symmetry shown in parentheses below. The five trigonal groups appear twice, once in the *R* lattice and once in the *P* lattice (Donnay, 1969).

Lattice	I	II
Triclinic	1	
	($\bar{1}$)	
Monoclinic	2	
	m	
	(2/m)	
Orthorhombic	222	
	$mm2$	
	(mmm)	
Tetragonal	4	4
	$\bar{4}$	$\bar{4}$
	(4/m)	$4/m$
	422	
	$4mm$	
	$\bar{4}2m$	
	(4/mmm)	(4/mmm)
Rhombohedral	31	31
	($\bar{3}1$)	$\bar{3}1$
	32	
	$3m$	
	($\bar{3}m$)	($\bar{3}m$)
Hexagonal	311	311
	($\bar{3}11$)	$\bar{3}11$
	321	321
	$3m1$	$3m1$
	($\bar{3}m1$)	$\bar{3}m1$
	6	6
	$\bar{6}$	$\bar{6}$
	(6/m)	$6/m$
	622	
	$6mm$	
	$\bar{6}2m$	
	(6/mmm)	(6/mmm)
Cubic	23	23
	($m\bar{3}$)	$m\bar{3}$
	432	
	$\bar{4}3m$	
	($m\bar{3}m$)	($m\bar{3}m$)

Solution of the structure for twins by merohedry of class I

Let us investigate what may happen in the solution and refinement of a crystal structure, if the intensities have been collected on a twin of class I that was not recognized as such. The outcome will be different, if the correct space group or a wrong one is used.

Correct space group

The results are the same as if intensities from a single crystal had been used, even though the quality of the results can be worse. Broadening, possibly asymmetrical, of diffraction peaks may take place (*cf.* Catti, Ferraris & Franchini-Angela, 1976); distortions of contact surfaces on the atomic scale may be caused by twinning: if a large fraction of the twin is involved in the phenomenon (*e.g.*, polysynthetic twinning), an increase of the apparent thermal motion can result.

Several reasons may have led to the correct space group: (i) the space group is already known for certain; (ii) statistical tests on the intensities show a lower symmetry than the Laue symmetry; in fact, the statistical distribution of intensities depends on the symmetry of the cell content only; (iii) information on the space group has been given by vector-space analysis (Buerger,

1959); (iv) the number of molecules per cell is equal to the general multiplicity of a space group in a merohedral point group, and so it is lower than the multiplicity of the point group corresponding to the observed Laue symmetry; besides, there are good reasons to believe that the formula unit cannot be in a special position; (v) the correct space group is found by trial and error.

Wrong space group

The crystal structure usually cannot be solved. However, if the symmetry of the crystal is close to the twin symmetry, a partial solution (*cf.* Catti, Ferraris & Franchini-Angela, 1976) or even a complete solution can be achieved; in the latter case, some structural features will be ascribed to disorder. In fact, in such a solution, because of the higher symmetry of the space group considered the atoms will appear either in special positions (which correspond only approximately to the positions in the correct space group) or in general positions with the following two possibilities: (*a*) the atoms seem to lie statistically on sites related by false symmetry elements; (*b*) two sets of positions, which are independent in the true space group, by twinning simulate a single set of equivalent positions in the wrong space group.

Conclusions

It is probable that many crystal structures solved and described in the literature come from twins by merohedry, which have not been recognized as such. If twinning is suspected, one should try to solve the structure in the space group obtained by removing, with due mathematical precautions (*cf.* Rae, 1974), the elements for which atoms lie in special positions. It should be kept in mind that twins by merohedry with symmetry $\bar{1}'$ (formed by two crystals with symmetry 1) are also possible.

In any case the term 'twinning by merohedry', should be used properly: only a crystal can be 'merohedral', not a twin; 'twinning by merohedry', 'twinning by pseudo-merohedry with obliquity (apparently) equal to zero', and 'twinning by reticular (lattice) merohedry' have distinct and well-defined meanings. In this respect a recent short note (Hawthorne, 1974) with the title *Refinement of Merohedrally Twinned Crystals* is misleading in respect of its content.

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