Introduction to Twinning

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Introduction

Although twinning has long been considered to be one of the most serious potential obstacles to structure determination,[1, 2] computer software has also now been developed to such an extent that previously intractable twinning problems have yielded results of comparable precision to those obtained with untwinned samples.[3-5] Structure determinations from twinned crystals are therefore becoming more common, and the aim of this lecture will be to present an introduction to the phenomenon of twinning.

A twinned crystal is an aggregate in which different domains are joined together according to a specific symmetry operation - the twin law. The diffraction patterns derived from different domains are rotated, reflected or inverted with respect to each other, 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. 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, the latter occurs when the twin law is a symmetry operation belonging to a higher symmetry supercell.

A Simple Example

Twinning may occur when a unit cell (or a supercell) has higher symmetry than implied by the space group of the crystal structure. An example of a system which might be susceptible to twinning is a monoclinic crystal structure in $P2_1/c$ where the unique angle, β, is equal, or very close, to 90°. In this case the crystal structure has point group $2/m$, but the lattice has point group *mmm*. The elements of these point groups are:

$2/m$: $1, m \perp \mathbf{b}, 2 \,//\, \mathbf{b}, \bar{1}$

mmm: $1,\ m \perp \mathbf{a}, 2 \,//\, \mathbf{a}, m \perp \mathbf{b}, 2 \,//\, \mathbf{b}, m \perp \mathbf{c}, 2 \,//\, \mathbf{c}, \bar{1}$

The important issue is that *mmm* contains symmetry elements which do not occur in $2/m$. Twinning can occur if different regions of the crystal (domains) have their unit cells related by symmetry operations which are elements of *mmm* but not $2/m$ - a two-fold axis about **a** for example.

Diffraction Patterns from Twinned Crystals.

Each domain of a twinned crystal gives rise to its own diffraction pattern, and what is measured on a diffractometer is a superposition of all these patterns with intensities weighted according to the contribution of each domain (the domain scale factor). Fig. 1[6] shows this for a twinned monoclinic crystal structure for which β = 90°. Rotated versions of the same diffraction pattern are shown in Figs. 1*a* and *b*. Figs. 1*c* and *d* show superposition of these patterns with different weights. Twinning is a problem in crystallography because it causes superposition or overlap between reflections which are not related by symmetry. In Fig. 1*c*, for example, the reflection which would have been measured with indices 102 is actually a superposition of the 102 reflection from domain 1 (Fig. 1*a*) and the −102 reflection from domain 2 (Fig. 1*b*). During structure analysis of a twinned crystal it is important to define exactly which reflections contribute to a given intensity measurement: this is the role of the twin law.

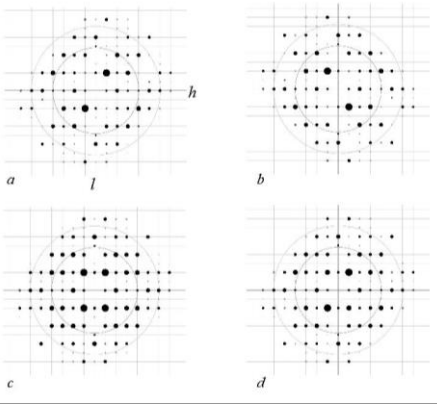

Figure 1. The effect of twinning by a two-fold rotation about **a** on the diffraction pattern of a monoclinic crystal with β = 90°. Only the *h*0*l* zone is illustrated; the space group is $P2_1/c$. *a*. *h*0*l* zone from a single crystal. *b.* The same pattern rotated about **a*** (or *h*) (which is coincident with the *a*-axis of the direct cell). *c*. Superposition of figures *a* and *b* simulating a twin with a domain scale factor of 0.5, *i.e.* both domains are present in equal amounts. *d.* Superposition of figures *a* and *b* simulating a twin with a domain scale factor of 0.2. The values of $|E^2-1|$ for each figure are: *a* and *b* 1.015; *c* 0.674; *d* 0.743.

In order to treat twinning during refinement the twin law must form part of the model. Usually it is input into a refinement program in the form of a 3×3 matrix. In the example shown in Fig. 1 the 2-fold axis about the *a* axis will transform **a** into **a**, **b** into −**b**, and **c** into −**c**. This is the transformation between the cells in different domains of the crystal; written as a matrix this is:

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

The same matrix relates the indices of pairs of overlapping reflections:

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

This two-component twin can be modelled using a quantity $|F_{twin,calc}|^2$ which is a linear combination (Equation 1)[7] consisting of $|F|^2$ terms for each component reflection weighted according to the twin scale factor, x, which can be refined.

$$\left|F_{twin,calc}(h,k,l)\right|^2 = (1-x)|F_{calc}(h,k,l)|^2 + x|F_{calc}(h,-k,-l)|^2 \qquad (1)$$

In the single crystal reciprocal lattice plots shown in Figs. 1*a* and *b*, although two-fold axes and mirror planes about the *a** and *c** axes relate the *positions* of the spots, this symmetry is not expressed in the *intensities* of the spots (for example, the −102 and 102 reflections have different intensities in Fig. 1*a*). However, in the composite, twinned, pattern (Fig. 1*c*), both the positions *and* the intensities of the spots exhibit the same mirror or two-fold symmetry with respect to both of these axes. The composite pattern with equal domain volumes (that is x = 0.5, Fig. 1*c*) appears to have orthorhombic diffraction symmetry even though the crystal structure is monoclinic. In general, for a two-component twin, if x is near 0.5 then merging statistics will appear to imply higher point symmetry than that possessed by the crystal structure. As x deviates from 0.5 then the merging in the higher symmetry point group gradually becomes poorer relative to merging in the point group which corresponds to the space group of the crystal structure (Fig. 1*d*). Although it is impossible to give a definitive range, merging in the higher symmetry point group may yield a merging residual of 0.10-0.35; values of around 0.60 might be expected for untwinned samples (though pseudo-symmetry in, for example, heavy atom positions can give rise to a similar effect).

Another striking feature of the twinned diffraction pattern shown in Fig. 1*c* is that it appears to have a more acentric intensity distribution than the component patterns. The superposition of the diffraction patterns arising from the different domains tends to average out intensities because strong and weak reflections sometimes overlap. The quantity $|E^2 - 1|$, which adopts values of 0.97 and 0.74 for ideal centric and acentric distributions, respectively, may assume a value in the range 0.4-0.7 for twinned crystal structures.[1]

Common signs of twinning have been listed by Herbst-Irmer and Sheldrick.[1] Additional signs to those described above include: an inability to solve a structure even though the data appear to be of good quality; or, if a structure can be solved, a high R-factor or a noisy, inexplicable difference electron density map. Since reflections from one domain may overlap with systematic absences from another, the observed systematic absences may

either not be consistent with any known space group, or appear to imply a very rare space group.

Merohedral and Pseudo-merohedral Twins

Crystal structures in low symmetry tetragonal, trigonal, rhombohedral, hexagonal and cubic space groups are susceptible to *merohedral twinning*. For example, a tetragonal structure in point group $4/m$ may twin about the two-fold axis along [110], which is a symmetry element of the higher symmetry tetragonal point group, $4/mmm$. The twin law in this case is:

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

An exhaustive list of possible merohedral twin laws has been given by Flack and Wörle.[8]

Merohedral twinning should be carefully distinguished from the example described above where a monoclinic crystal structure 'accidentally' had a β-angle near 90°. There is nothing 'accidental' about a low symmetry tetragonal structure having a lattice with $4/mmm$ symmetry: all low symmetry tetragonal structures have this property, and the higher $4/mmm$ symmetry is exact. By contrast, a monoclinic crystal structure which happens to have $\beta \sim 90°$ has a lattice with approximately *mmm* symmetry. This higher symmetry may be very close, but it is not fixed by symmetry. This type of effect is instead referred to as *pseudo-merohedral twinning*.

Derivation of Twin Laws

In the case of a monoclinic crystal where $\beta \sim 90°$ it was shown above that twinning could occur about a two-fold axis about **a**. This leads to overlap between reflections with indices $h\ k\ l$ and $h\ -k\ -l$. Twinning via a two-fold axis about **c** would lead to overlap between reflections with indices $h\ k\ l$ and $-h\ -k\ l$. However, since reflections $h\ -k\ -l$ and $-h\ -k\ l$ are related by the monoclinic two-fold axis about **b***, which must be present if the crystal point group is 2 or $2/m$, these twin laws are equivalent. If the point group is *m* they are not equivalent.

It is usually the case that several equivalent descriptions may be used to describe a particular twin. However, several distinct twin laws may be possible, and they can be expressed simultaneously. There clearly exists a potential for possible twin laws to be overlooked during structure analysis. Flack[9] has described the application of *coset decomposition* to this problem, enabling this danger to be systematically avoided. The procedure has been incorporated into the computer program TWINLAWS.[10]

Non-merohedral Twinning

In merohedral and pseudo-merohedral twinning integral Miller indices in one domain are converted into other integer triples in the twinned domain, so that all reciprocal lattice points overlap. This usually means that all reflections are affected by overlap, although reflections from one domain may overlap with systematic absences from another. Twins in which only certain zones of reciprocal lattice points overlap are classified as being *non-merohedral*.

In these cases only reflections which meet some special conditions on *h*, *k* and/or *l* are affected by twinning. An example might be where only reflections where *h* is an even number are affected by overlap.

A non-merohedral 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 $2a \sim b$ (Fig. 2). A metrically tetragonal supercell can be formed by doubling the length of *a* so that there is a pseudo-four-fold axis about **c**. The diffraction pattern from one domain of the crystal is related to that from the other by a 90° rotation about **c***. Superposition of the two diffraction patterns shows that data from the first domain are only affected by overlap with data from the second domain when *k* is even (Fig. 2*d*). For the purposes of structure analysis this twin law needs to be expressed with respect to the axes of the true orthorhombic cell.

From Fig. 2*a*,

a' = -0.5**b**

b' = 2**a**

c' = **c**

so that the twin law is:

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

The effect of this matrix on the data is:

$$\begin{pmatrix} 0 & -0.5 & 0 \\ 2 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix} = \begin{pmatrix} -k/2 \\ 2h \\ l \end{pmatrix},$$

confirming that only data with $k = 2n$ are affected by the twinning.

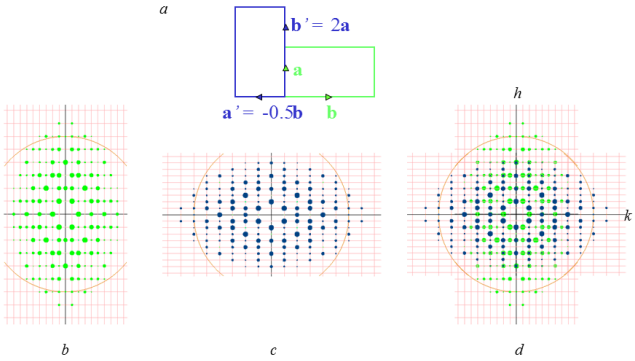

Figure 2. Non-merohedral twinning in an orthorhombic crystal where $2a = b$. *a*. The relationship of the unit cells in different domains is a 90° rotation about **c**. *b*. and *c*. Diffraction patterns from the two different domains in the crystal. *d*. Superposition of *b* and *c* to illustrate the diffraction pattern that would be measured for the twinned crystal. Note that spots only overlap where *k* is an even number.

It is likely that the example given here would index readily on the tetragonal supercell, but notice the bizarre systematic absences in Fig. 2*d*. Zones of unusual systematic absences are frequently a sign that a crystal is non-merohedrally twinned. This pseudotranslational symmetry should enable the true orthorhombic cell to be inferred, and it can be readily identified in a Patterson synthesis.

Derivation of Non-Merohedral Twin Laws

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, requiring more than one orientation matrix to index all the observed spots.[11] Options in indexing software need to be selected to activate the twin-indexing algorithms.

The relationship between two orientation matrices yields a twin law. It is usually the case that twinning can be described by a two-fold 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. The program CREDUC and the LePAGE routine in PLATON are extremely useful for investigating this.[12-14]

Overlap between reflections may be imperfect in some or all zones of data affected, and integration and data reduction needs to be performed taking into account the possibility of partially overlapping reflections. This can be accomplished by integrating diffraction images simultaneously with multiple orientation matrices. Specialised routines for correction of systematic errors

have been developed for handling twinned data and form the part of software suites distributed with diffractometers.

It is sometimes the case that the first intimation that the analyst has that a crystal is twinned is during refinement. Symptoms such as large, inexplicable difference Fourier map 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 $|F_{obs}|^2$ is systematically larger than $|F_{calc}|^2$. The programs TwinRotMat (part of PLATON)[14] and ROTAX[15] are designed to suggest possible twin laws that can then be incorporated into a refinement model.

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