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The Indexing of Reflexions in Investigations Involving the Use of the Anomalous Scattering Effect

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The assignment of the right sign to the index triplet of a reflexion in the calculation of structure factors and in the indexing of the diagram in the Weissenberg technique is discussed.

The possible use of anomalous scattering for the determination of the phase angle in the single-heavy-atom technique is pointed out.

Introduction

When anomalous scattering occurs in a non-centrosymmetric crystal, Friedel's law no longer holds and the signs of the phase angles can be determined, which implies the determination of absolute configuration (Peerdeman, Bommel & Bijvoet, 1951; Peterson, 1955). In this case it is imperative to assign the reflexion triplets their right sign in indexing the diagrams and in calculating structure factors.

On the basis of the equation

$$E(x, t) = E_0 \exp\left[+2\pi i(\nu t - x/\lambda)\right] \qquad (1)$$

for the propagation of a wave, with wavelength λ, along the x direction, the phase is defined according to:

$$\varphi(x, t) \equiv +2\pi(\nu t - x/\lambda)\ . \qquad (2)$$

With the phase thus defined, the phase change by passing from normal to anomalous scattering has been shown to be positive (James, 1948). Accordingly, when the anomalous scattering power $f_j \exp[i\delta_j]$ of an atom j is written in terms of the normal scattering power f^0 and the real and imaginary correction terms $\Delta f_j'$ and $i\Delta f_j''$ as in (3)

$$f_j \exp[i\delta_j] = f_j^0 + \Delta f_j' + i\Delta f_j'' \qquad (3)$$

with positive $\Delta f_j''$, then δ_j gives the *increase* in phase as a result of anomalous scattering. In the expression for the structure factor, namely

$$F_{hkl} = \sum_j f_j \exp\left[i(\delta_j + \varphi_j)\right]\ , \qquad (4)$$

the phase term φ_j then has to denote the *increase* in phase that results from the differences in path length which occur.

When for practical purposes φ is calculated with the use of the reflexion indices $h_1h_2h_3$ according to

$$\varphi = h_1x + h_2y + h_3z\ , \qquad (5)$$

the definition of δ_j allows no other definition of $h_1h_2h_3$ than that originally given by von Laue (1923), which may be rendered as: $h_1h_2h_3$ are the numbers of cycles with which *the phase* increases when a diffracting point is displaced over one cell edge in the positive direction of the a, b and c axes respectively.

With (3) and (5), the expression (4) then gives the structure factor—that is amplitude and phase—of a beam diffracted by the cell, relative to the radiation scattered by a free electron at the origin.

As the Laue indices are defined in several text books as the corresponding increases in *light path* (expressed in wavelengths), one should be prudent. In normal diffraction, where Friedel's law holds, the difference is immaterial; but in the case of anomalous scattering the latter definition would cause a given reflexion to be indexed $h_1h_2h_3$ instead of $\bar{h}_1\bar{h}_2\bar{h}_3$, thus changing the intensities of reflexion and counter-reflexion. This would in fact reverse the conclusion concerning the absolute configuration. It should therefore be ensured that in using (4) and (5) the signs of δ_j and $h_1h_2h_3$ correspond.

Application to the orthorhombic system

We will describe the indexing of reflexions, paying due attention to the correct sign of the index triplet, in the case of an orthorhombic crystal and the Weissenberg technique for recording intensities; after that, the differences in other crystal classes and other recording techniques will be discussed briefly.

In an orthorhombic crystal we have to do with a rectangular coordinate system, the axes of which are parallel to the twofold axes of the crystal. All directions normal to these axes are non-polar, and therefore the equator reflexions $0kl$, $h0l$ and $hk0$ are irrelevant for our purpose. In order to obtain the intensities of general reflexions hkl an equi-inclination Weissenberg diagram is made of a higher layer line. The arrangement of the Weissenberg camera is given in Fig. 1(*a*), which shows the crystal with incident and diffracted beams i and d and the moving film f around it. The first point to be discussed is the relation between the sense of rotation of the crystal and the coupled translation of the film. This relation is indicated by the arrows r and t in the figure; in the case represented, the rotation of the crystal and the movement of the crystal

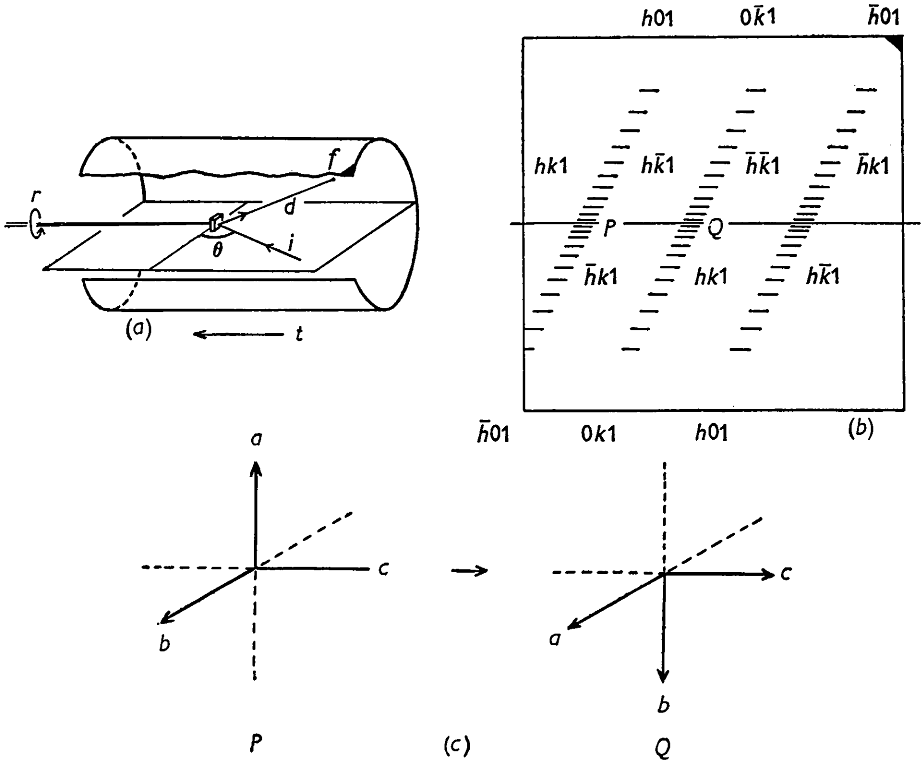

Fig. 1. Indexing of equi-inclination Weissenberg diagrams. (a) Camera arrangement; (b) corresponding position of film; (c) orientation of coordinate system to P and Q.

relative to the film (the latter imagined stationary) are in a right-handed screw relation.

The consequence of this right-handed screw motion is that, looking at the film from the position of the crystal, the 'axis' reflexions are found on a line sloping upwards from left to right (Fig. 1(*b*)). This is seen when visible light and a mirror are imagined to take the place of the X-rays and reflecting plane.

A rotation according to the arrow r brings the reflexion higher up on the film and, because of the coupled translation, more to the right. However, the knowledge of the slope of the 'axis' reflexions does not suffice to reconstruct the position of the film in the camera after developing and fixing have taken place. It cannot be decided whether, in the position shown by Fig. 1(*b*), the film has to be rotated through 180° in its plane. Consequently, it is necessary to mark the film in one of the corners for the purpose of reconstructing the original position. Evidently the relation between rotation of the crystal and translation of the film can then be derived from the film. It will be clear that this marking of the film is never required in normal X-ray diffraction work since the difference between hkl and $\bar{h}\bar{k}\bar{l}$ reflexions is then immaterial.

Let us suppose that the crystal is rotated around the c axis and that the first layer-line reflexions are recorded on the film (Fig. 1(*b*)). On this film all reflexions can at once be assigned their indices apart from sign. In the position of the crystal corresponding with the point P on the film the a axis was vertical. The orientation of the right-handed coordinate system in that point may be taken as in Fig. 1(*c*). Other possible orientations which follow from that by a rotation of 180° around the axes are equivalent by symmetry, the axes of the crystal being twofold axes.

The second decisive point in the assigning of indices is the inclination angle θ (Fig. 1(*a*)). The sign of the l index ($l = 1$) depends on whether the inclination is to the right or to the left. In this orthorhombic crystal the side of the inclination is the only one of the experimental data that cannot be ascertained from a marked film. In the situation of Fig. 1 the sign of the l index for the coordinate system of Fig. 1 is positive (the path length is seen to decrease, hence the phase to increase, when the scattering point is shifted in the direction of the positive c axis). As in the point P (Fig. 1(*b*)) the positive a axis is directed upwards, a rotation of the crystal from this position, as indicated by the arrow in Fig. 1(*a*) gives $h0l$ reflexions with positive h on the upper side of the film. After a rotation of 90° in this direction the positive b axis is pointing vertically downwards (Fig. 1(*c*)). In this position it corresponds to the point Q on the film. Accordingly, the $0kl$ reflexions above Q on the film have negative k values. With the signs of h and k of these reflexions, the signs of the indices in every section of the diagram are fixed.*

Coordination of calculated and observed intensities in other cases

A crystal with higher symmetry than orthorhombic presents no further difficulties. The only difference is that, in e.g. class 422, a given polar direction occurs eight times instead of four. There are therefore eight sets of possible indices for a reflexion. All of these are equivalent by symmetry.

A difficulty arises, however, in the case of lower symmetry. One example will suffice to illustrate this.

We will consider a monoclinic crystal which is rotated about the c axis (b axis unique); the intensities of the zero layer-line are recorded. The Weissenberg diagram will have the same appearance as in Fig. 1(b), the index l being zero. The orientation of the coordinate system corresponding to Q may be either that of Fig. 2(a) or that of Fig. 2(b). These orientations are not equivalent as they are changed into each other by a rotation of 180° about the c axis, which is *not* a symmetry axis. As the decision between the two possible orientations cannot be made from the diagram it has to be reached separately by observing some reflexion outside the ab plane.

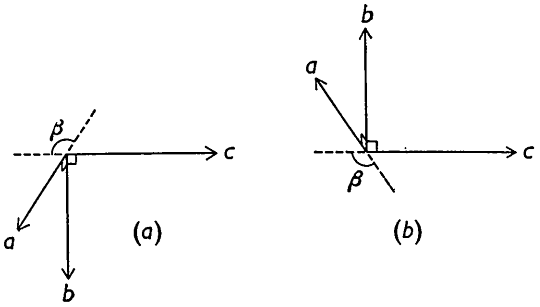

Fig. 2. Non-equivalent orientations of coordinate system to be distinguished in anomalous diffraction from monoclinic crystals.

Of the other recording techniques, the Geiger-counter technique presents no difficulties: in this case the relation between the sequence of the reflexions and the sense of rotation of the crystal is observed directly. When the intensities are recorded on an oscillation photograph difficulties are met with. The relation between sequence of the reflexions and the sense of rotation of the crystal can then be determined only in connection with a second oscillation photograph. It goes without saying that the same—say right-handed—coordinate system must be used throughout the investigation.

Use of anomalous scattering for determining phase angles

The use of anomalous scattering in the centrosymmetrical case, using the real part of the anomalous scattering, has been well known from early times in distinguishing between atoms of about equal normal scattering power.

In the Fourier technique of non-centrosymmetrical structures the imaginary part of the anomalous scattering factor $\Delta f''$ has been used in the determination of the *sign* of phase angles in connexion with the isomorphous substitution method. It may be remarked that, as seen from Fig. 3, it can obviously be used in the simple heavy-atom technique for determining sign *and value* of the phase angle φ. In Fig. 3 F_A denotes the contribution of the heavy atom to the structure factor, F the structure factor of unknown phase. The increase of $|F|$ on addition of Δ, the resultant of the contributions $\Delta f''$, is seen to be the greater the nearer φ is to $\frac{1}{2}\pi$. This correlation enables us to calculate φ from the intensity difference between I_{hkl} and $I_{\bar{h}\bar{k}\bar{l}}$.

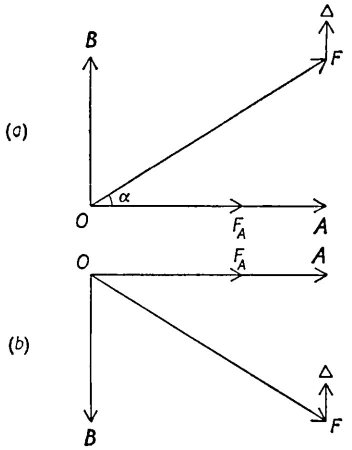

Fig. 3. Determination of the phase angle in sign and magnitude from the observed intensity difference between reflexion (a) and counter-reflexion (b).

If A and B denote respectively the real and imaginary parts of F, the effect of $\Delta f''$ not included, then

$$\Delta I \equiv I_{hkl} - I_{\bar{h}\bar{k}\bar{l}} = [A^2 + (B+\Delta)^2] - [A^2 + (B-\Delta)^2] = 4B\Delta\,.$$

I being measured and Δ being calculable, B can be determined from this equation (sign included) and hence φ according to

$$\sin\varphi = B/|F|\ .^*$$

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* Starting with the coordinate system in one of the other possible orientations, the reflexions indexed hkl could have had the indices $\bar{h}\bar{k}l$, $\bar{h}k\bar{l}$ or $h\bar{k}\bar{l}$, which, as has been remarked, are equivalent by symmetry. Their structure factors will therefore be found to be identical.

* The remaining ambiguity between φ and $\pi-\varphi$ is of no practical importance, as the angle between F and F_A is small in all cases where F is not very small.

In due time an example of this technique will be given.

The use of anomalous scattering in the Patterson technique has been outlined by Pepinsky (Okaya, Saito & Pepinsky, 1955).

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The Crystal Structure of $Ce(IO_3)_4$*

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The crystal structure of $Ce(IO_3)_4$ has been determined by single-crystal methods. Refinement of the structure was made by the method of least squares. $Ce(IO_3)_4$ is tetragonal, space group $P4_2/n$, with $a = 9{\cdot}90$ and $c = 5{\cdot}32$ Å. The cerium atoms are surrounded by eight oxygens at the corners of a distorted Archimedes antiprism. Two of the three oxygens in each iodate group are coordinated to cerium while the third oxygen is isolated. The three I–O bond lengths are 1·78, 1·84 and 1·83 Å, all ±0·09 Å. The average Ce–O distance is 2·33 Å. Within the limits of error, the iodate group has trigonal symmetry. Each iodine atom has five oxygen neighbors in addition to the three in the iodate group.

Introduction

In connection with some work being done in this laboratory by Dr Burton Lewis on magnetic properties of plutonium compounds it was desirable to know the crystal structure of $Pu(IO_3)_4$, particularly the coordination of the oxygen atoms about the plutonium. Instead of studying $Pu(IO_3)_4$ itself, the structure determination of the isomorphous $Ce(IO_3)_4$ was undertaken, primarily because Ce has a lower scattering power than Pu and also because of the health hazard of working with Pu compounds.

Experimental

The preparation of $Ce(IO_3)_4$, its morphology, optical properties and X-ray diffraction data have already been published (Staritzky & Cromer, 1956).

Weissenberg and precession photographs with Cu and Mo radiations showed $Ce(IO_3)_4$ to be tetragonal with

$$a = 9{\cdot}90 \pm 0{\cdot}02,\ c = 5{\cdot}32 \pm 0{\cdot}01\ \text{Å}\,.$$

Reflections of the type $hk0$ were observed only with $h+k = 2n$, and of the type $00l$ only with $l = 2n$. The space group is thus uniquely established as C_{4h}^4–$P4_2/n$. The calculated density with two formula units per cell is 5·35 g.cm.$^{-3}$. The observed density is 5·4 g.cm.$^{-3}$. Most of the crystals gave streaked diffraction spots, although the crystals were externally well developed.

A small crystal that gave a good diffraction pattern was ultimately found. This crystal showed the forms {001}, {111}, {100} and {110}. The distance across the crystal was 0·073 mm. and the distance between {001} faces was 0·032 mm. The cross-section normal to the c axis was an octagon, a favorable shape for minimizing absorption errors. As a rough approximation, the over-all shape of the crystal was that of an oblate spheroid. This crystal was mounted on the c axis and hkl data for $l = 0$–3 were obtained with a Geiger-counter attachment on the Weissenberg camera (Evans, 1953), using Mo $K\alpha$ radiation. Intensities were corrected for the Lp factors and converted to structure factors on a relative scale. No absorption corrections were made.

Determination of the structure

There were two Ce atoms and eight iodate groups to be located in the unit cell. In $P4_2/n$ there are two equivalent sets of twofold positions. The Ce atoms were therefore placed in 2(a) at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. (The origin at $\bar{4}$ is used throughout this paper.) This special position contributes only to reflections with $h+k+l = 2n$ and it was observed that these reflections were in

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* Work done under the auspices of the Atomic Energy Commission.