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A Chart for Interpreting the Weissenberg Photographs of Pseudo-Merohedral Twins

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A chart is presented on which the appropriate zero-level Weissenberg photograph of a pseudo-merohedral twin may be superimposed. This enables the separation of twin-pairs of reflexions at any point on the film to be related to the twin obliquity angle. A separate chart which may be used with the zero-level Weissenberg photograph of any crystal, twinned or untwinned, gives the film-to-reciprocal-lattice magnification ratio corresponding to any short interval measured along a festoon.

Introduction

Pseudo-merohedral twinning can occur when a crystal lattice almost possesses greater symmetry than is required by the crystal system to which it belongs. For example, in a monoclinic crystal the third angle of the unit cell may be *almost* 90°, so that the lattice is almost orthorhombic. Rotation and reflexion twins are found to occur under these circumstances (Cahn, 1954). The effect of such twinning is that each reciprocal lattice point due to one individual of the twin either coincides or almost coincides with a point belonging to the other individual, as described below. Such patterns have sometimes been recognized only with difficulty (*e.g.* Herbstein, 1964, 1965).

An example of pseudo-merohedral twinning

Fig. 1 depicts the zero-level reciprocal lattice of a twinned monoclinic crystal when viewed parallel to the symmetry (b) axis which is common to both individuals. The a^* axes coincide, while the c^* axes almost coincide, the angle between them being 2χ where χ is the so-called twin obliquity (angle) which represents the difference between the angle β and 90°. The obliquity is frequently much smaller than shown here. The lattice points belonging to the two components are distinguished by open and filled circles. This Figure could equally well represent either a rotation twin having c as the twin axis, or a reflexion twin having (100) as the twin plane, for the geometry of the reciprocal lattice would be the same in either case (although the internal configuration of the individuals would not). The choice of axes is not intended to indicate the type of twinning, and is convenient for the present purpose.

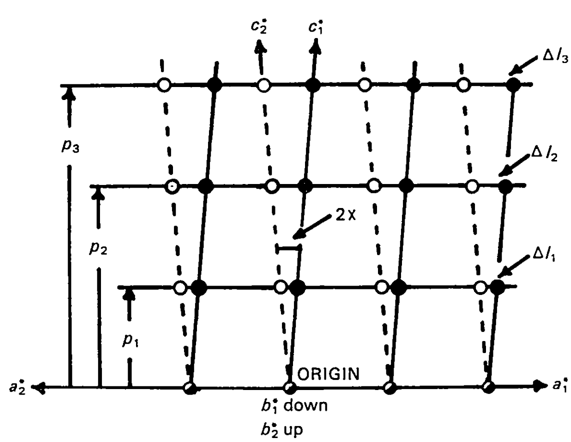

Fig. 1. The zero-layer reciprocal lattice of a monoclinic crystal twinned by pseudo-merohedry. The twin obliquity angle χ is here about 5°. The separation of a 'twin-pair' of reflexions is $\Delta l = 2p \tan \chi$, where p is the perpendicular distance of the lattice row concerned from the origin.

The pattern of the twinned reciprocal lattice is seen to be characterized by pairs of reflexions, herein termed 'twin-pairs', along the rows parallel to the a^* axes. The reciprocal-lattice separation of the points comprising a twin-pair is constant within a given row (or, in three dimensions, within a given plane), but varies from row to row. This separation may be expressed as $\Delta l = 2p \tan \chi$, where p is the perpendicular distance of the particular lattice row from the origin.

When the Weissenberg method is used for such a layer, interpretation can be surprisingly difficult, and the pattern may not even be recognized as belonging to a twinned crystal. The difficulty is still greater if the obliquity angle is very small, for then the twin-pairs may not be resolved on parts of the photograph. Resolution depends upon the spot size and shape, but is also influenced in a complicated way by the Weissenberg geometry. In particular, since the effective linear magnification of the reciprocal lattice varies from point to point along a festoon, the spots corresponding to one of the horizontal rows in Fig. 1 may be resolved at one part of a festoon and not at another part of the same festoon.

Chart for twinned crystals (Fig. 2)

When during the course of a recent investigation (Grainger & McConnell, 1969) such pseudo-merohedral twinning was encountered, the need was felt for a simple method of determining how the separation of twin-pairs varies over the Weissenberg photograph. It proved possible to express this information most simply in the form shown in Fig. 2 which applies specifically to the zero-level of interest. The manner of use is described in the caption.

The chart may be employed in several ways. If split spots are encountered during the early stages of an investigation, and pseudo-merohedral twinning is suspected, one can measure the separation of the split pairs on various parts of the film, and deduce χ for each pair with the aid of Fig. 2. If the values agree, the presence of this type of twinning is confirmed. If, on the other hand, the twin obliquity angle is known, the expected separation of the twin-pairs in millimetres is simply $\tan \chi$ multiplied by the appropriate contour label. This knowledge is of value for indexing the reflexions belonging to the two individuals, for determining whether resolution can be expected at a given point on the film – whether, for example, a given spot is compound or single – and for distinguishing, in some cases, twin-pairing from α_1,α_2 splitting.

It is, therefore, expected that the use of Fig. 2 will assist in the speedy recognition of pseudo-merohedral twinning, and enable indexing to be achieved more reliably.

Theory

In Fig. 3(*b*) the reciprocal lattice row *BP* is at a perpendicular distance $OB=p$ from the origin *O*. The row is in the reflecting position for a point *P*. Let $PB=l$ and $PO=r$. The coordinates of the corresponding point

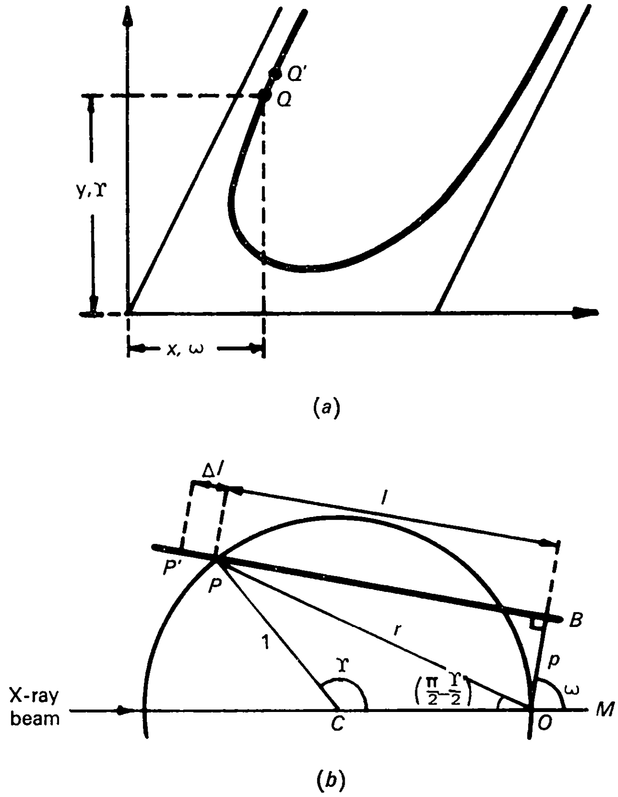

Fig. 3. (*a*) Two close points *Q* and *Q'* on a Weissenberg festoon, related to the usual coordinate system. (*b*) The corresponding points *P* and *P'* of the reciprocal lattice with *P* in the reflecting position.

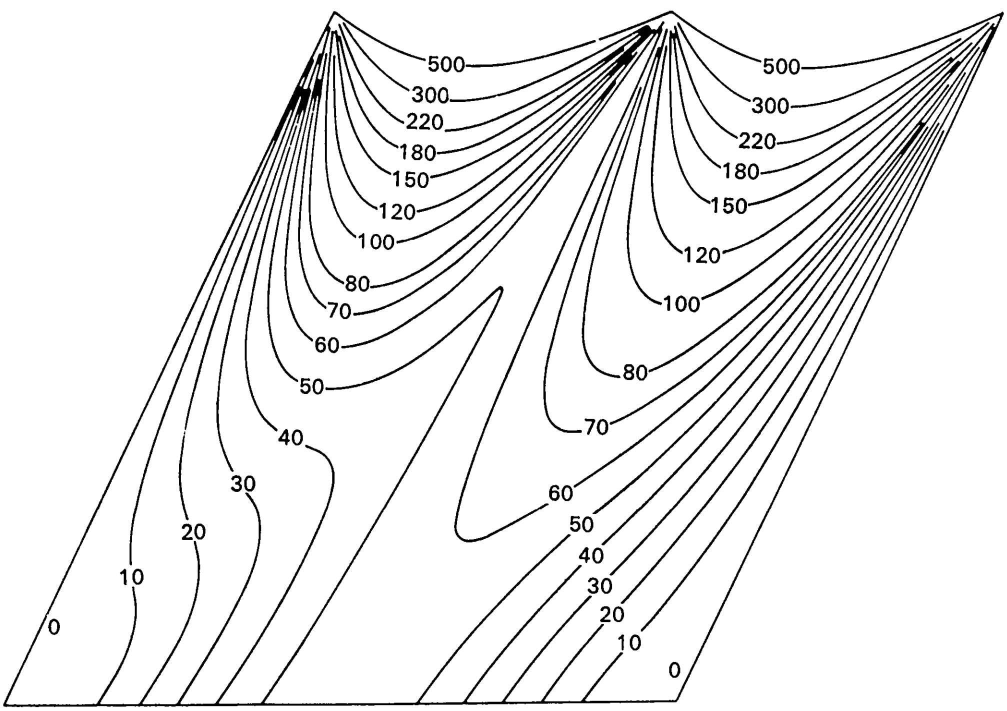

Fig. 2. Chart for pseudo-merohedral twins. Contours give *(film separation of twin-pair in mm)/tan* χ, where χ is the obliquity. The Weissenberg film is placed on the chart with the axis parallel to the row of interest on the zero contours.

Q on the Weissenberg film, Fig. 3(a), are called ω and Υ, as usual in Buerger's notation, equal respectively to angles BOM and PCO.

Let P' be a nearby point on the same lattice row at a distance Δl from P. In order to bring P' into a reflecting position, the crystal must be rotated by $\Delta\omega$, and the reflexion will occur at Q' at the angular position $\Upsilon+\Delta\Upsilon$ on the film. On a standard Weissenberg camera, Q' will be displaced from Q by vertical and horizontal distances

$$\Delta y=\frac{90}{\pi}\cdot\Delta\Upsilon\,,$$

$$\Delta x=\frac{90}{\pi}\cdot\Delta\omega\,, \qquad (1)$$

where $\Delta\Upsilon$ and $\Delta\omega$ are measured in radians and Δy and Δx in millimetres.

The distance QQ' on the film is

$$\Delta s=(\Delta x^2+\Delta y^2)^{1/2}\,. \qquad (2)$$

The required expressions for $\Delta\Upsilon$ and $\Delta\omega$ in terms of Δl are derived as follows.

From Fig. 3(b),

$$r=2\sin\frac{\Upsilon}{2}\,, \qquad (3)$$

$$r^2=l^2+p^2\,, \qquad (4)$$

$$\pi=\omega+\cos^{-1}\left(\frac{p}{r}\right)+\left(\frac{\pi}{2}-\frac{\Upsilon}{2}\right). \qquad (5)$$

Differentiating these,

$$\Delta r=\Delta\Upsilon\cos\frac{\Upsilon}{2}\,, \qquad (6)$$

$$r\,.\,\Delta r=l\,.\,\Delta l\,, \qquad (7)$$

$$0=\Delta\omega+\frac{p\,.\,\Delta r}{lr}-\frac{\Delta\Upsilon}{2}\,. \qquad (8)$$

The perpendicular p can be expressed in terms of ω and Υ as follows.

$$p=r\cos\left(\frac{\pi}{2}+\frac{\Upsilon}{2}-\omega\right) \text{ from equation (5)}$$

$$=r\sin\left(\omega-\frac{\Upsilon}{2}\right) \qquad (9)$$

$$=2\sin\frac{\Upsilon}{2}\sin\left(\omega-\frac{\Upsilon}{2}\right) \text{ from equation (3)} \qquad (10)$$

$$=\cos(\Upsilon-\omega)-\cos\omega\,. \qquad (11)$$

$\Delta\Upsilon$ may be expressed in terms of Δl, ω and Υ, using equations (6), (7), (4) and (9):

$$\Delta\Upsilon=\frac{\Delta l\,.\cos\left(\omega-\frac{\Upsilon}{2}\right)}{\cos\frac{\Upsilon}{2}}\,. \qquad (12)$$

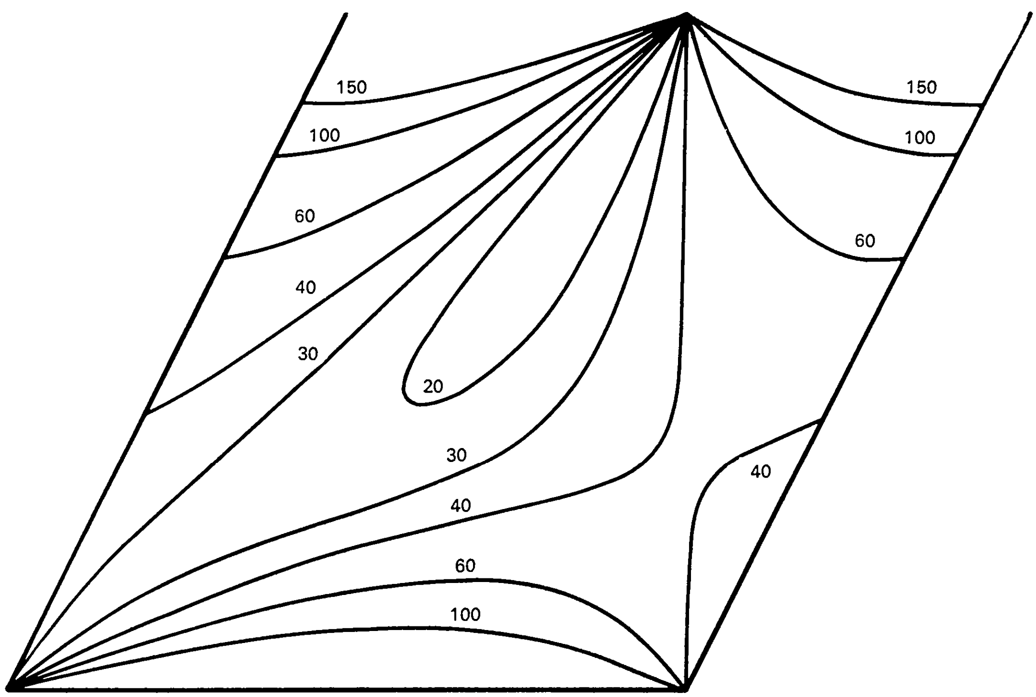

Fig. 4. Magnification chart for any zero-layer Weissenberg film. Contours give the Weissenberg magnification factor, *i.e. (the separation in mm of any two close points on a festoon)/(the separation in r.l.u. of the corresponding reciprocal lattice points).* The Weissenberg film is placed on the chart with an axis superimposed on the boundary lines, as with an ordinary Buerger chart.

This allows $\Delta\omega$ to be expressed in terms of the same quantities using equations (7), (8), (3), (10) and (12):

$$\Delta\omega = \frac{\Delta l \,.\, \sin(\Upsilon-\omega)}{\sin \Upsilon}\,. \tag{13}$$

One then obtains the following expression using equations (1), (2), (12) and (13):

$$M = \frac{\Delta s}{\Delta l} = \frac{90}{\pi}\cdot\left[\frac{\cos^2\left(\omega-\frac{\Upsilon}{2}\right)}{\cos^2\frac{\Upsilon}{2}} + \frac{\sin^2(\Upsilon-\omega)}{\sin^2\Upsilon}\right]^{1/2}. \tag{14}$$

The quantity M ('magnification') represents the ratio of the film separation Δs in millimetres of any two close reflexions, measured along a festoon, to their reciprocal-lattice separation Δl in reciprocal-lattice units. M is graphed in Fig. 4. Fig. 4 differs from Fig. 2 in that it can be applied to *any* two close points on a festoon belonging to *any* crystal, twinned or untwinned, whereas Fig. 2 applies only to *twin-pairs* belonging to a pseudo-merohedral twin. It is expected that Fig. 4 will be useful in interpreting unusual patterns other than those covered by Fig. 2.

In the case of pseudo-merohedral twinning we are especially concerned with the separation of the twin-pairs, and so must introduce the additional restriction

$$\Delta l_t = 2p \tan\chi\,, \tag{15}$$

where the subscript t serves to remind us we are dealing with twin-pairs. Substituting this relation in equation (14), and using equation (11) for p, we get

$$\frac{\Delta s_t}{\tan\chi} = \frac{180}{\pi}\left[\frac{\cos^2\left(\omega-\frac{\Upsilon}{2}\right)}{\cos^2\frac{\Upsilon}{2}} + \frac{\sin^2(\Upsilon-\omega)}{\sin^2\Upsilon}\right]^{1/2} \times [\cos(\Upsilon-\omega) - \cos\omega]\,. \tag{16}$$

The calculations for Figs. 2 and 4 were performed with the use of a FORTRAN program to compute the expressions given by (16) and (14) respectively, at all points on the Weissenberg film, with a grid interval of 0·5 mm along x and y. With the help of another program for linear interpolation, contours were constructed as shown in the Figures.

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The Structure of NH_4F as Determined by Neutron and X-ray Diffraction

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Neutron and X-ray intensities of NH_4F were measured at −196°C and −155°C respectively. The wurtzite type structure and space group $P6_3mc$ were confirmed. The displacement of the two h.c.p. sublattices, formed by each of the F^- – and NH_4^+ – ions, is such that all bond-distances are equivalent. The N–H bond distances as found from the X-ray data are about 0·1 Å shorter than those obtained from the neutron data. The final weighted R values were 1·9% and 2·6% for the X-ray and neutron data respectively.

Introduction

The structure of NH_4F was solved by Zachariasen (1927). The accuracy of the methods at that time was not high enough to show hydrogen atoms and provide information on bonding effects. Looking for compounds with small asymmetric units consisting of light atoms only, we decided to repeat the structure determination, this time by X-ray and neutron diffraction methods.

Previous work

In the following some previous work on NH_4F is summarized. Zachariasen (1927) established the space group to be $P6_3mc$ and found the following cell constants: