Short Communications

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The interpretation of X-ray powder photographs of crystals of low symmetry.

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Ito (1949, 1950) has recently devised a method by which the powder photograph of a crystal may be indexed regardless of its symmetry. The method, which is discussed in the *International Tables for X-ray Crystallography* (1952), involves finding an arbitrary triclinic unit cell in reciprocal space, by reference to which the observed reflexions may be indexed. The true unit cell is then obtained from the arbitrary unit cell by a reduction method first described by Delaunay (1933).

It is not difficult to find an arbitrary triclinic unit cell which will explain most of the observed reflexions but the method as a whole requires that two conditions be satisfied, namely that the arbitrary triplet in reciprocal space must be primitive (and must therefore explain all the observed reflexions) and that the values of $1/d^2$ for the observed reflexions must be extremely accurate throughout. It is not always possible to satisfy these conditions and it seems worth while, therefore, describing a method developed by the authors which is a variation on that of Ito and which is not so rigorous in its demands. As might be expected, the method is correspondingly less powerful than Ito's, leading to the Laue symmetry group (and thence to the unit cell) instead of to the Bravais lattice.†

The method

An arbitrary triclinic unit cell is found in reciprocal space, as described by Ito, but no account need be taken of one or two unexplained reflexions as long as the rest of those observed are satisfactorily accounted for. The poles of those planes whose reflexions are thus indexed are then plotted on a stereographic projection, remembering that the direction of the line joining the origin to any reciprocal-lattice point is that of the normal to the corresponding crystallographic plane, and using the following formulae for the angles, φ_{a^*}, φ_{b^*}, φ_{c^*}, between each of the directions concerned and the three reciprocal-lattice axes:

$$\cos \varphi_{a^*} = \frac{1}{d^*}(ha^* + kb^* \cos \gamma^* + lc^* \cos \beta^*) ,$$

$$\cos \varphi_{b^*} = \frac{1}{d^*}(ha^* \cos \gamma^* + kb^* + lc^* \cos \alpha^*) ,$$

$$\cos \varphi_{c^*} = \frac{1}{d^*}(ha^* \cos \beta^* + kb^* \cos \alpha^* + lc^*) ,$$

where the symbols have their usual significance. One is then in a position resembling that of the classical crystallographer dealing with a macro-crystal in which some faces are developed and others are not, with the exception that the X-rays will have added a centre of symmetry. It is then not difficult to determine the Laue symmetry group. In the present connexion only three are likely to be of much interest, namely those characteristic of the orthorhombic, monoclinic and triclinic systems respectively: i.e. *mmm*, 2/*m* and $\bar{1}$. The unit cell may then be determined on the lines given below. In general, there will be more points on the stereographic projection than there are powder lines observed since many of these lines will correspond to two or more sets of triclinic indices. Indeed, clues to the symmetry can be obtained by observing the relationships between those points on the stereographic projection that correspond to the same observed X-ray reflexion. Slight inaccuracies in spacing measurement are not serious, leading to the plotting of poles which are somewhat displaced from their true positions or, in the case of wrong indexing, to isolated poles having no obvious connection with the rest of the projection. In either event the situation is easily recognised and dealt with.

Determination of the unit cell

Laue symmetry mmm

The intersections of the three mirror planes give the axes of the orthorhombic unit cell at once. Reference to the corresponding spacings will give the lengths of these axes in real space, or sub-multiples of them. The correct values can readily be obtained by trial and error.

Laue symmetry 2/*m*

The b^* direction is defined by the twofold axis, and the length of the b axis, or a sub-multiple of it, may be derived as above.

The choice of points corresponding to a^* and c^* will be limited to points situated 90° from b^* on the stereographic projection and of these some will be suggested more strongly than others by a consideration of the observed zones. The best fit may then be obtained by trial and error, taking these points in pairs.

Laue symmetry $\bar{1}$

A centre of symmetry will always appear, but if no other symmetry elements are observed it must be concluded that the structure is triclinic. Each case will then have to be treated on its own merits, but such

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† The Ito method leads actually to one of 24 different types of reduced cell for the 14 Bravais lattices.

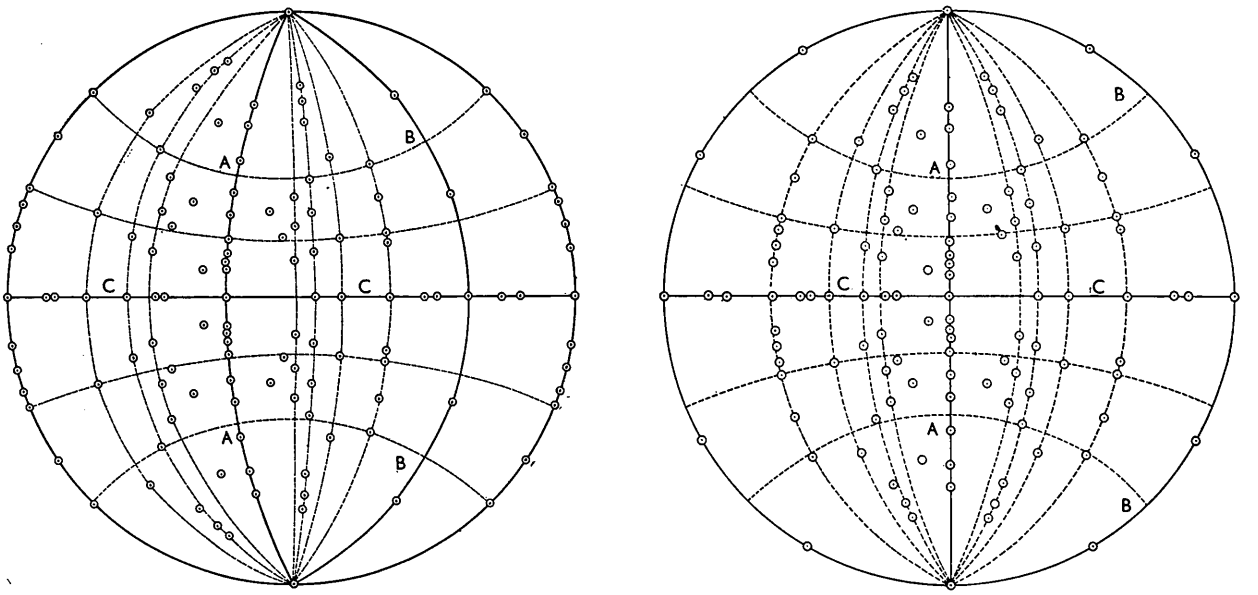

Fig. 1. Stereographic projections of arbitrary unit cell. (*a*) Original projection. (*b*) Re-projection.

features as intersections of zones may be used in a search for the reciprocal axes.

Application of the method

The method has been applied successfully to α-uranium, using the results of Jacob & Warren (1937). The 'triclinic' unit cell obtained actually turned out to be monoclinic with $\beta^* = 64° 9'$ and this led to an orthorhombic unit cell which is compared below with that given by Jacob & Warren:

	a	*b*	*c*
Jacob & Warren	2·852	5·865	4·945
Present authors	2·852	5·862	4·945

The units are probably kX. (see Thewlis, 1951).

No attempt was made to refine the values obtained, but it may be noted that when such a refinement is carried out the difference between the values of $1/d^2$ obtained for the various 'triclinic' planes which correspond to the same observed reflexion, by virtue of symmetry, is a guide to the accuracy of the values originally chosen for the axes.

Fig. 1 gives the two relevant stereographic projections. Fig. 1(*a*) is that produced from the original arbitrary cell, which suggested that the circles *AA* and *BB* as well as *CC* (which arises from the monoclinic symmetry of the cell) corresponded to mirror planes. Measurement confirmed this and a re-projection with the point of intersection of *AA* and *CC* as the central pole gave Fig. 1(*b*). A few zones are shown, the same ones in each projection, as well as small circles which help in seeing the mirroring of the poles.

An attempt was made to index the powder photograph of β-uranium by the above method but on this occasion no success was achieved. When the full details of Ito's method became available (through the kindness of Prof. Kathleen Lonsdale) this method too was applied; but with little success. As already reported (Thewlis, 1951, 1952), Ito's method led to a monoclinic unit cell which bears no obvious relationship to the tetragonal unit cell proposed by Tucker (1950, 1951) and confirmed, with some changes in size, by one of the authors. It therefore appears that, neither by using the Delaunay reduction method nor the method of reduction described in the present note, can success be guaranteed. The spacing measurements in the present instance were certainly less accurate than those required by Ito for the Delaunay method of reduction, and this fact might possibly account for the lack of success obtained. But great accuracy of measurement is not demanded by the stereographic-projection method and the failure here is believed to be due to the large size of the unit cell.

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