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A General X-ray Method for Orienting a Crystal

BY E. J. BROOKER AND E. W. NUFFIELD

Department of Geology, University of Toronto, Canada

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A method for ascertaining the orientation of a randomly set crystal and adjusting it to a preferred orientation is described. Normal-beam, flat-film rotation photographs yield data from which are calculated (ϱ) angles that define the directions of reciprocal lattice vectors with reference to the rotation axis and the planes of the goniometer arcs. The method of plotting the vectors reveals the principal zones and their orientation. The use of monochromatic radiation provides a quantitative estimate of the relative 'importance' of each zone.

The method has several advantages. It is systematic and thereby eliminates the customary search through a series of trial and error photographs for a useful expression of the crystal's structure. It circumvents the complex problem, encountered in cylindrical-film methods, of dealing with the movement of reciprocal points on a curved surface. The magnitude of arc movements required to adjust a zone axis to a desired setting can be evaluated by inspection with a Wulff net. The method is particularly effective for low-symmetry crystals.

Introduction

The Laue, oscillation and precession methods all include systematic techniques for detecting and correcting errors in the orientation of a crystal. However the techniques are limited to the evaluation of small misalignments and are therefore not satisfactory for orienting unknown crystals, or even known crystals with no diagnostic morphological traits.

Most practical X-ray methods for determining the orientation of a randomly-set crystal are based on a preliminary trial and error approach involving a search through a number of photographs of the crystal in different arbitrary orientations, for some sign of a symmetry plane or prominent zone or axis. They are best suited to crystals of high symmetry.

The method described here is a systematic method for ascertaining the orientation of a randomly set known crystal and adjusting it to within about 1° of a preferred orientation. The final adjustment is made with one of the techniques especially suited to correcting small misalignments. The data are plotted in such a manner that the principal zones in the crystal become apparent and thus the method can be applied in the general case to locate a principal zone axis in an unknown, randomly oriented crystal and set it for rotation or precession in one of the standard single-crystal methods of analysis. In contrast to orientation procedures that use Laue photographs, application of this method is simplified by a decrease in crystal symmetry.

An expression for the orientation of a randomly set reflecting plane

The locus of a reciprocal point Q, representing a randomly oriented direct-lattice plane (hkl), is confined to the surface of a sphere, centered at the origin P and having a radius of $PQ=\lambda/d_{hkl}$. This may be called the sphere of location. If the point is rotated about an axis (which passes through P) it will trace out a circle (the circle of location) on the surface of the sphere of location. Fig. 1 shows the case for a rotation axis situated normal to the incident beam. In general the point will pass through the surface of the reflexion sphere twice (at Q' and Q'') in one complete rotation, and therefore satisfy the condition for reflexion twice. If the reflexions (R' and R'') are intercepted on a flat film placed normal to the beam, they will lie on a line normal to the rotation axis (Fig. 2). For every reciprocal point Q there is an opposite point $\bar{Q}$ and consequently the film will show a second pair of reflexions $\bar{R}'$ and $\bar{R}''$. The half-distance s, between the two sets of reflexions is equal to $s^* . F$, where $s^* = SP$ (Fig. 1), is the projection of the vector PQ onto the rotation axis, and F is the crystal to film distance. Therefore $s^* = s/F$.

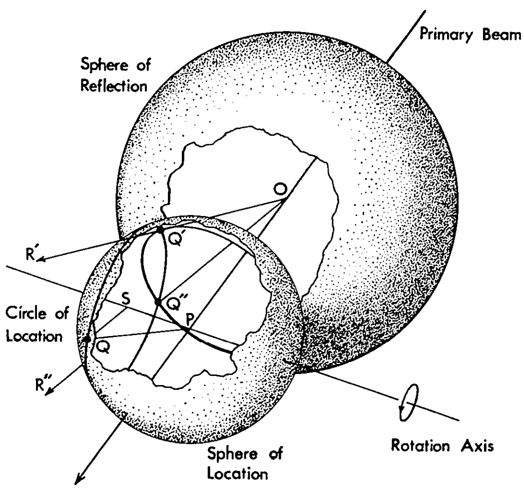

Fig. 1. A reciprocal point Q intersecting the reflexion sphere twice (at Q' and Q'') to cause two reflexions (R' and R'') as it rotates about an axis normal to the beam.

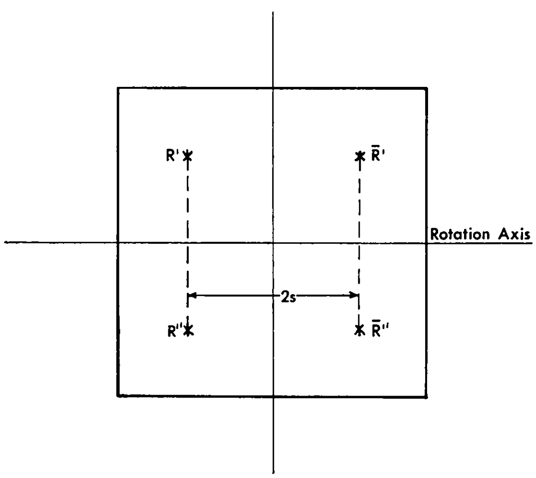

Fig. 2. Reflexions produced by reciprocal points Q and $\bar{Q}$ on a normal-beam flat-film rotation photograph. The half distance s is the projection of SP in Fig. 1.

Suppose one of the arcs (say the small or S arc) of the goniometer head on which the crystal is mounted, is moved through an angle α_S while the setting of the other arc is maintained at zero to confine motion of the crystal to the plane of the arc moved. Then the vector's projection in this plane will also move through an angle α_S from PQ_1' to PQ_2', and its projection on the rotation axis will change from s_1/F to s_2/F (Fig. 3). The angle ϱ_S between PQ_1' and the rotation axis defines the original position of the vector as measured in the plane of the small arc. From Fig. 3

$$\cos \varrho_S = \frac{s_1/F}{PQ_1'}$$

and

$$\cos(\varrho_S + \alpha_S) = \frac{s_2/F}{PQ_2'} = \frac{s_2/F}{PQ_1'}$$

since $PQ_1' = PQ_2'$.
Hence

$$PQ_1' = \frac{s_1/F}{\cos \varrho_S} = \frac{s_2/F}{\cos(\varrho_S + \alpha_S)}$$

and

$$\frac{s_2}{s_1} = \frac{\cos(\varrho_S + \alpha_S)}{\cos \varrho_S}$$

$$= \frac{\cos \varrho_S \cos \alpha_S - \sin \varrho_S \sin \alpha_S}{\cos \varrho_S}$$

$$= \frac{\cos \varrho_S \cos \alpha_S}{\cos \varrho_S} - \frac{\sin \varrho_S \sin \alpha_S}{\cos \varrho_S}$$

$$= \cos \alpha_S - \tan \varrho_S \sin \alpha_S .$$

This can be rearranged into a more useful form:

$$\varrho_S = \tan^{-1} \left[\frac{\cos \alpha_S - \dfrac{s_2}{s_1}}{\sin \alpha_S} \right]$$

The expression permits ϱ_S to be calculated from an instrumental setting (α_S) and two film measurements ($2s_1$ and $2s_2$). A similar relation holds for the large arc provided that the small arc is set at zero to confine motion of the crystal to the plane of the large arc. The values ϱ_S and ϱ_L for a reciprocal point Q define the position of the point on the sphere of location, as measured against the rotation axis in the planes of the two arcs.

The expression for ϱ leads to a negative, a positive or a zero value depending on whether s_2/s_1 is greater than, less than or equal to $\cos \alpha$. The signs of ϱ_L and ϱ_S signify the quadrant of the sphere of location in which Q occurs. Fig. 4 illustrates the three possibilities (for one arc) which result from a right rotation of the arc in the plane of the page.

The sphere of location may be represented by a stereographic sphere in which the rotation axis coincides with the vertical or polar axis of the stereogram and the planes of the two arcs are normal to the projection plane and occupy the N–S, E–W directions. The reciprocal point Q (when the two arcs have zero settings) is located at the intersection of two great circles which make angles of ϱ_L and ϱ_S with the planes of the small and large arcs respectively.

For purposes of standardization the following orientation of the various components and view of the projection has been taken. The view along the rotation axis is from the crystal to the arcs. The standard settings are obtained with right-handed rotational movements of the arcs. It follows that positive values of ϱ_S fall on the upper half of the projection and positive values of ϱ_L on the right-handed half (Fig. 5). If the arc movements are reversed, the signs are reversed.

Procedure for determining a plane's orientation

1. With both goniometer arcs set at zero, a flat-film rotation photograph is prepared and the s_1 distance for the reflexion measured. (For known crystals a single crystal diffractometer may be used to solve the orientation of a selected plane at this point. The ν and Υ settings of the counter on a Buerger equi-inclination device, for example, can be calculated from the measured film distances $R'-\bar{R}'$ and $R'-R''$ (Fig. 2) after which the φ setting of the plane is found by rotating the crystal until the reflexion is received).

2. With one of the arcs (say the large arc) set at an angle α (15° is a practical setting), a second rotation photograph is prepared and the $s_2(L)$ distance measured.

3. The value of ϱ_L is calculated from the relation

$$\varrho_L = \tan^{-1}\left[\frac{\cos\alpha - \dfrac{s_2}{s_1}}{\sin\alpha}\right]$$

4. With the large arc set at zero and the small arc at an angle α, a third rotation photograph is prepared and the distance $s_2(S)$ measured.

5. The value of ϱ_S is calculated.

6. The point of intersection of the two great circles which make angles of ϱ_L and ϱ_S with the small and large arc-planes respectively, is plotted on the stereogram. This point is the stereographic projection of the plane (represented by the reciprocal point Q) when both arcs have zero settings.

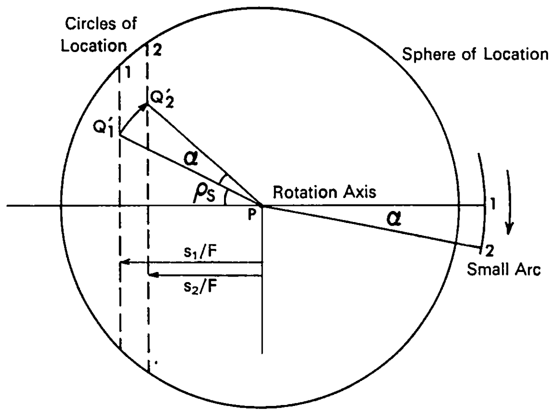

Fig. 3. Projection in plane of small arc showing projected angular displacement (α) of PQ caused by an angular movement α of the arc.

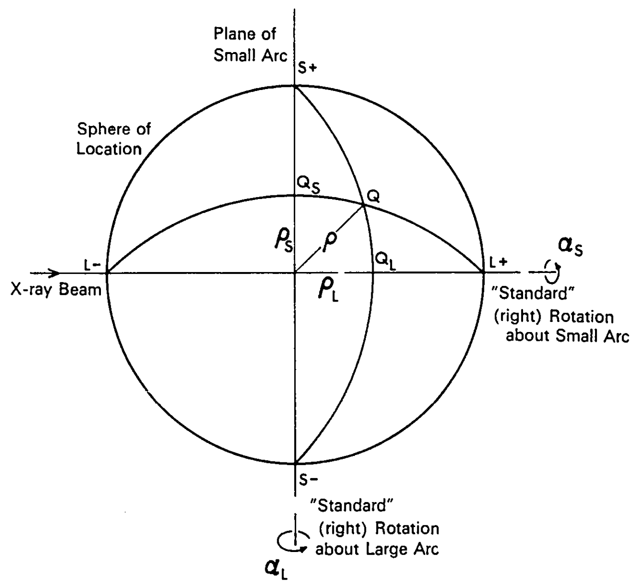

Fig. 5. 'Standard' orientation and rotational movements of arcs. View along rotation axis is from crystal to arcs.

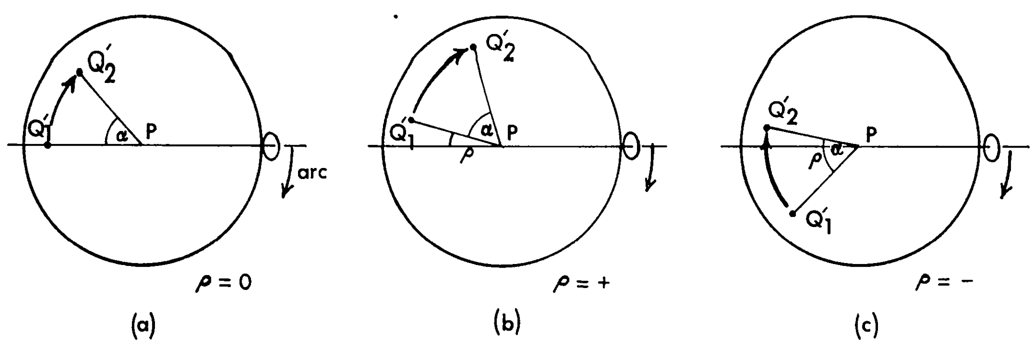

Fig. 4. The sign of ϱ.

Not all of a crystal's planes will necessarily give values for ϱ. Reciprocal lattice vectors within a few degrees of the rotation axis may not enter the sphere of reflexion as the crystal is revolved, or may be moved permanently outside the sphere by the α setting of one of the arcs.

All equivalent reciprocal points reflect to positions equidistant from the film center – that is, to the circumference of a circle. In general then, the higher the symmetry of the crystal, the more densely populated is the circle and the more difficulty may be encountered in sorting out the movement of reflexions caused by the settings. Thus the method is best suited to crystals of low symmetry.

Application of the method

The Buerger precession goniometer is a convenient instrument for applying the new method. The instrument is readily converted to the required flat-film rotation technique by setting the precession angle at zero, and rotating the drum axis independently by means of a belt drive from a small 1 r.p.m. motor. Furthermore, crystal settings derived from application of the method can be readily tested and precisely adjusted with the aid of precession-orientation photographs on the same instrument.

Important direct-lattice rows are axes of zones that include a high proportion of simple-index planes. Reflexions from these planes are generally well represented in the low 2θ region of a film obtained with monochromatic radiation. Therefore a systematic procedure for locating such an axis is to plot the stereographic poles of the low-2θ reflecting planes according to the scheme described in the preceding section, and analyse the projection for important zones.

A randomly set crystal of the triclinic compound $CuSO_4 . 5H_2O$ provides a test of the method in the general case, for locating a principal zone in the crystal and defining its orientation in a useful way. Table 1 gives the s measurements and calculated ϱ values obtained for the first 15 reflexions from such a crystal, beginning with the reflexion nearest the film center and working outward to larger 2θ values*.

Fig. 7 shows the ϱ values plotted on a stereogram according to the scheme illustrated in Fig. 5. The most notable feature of the projection is the appearance of 3 prominent zones. The zones are numbered from 1 to 3 in decreasing order of importance, the estimation of importance being based on the abundance of low 2θ (large spacing, simple index) reflecting planes.

Table 2 shows a comparison between the d values determined from measurements of r for the 15 reflexions, and d values calculated for the $CuSO_4 . 5H_2O$ cell. The table establishes that the 3 zones are composed of planes with general indices, respectively: $(hk0)$, $(0kl)$ and (hkh). The zones axes are therefore [001], [100] and [101]. It is noteworthy that the two most important zones are axial zones. The orientation of the crystal when both arcs are set at zero is now established and the pole of any additional plane or axis may be plotted with the aid of standard crystallographic data for the compound.

Although 15 reflexions were used in this illustration, the three zones would have been discovered by measurement of the first nine reflexions. The two axial zones are defined by the first four and six poles respectively.

* The simple relation $r/F = \tan 2\theta$ (in which r is the film center to reflexion distance, and F is the crystal to film distance) holds for all reflexions in a monochromatic normal-beam, flat-film rotation method. It enables the d spacing, and if the cell dimensions are known, the index of each reflecting plane to be determined with a single film measurement on any of the three preliminary rotation photographs.

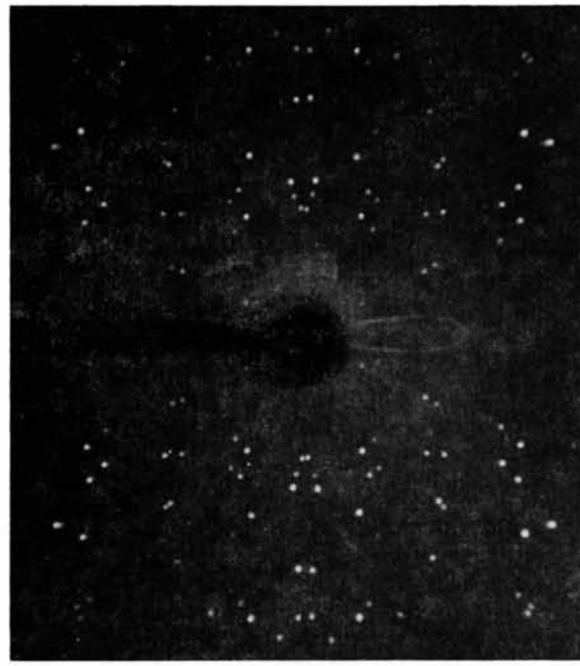

Fig. 6. Normal-beam flat-film rotation photograph of $CuSO_4 . 5H_2O$. Fe-filtered Co radiation; $F = 50$ mm.

Table 1. *Values of ϱ calculated from film* measurements of a $CuSO_4 . 5H_2O$ crystal*

Reflexion	s_1	$s_2(L)$	ϱ_L	$s_2(S)$	ϱ_S
1	3·6 mm	2·8 mm	$36\frac{1}{2}°$	1·9 mm	$59\frac{1}{2}°$
2	10·2	10·1	−1	12·3	$-42\frac{1}{2}$
3	0·3	3·1	$-88\frac{1}{2}$	1·7	87
4	13·8	12·6	$12\frac{1}{2}$	14·3	−14
5	7·4	5·7	38	4·0	59
6	3·4	5·6	−69	0·3	$73\frac{1}{2}$
7	4·1	0·3	74	3·7	14
8	13·8	15·9	−35	12·9	$7\frac{1}{2}$
9	10·1	13·1	−52	10·8	−21
10	6·7	7·3	−25	10·5	$-66\frac{1}{2}$
11	18·1	15·7	$21\frac{1}{2}$	16·8	9
12	17·9	19·7	$-26\frac{1}{2}$	15·0	$26\frac{1}{2}$
13	7·3	8·9	−44	2·3	68
14	6·5	10·5	−68	9·0	−58
15	8·0	2·7	67	6·0	$40\frac{1}{2}$

* Cu radiation, $F = 50$ mm

Table 2. *Identification of the first* 15 *reflexions on a flat-film rotation photograph of* $CuSO_4 . 5H_2O$

Reflexion	Measured* 2θ	Measured* d	Reflecting plane†	Calculated d_{hkl}
1	8·45°	10·4 Å	$(0\bar{1}0)$	10·42 Å
2	15·45	5·74	$(\bar{1}00)$	5·75
3	15·5	5·72	(001)	5·68
4	16·6	5·34	$(\bar{1}\bar{1}0)$	5·48
5	16·95	5·27	$(0\bar{2}0)$	5·21
6	17·2	5·16	$(0\bar{1}1)$	5·15
7	18·35	4·84	$(0\bar{1}\bar{1})$	4·84
8	18·7	4·75	$(\bar{1}\bar{1}1)$	4·72
9	18·7	4·75	$(\bar{1}01)$	4·75
10	19·0	4·67	$(\bar{1}10)$	4·68
11	20·7	4·29	$(\bar{1}\bar{2}0)$	4·28
12	22·3	3·99	$(\bar{1}\bar{2}1)$	3·96
13	22·3	3·99	$(0\bar{2}\bar{1})$	3·99
14	22·3	3·99	$(\bar{1}11)$	4·01
15	23·9	3·72	$(0\bar{2}\bar{1})$	3·71

* On a film obtained with unfiltered Cu radiation and an F setting of 50 mm.

† For the cell with $a=6·122$, $b=10·695$, $c=5·962$ Å; $\alpha=97·58°$, $\beta=107·17°$, $\gamma=77·55°$.

This suggests that a principal zone in an unknown crystal should be located by measurement of the first five or six reflexions. If the crystal is known, one or two *selected* reflexions indicate the orientation. In practice, it is essential to ensure that the very low angle reflexions are recorded. This may involve the use of long-wavelength radiation and extended exposure times for some crystals.

Setting the crystal

The next step, whether the crystal is known or not, is to orient one or more chosen axes for further investigation with the precession, Weissenberg or other method. To photograph the reciprocal lattice it is necessary to orient an important direct-lattice row (preferably an edge of the conventional unit cell) parallel with the beam (which is left to right in the standard orientation adopted in Fig. 5) for precession studies, and normal to it for Weissenberg work. The precession condition is met with arc adjustments to bring the row

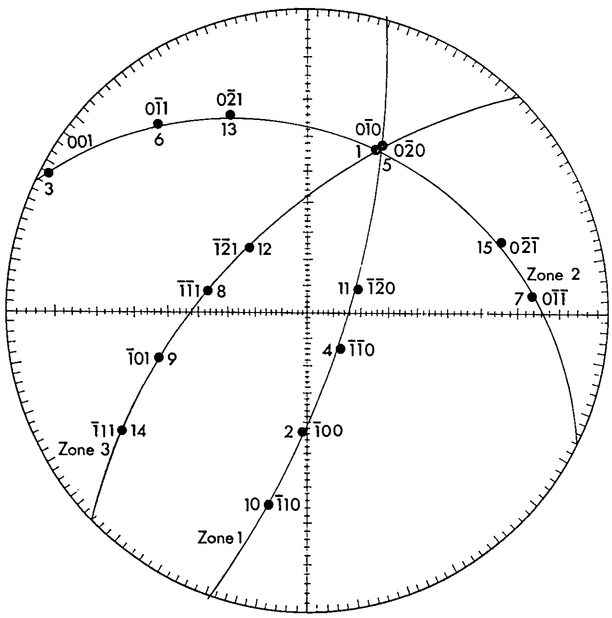

Fig. 7. ϱ values for first 15 reflexions of $CuSO_4 . 5H_2O$ (Table 1) plotted on stereogram according to scheme of Fig. 5. Indices from Table 2.

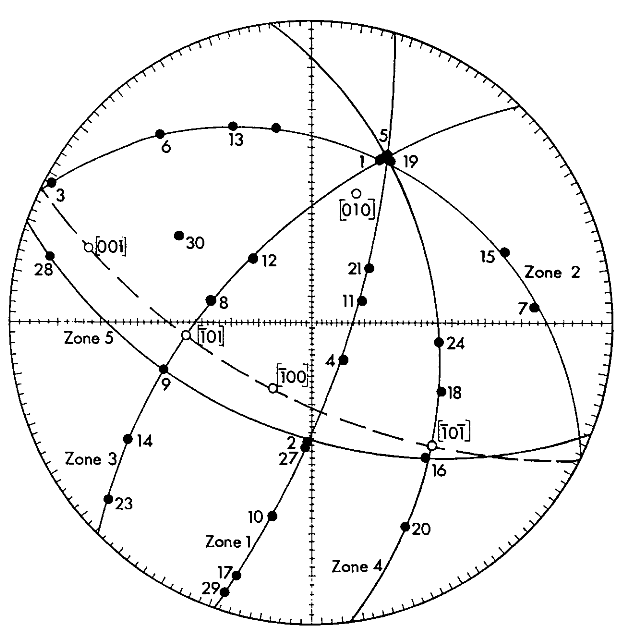

Fig. 9. Crystal geometry of $CuSO_4 . 5H_2O$ displayed by a plot of the first 30 reflexions.

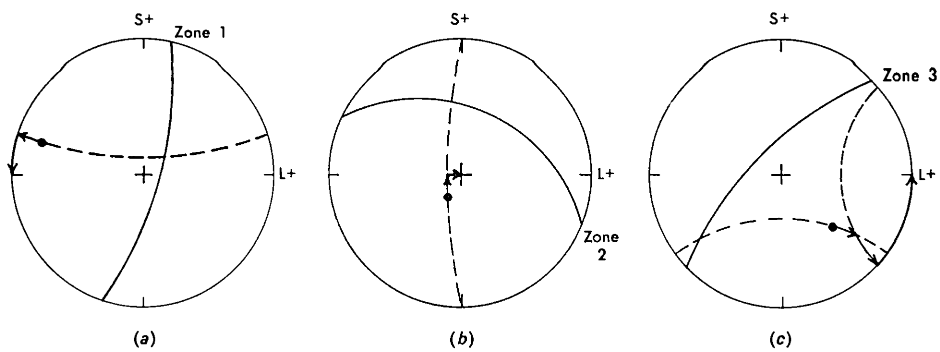

Fig. 8. Arc movements to bring three zones of Fig. 7 to a desired alignment.

into the plane of projection, and a drum movement to rotate the axis into the beam. An advantage of plotting orientation data in the manner illustrated in Fig. 7 is that the arc and drum adjustments can be read directly from the stereogram. An arc adjustment moves a point along a small circle, parallel to the plane of the arc; a drum adjustment rotates the point about the center of the projection. A consideration of Fig. 8(*a*), which shows only the (*hk*0) zone and the pole representing its axis, indicates that the large arc must be given a 15° left rotation to bring the axis into the plane of projection. An anti-clockwise rotation of 18° of the drum aligns the axis with the beam. A precession-orientation photograph for this setting revealed a misalignment of less than 1°.

The axis of zone 2 is clearly beyond reach of the arc adjustments for precession studies. However, the Weissenberg method requires the chosen axis to be coincident with the axis of the goniometer head [(that is, normal to the plane of projection in Fig. 8(*b*)]. This condition is easily within reach. It requires a right rotation of 14° about the large arc and a right rotation of 24° about the small arc.

Zone 3 presents another situation. It requires a right rotation of 41° about the large arc to bring the axis into the plane of projection. This is beyond the limit of a single arc movement, but by combining the movements of both arcs the axis can be brought into the desired position. The rotation of an arc moves the pole representing an axis along a small circle parallel to the arc. A trial investigation with the pole marked on a transparent sheet overlying a Wulff net soon establishes the magnitude of equal angular movements to bring the pole onto the primitive circle. It was found in the present case that this procedure called for a right rotation of 23° about the large arc and a left rotation of 23° about the small arc. A left rotation of 50° of the drum brought the axis into near coincidence with the beam.

The recognition of crystal symmetry

The principal advantage of the orientation method described above derives from instrumental arrangements (normal-beam monochromatic radiation, flat film) that allow the spacing corresponding to each reflexion to be rapidly determined. As a consequence the stereographic projection of reflecting planes has an important advantage over a similar plot obtained from a Laue photograph. It is possible, as shown in the preceding section, to estimate the relative importance of zones and thereby locate simple-index direct-lattice rows. The angles between these rows are conveniently measured with the Wulff net. They provide information about the geometry of the cell and, indirectly, its symmetry. This is naturally of great value in the preliminary investigation of an unknown crystal.

The use of these data, in the case of $CuSO_4 . 5H_2O$, is illustrated by the analysis of the stereogram obtained from measurement of the first 30 reflexions of this compound (Fig. 9). The stereogram shows four prominent zones. The zone axes lie in a common plane, identified in the projection by the dashed great circle. The pole of this plane coincides with the intersection of the four zone circles. It represents an important crystal plane as evidenced by the multiple order reflexions 1, 5 and 19, but its normal is not a direct-lattice row because no stereographic poles fall on the dashed great circle. If the axes of zones 1 and 2 are crystal axes, it follows that the third crystal axis is not a right angles and the crystal is triclinic (the angle between the first two axes is clearly not 90°). Since the interedge angles in conventionally selected triclinic cells are generally within 15° of being right angles, the pole of the third axis should occur near the intersection of the zones. The zone of the axis should lie in the vicinity of the dashed great circle. A fifth zone, comprising poles 2, 9, 16, 27 and 28 does indeed occur in this region of the stereogram.

The angles between the axes of zones 1, 2 and 5, as measured graphically on the projection, confirm the deduction that they are the principal axes in the crystal:

Measured (graphically)	Standard angles*
$1 \wedge 2 = 72\frac{1}{2}°$	$[001] \wedge [\bar{1}00] = 72°50'$
$1 \wedge 5 = 82\frac{1}{2}$	$[001] \wedge [0\bar{1}0] = 82\ 25$
$2 \wedge 5 = 78$	$[\bar{1}00] \wedge [0\bar{1}0] = 77\ 33$

The example of copper sulphate cited above calls attention to the similarity between the stereogram that results from application of the orientation method, and the stereogram obtained by plotting the face-normals of a morphologically well-developed crystal. The important zones are immediately evident — from the relative abundance of low-2θ reflexions in the first case, and from an examination of the crystal in the second. The relations between these zones are equally useful for deducing cell geometry and symmetry.

We wish to thank Mr Kenneth Davison for preparing the drawings.

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* From *Dana's System of Mineralogy* (1951).