Chapter 16

Orientation of Single Crystals

16-1 INTRODUCTION

Many of the properties of polycrystalline materials have been explained by studies of isolated single crystals, since such studies permit measurement of the properties of the individual building blocks in the composite mass. Because single crystals are anisotropic, research of this kind always requires accurate knowledge of the orientation of the single crystal test specimen in order that measurements may be made along known crystallographic directions or planes. By varying the crystal orientation, data on the property measured (e.g., yield strength, electrical resistivity, corrosion rate) is obtained as a function of crystal orientation.

There is also an increasing production of single crystals, not for research studies, but for use as such in various devices, mainly electrical, optical and magnetic. One example is silicon crystals for central processor units and random access memory in computers and for semiconductor based consumer products. Another example is single-crystal nickel-based super alloy turbine blades which have very high creep resistance. These crystals must all be produced with particular orientations.

Described below are the three main methods of determining orientation; back-reflection Laue, transmission Laue, and diffractometer methods. Nor should the old etch-pit method be overlooked. This is an optical method, involving the reflection of visible light from the flat sides, of known Miller indices, of etch pits in crystal surfaces. Although not universally applicable, this method is fast and requires only simple apparatus [G.10].

16-2 BACK-REFLECTION LAUE METHOD

As mentioned in Sec. 3-8, the Laue pattern of a single crystal consists of a set of diffraction spots on the film and the positions of these spots depend on the orientation of the crystal. This is true of either Laue method, transmission or back-reflection, so either can be used to determine crystal orientation. However, the back-reflection method is the more widely used of the two because it requires no special preparation of the specimen, which may be of any thickness, whereas the transmission method requires relatively thin specimens of low absorption.

In either case, since the orientation of the specimen is to be determined from the location of the Laue spots on the film, it is necessary to orient the specimen relative to the film in some known manner. The single crystal specimens encountered in materials work are usually in the form of wire, rod, sheet, or plate, but crystals of irregular shape must occasionally be analyzed. Wire or rod specimens are best mounted with their axis parallel to one edge of the square or rectangular film; a fiducial mark on the specimen surface, for example on the side nearest the film, then fixes the orientation of the specimen completely. It is convenient to mount sheet or plate specimens with their plane parallel to the plane of the film and one edge of the sheet or plate parallel to an edge of the film. Irregularly shaped crystals must have fiducial marks on their surface which will definitely fix their orientation relative to that of the film.

The problem now is to determine the orientation of the crystal from the position of the back-reflection Laue spots on the film. The Bragg angle θ corresponding to each Laue spot could be determined from Eq. (8-2), but that would be no help in identifying the planes producing that spot, since the wavelength of the diffracted beam is unknown. The orientation of the normal to the planes causing each spot, is fixed, however because the plane normal always bisects the angle between incident and diffracted beams. The directions of the plane normals can then be plotted on a stereographic projection, the angles between them measured, and the planes identified by comparison with a list of known interplanar angles for the crystal involved.

The first problem, therefore, is to derive, from the measured position of each diffraction spot on the film, the position on a stereographic projection of the pole of the plane causing that spot. In doing this it is helpful to recall that all of the planes of one zone diffract beams which lie on the surface of a cone whose axis is the zone axis and whose semi-apex angle is equal to the angle ϕ at which the zone axis is inclined to the transmitted beam (Fig. 16-1). If ϕ does not exceed 45°, the cone will not intersect a film placed in the back-reflection region; if ϕ lies between 45° and

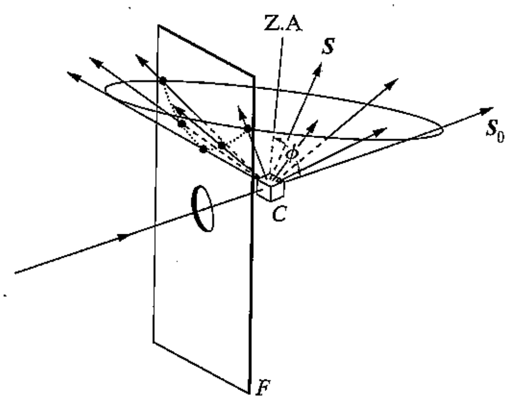


Figure 16-1 Intersection of a conical array of diffracted beams with a film placed in the back-reflection position. C = crystal, F = film, Z.A. = zone axis.

90°, the cone intersects the film in a hyperbola; and, if ϕ equals 90°, the intersection is a straight line passing through the incident beam. (If ϕ exceeds 90°, the cone shifts to a position below the transmitted beam and intersects the lower half of the film, as may be seen by viewing Fig. 16-1 upside down.) Diffraction spots on a back-reflection Laue film therefore lie on hyperbolas or straight lines, and the distance of any hyperbola from the center of the film is a measure of the inclination of the zone axis.

In Fig. 16-2 the film is viewed from the crystal. Coordinate axes are defined such that the incident beam proceeds along the z-axis in the direction Oz and the x- and y-axes lie in the plane of the film. The diffracted beam by the plane shown strikes the film at S. The normal to this plane is CN and the plane itself is assumed to belong to a zone whose axis lies in the yz-plane. If this plane were rotated about the zone axis, it would pass through all the positions at which planes of this zone in an actual crystal might lie. During this rotation, the plane normal would cut the film in the straight line AB and the diffracted beam in the hyperbola HK. AB is therefore the locus of plane normal intersections with the film and HK the locus of diffracted beam intersections. The plane which diffracts a beam to S, for example, has a normal which intersects the film at N, since the incident beam, plane normal, and diffracted beam are coplanar. Since the orientation of the plane normal in space can be described by its angular coordinates γ and δ, the problem is to determine γ and δ from the measured coordinates x and y of the diffraction spot S on the film.

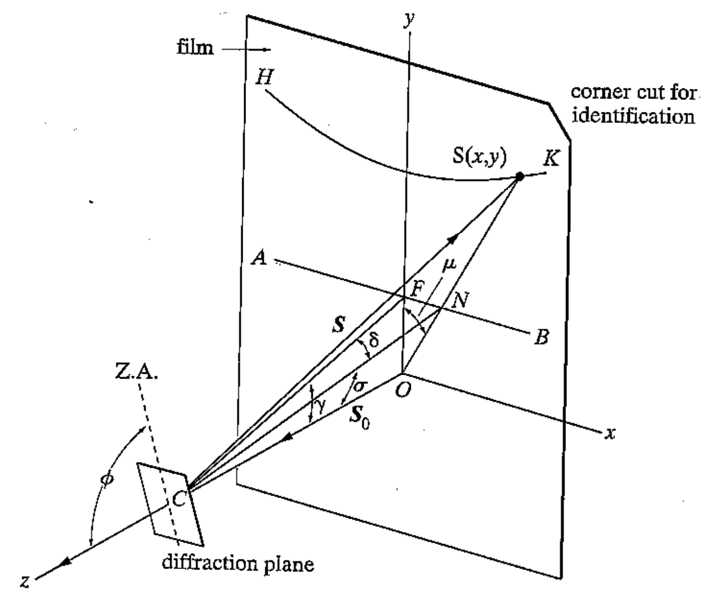


Figure 16-2 Location of back-reflection Laue spot. Note that $y = 90° - \phi$.

A graphical method of doing this was devised by Greninger [16.1] who developed a chart which, when placed on the film, gives directly the γ and δ coordinates corresponding to any diffraction spot. To plot such a chart, note from Fig. 16-2 that

$$x = OS \sin \mu, \; y = OS \cos \mu, \text{ and } OS = OC \tan 2\sigma, \tag{16-1}$$

where $OC = D$ = specimen-film distance. The angles μ and σ are obtained from γ and δ as follows:

$$\tan \mu = \frac{FN}{FO} = \frac{\mathrm{CF} \tan \delta}{CF \sin \gamma} = \frac{\tan \delta}{\sin \gamma} \tag{16-2}$$

$$\tan \sigma = \frac{ON}{OC} = \left(\frac{\mathrm{FN}}{\sin \mu}\right)\left(\frac{1}{CF \cos \gamma}\right) = \left(\frac{CF \tan \delta}{\sin \mu}\right)\left(\frac{1}{CF \cos \gamma}\right)$$

$$= \frac{\tan \delta}{\sin \mu \cos \gamma} \tag{16-3}$$

With these equations, the position (in terms of x and y) of any diffraction spot can be plotted for given values of γ and δ and any desired specimen-film distance D. The result is the Greninger chart, graduated at 2° intervals shown in Fig. 16-3 for D = 3.0 cm. The hyperbolas running from left to right are curves of constant γ, and any one of these curves is the locus of diffraction spots from planes of a zone whose axis is tilted away from the plane of the film by the indicated angle γ. If points having the same value of δ are joined together, another set of hyperbolas running from top to bottom is obtained. The lower half of the chart contains a protractor whose use will be described later. Greninger charts should have dark lines on a transparent background and are best printed on overhead projector transparencies using a computer plotting package and Eq. (16-1)-(16-3).

In use, the chart is placed over the film with its center coinciding with the film center and with the edges of chart and film parallel. The γ and δ coordinates corresponding to any diffraction spot are then read directly. Note that use of the chart avoids any measurement of the actual coordinate distances x and y of the spot. The chart gives directly, not the x and y coordinates of the spot, but *the angular coordinates γ and δ of the normal to the diffraction planes causing the spot.*

Knowing the γ and δ coordinates of any plane normal, for example CN in Fig. 16-2, the pole of the plane can be plotted on a stereographic projection. Imagine a reference sphere centered on the crystal in Fig. 16-2 and tangent to the film, and let the projection plane coincide with the film. The point of projection is taken as the intersection of the transmitted beam and the reference sphere. Since the plane normal CN intersects the side of the sphere nearest the x-ray source, the projection must be viewed from that side and the film "read" from that side. In order to know, after processing, the orientation the film had during the x-ray expo-

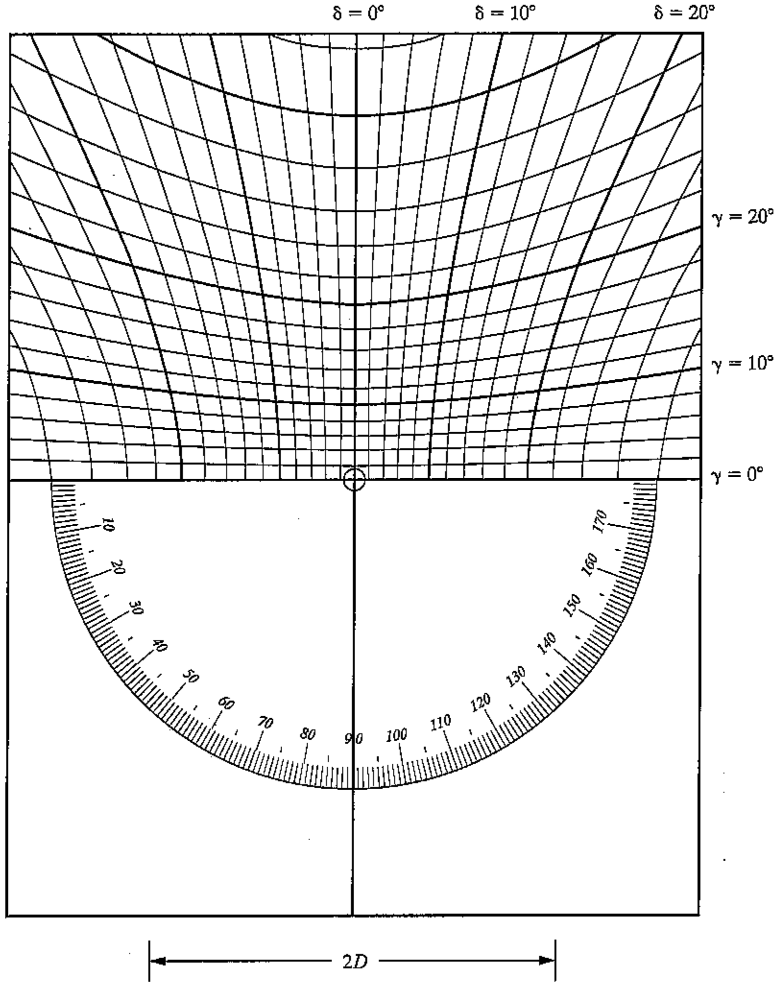


Figure 16-3 Greninger chart for the solution of back-reflection Laue patterns, reproduced in the correct size for a specimen-to-film distance D of 3 cm.

sure, the upper right-hand corner of the film (viewed from the crystal) is cut away before it is placed in the cassette, as shown in Fig. 16-2. When the film is read, this cut corner must therefore be at the upper left, as shown in Fig. 16-4(a). The angles γ and δ, read from the chart, are then laid out on the projection as indicated in Fig. 16-4(b). Note that the underlying Wulff net must be oriented so that its meridians run from side to side, not top to bottom. The reason for this is the fact that diffrac-

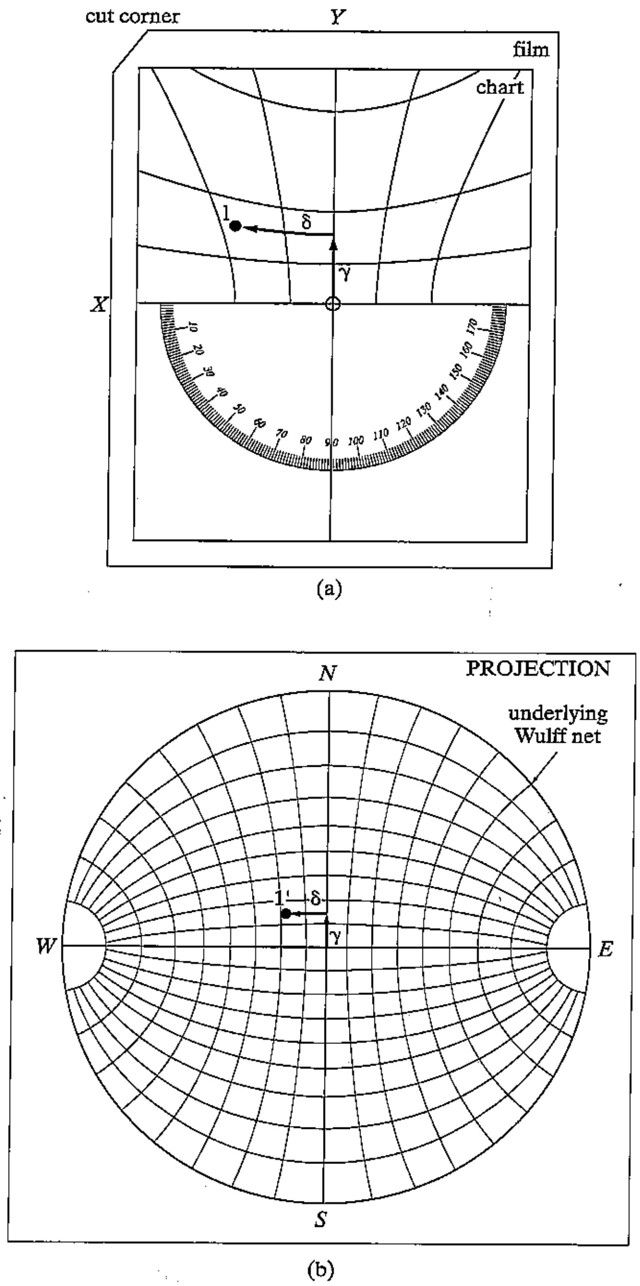


Figure 16-4 Use of the Greninger chart to plot the pole of a reflecting plane on a stereographic projection. Pole 1′ in (b) is the pole of the plane causing diffraction spot 1 in (a).

tion spots which lie on curves of constant γ come from planes of a zone, and the poles of these planes must therefore lie on a great circle on the projection. The γ, δ coordinates corresponding to diffraction spots on the lower half of the film are obtained simply by reversing the Greninger chart end for end.

It helps to remember that there are two frames of reference involved in analyzing Laue patterns. The first is the coordinate system of the laboratory, and the second is the coordinate system of the crystal. When the crystal is reoriented, this second system is also reoriented relative to the laboraotry coordinate system. The Wulff net and Greninger chart are in the laboratory frame of reference while the film and the tracing paper or transparency on top of the Wulff net represent the crystal. Since the laboratory, the x-ray generator and the Laue camera remain fixed in position, it is perhaps less confusing to keep the orientation of the Greninger chart and Wulff net fixed and to rotate only the film on the Greninger chart and the stereographic projection of the poles of the crystal on the Wulff net.

The procedure may be illustrated by determining the orientation of the aluminum crystal whose back-reflection Laue pattern is shown in Fig. 3-10(b). Fig. 16-5 is a tracing of this photograph, showing the more important spots numbered for reference. The poles of the planes causing these numbered spots are plotted stereographically in Fig. 16-6 by the method of Fig. 16-4 and are shown as solid circles.

The problem now is to "index" these planes, i.e., to find their Miller indices, and so disclose the orientation of the crystal. With the aid of a Wulff net, great circles are drawn through the various sets of poles corresponding to the various hyperbolae of spots on the film. These great circles connect planes of a zone, and planes lying at their intersections are generally of low indices, such as {100}, {110}, {111}, and {112}. The axes of the zones themselves are also of low indices, so it is helpful

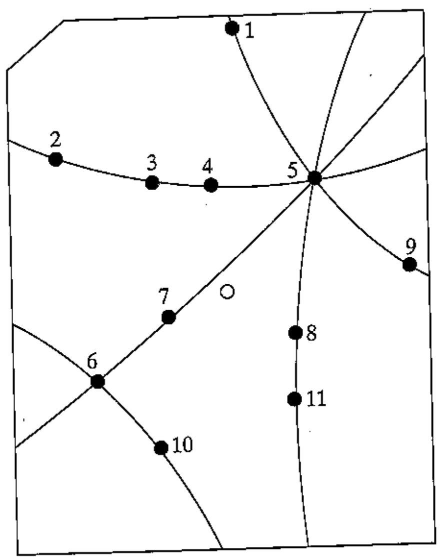


Figure 16-5 Selected diffraction spots of back-reflection Laue pattern of an aluminum crystal, traced from Fig. 3-10(b).

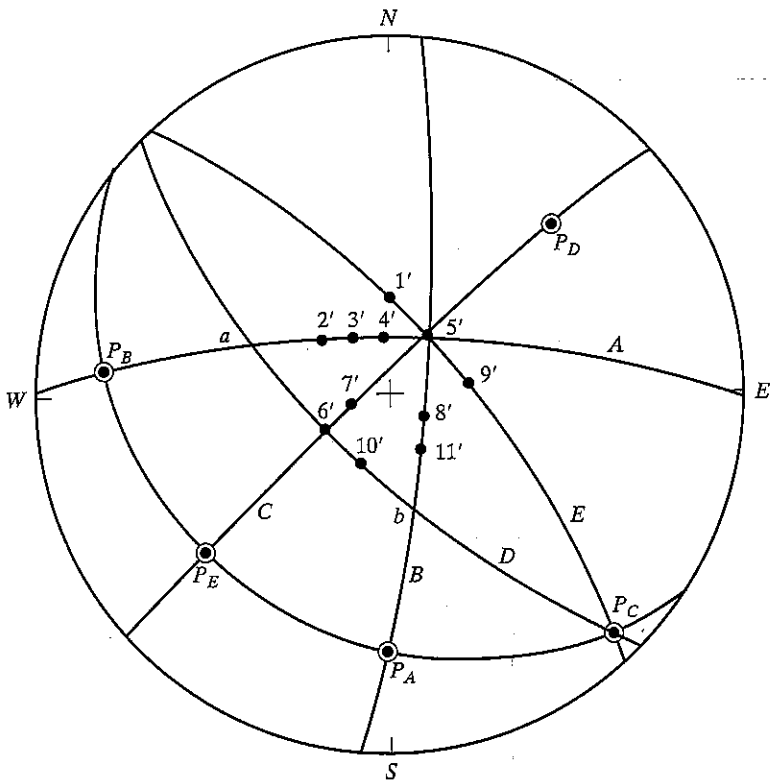


Figure 16-6 Stereographic projection corresponding to back-reflection pattern of Fig. 16-5.

to locate these axes on the projection. They are shown as open circles in Fig. 16-6, P_A being the axis of zone A, P_B the axis of zone B, etc. The angles between important poles (zone intersections and zone axes) are measured next and the poles are identified by comparing of these measured angles with those calculated for cubic crystals (Table 2-4). The method is essentially one of trial and error. Note, for example, that the angles P_A - P_B, P_A - 5′, and P_B - 5′ are all 90°. This suggests that one or more of these poles might be {100} or {110}, since the angle between two {100} poles or between two {110} poles is 90°. Suppose P_A, P_B, and 5′ are all {100} poles.[1] Then P_E, which lies on the great circle between P_A and P_B and at an angular distance of

[1] The reader may detect an apparent error in nomenclature here. Pole 5′ for example, is assumed to be a {100} pole and spot 5 on the diffraction pattern is assumed, tacitly, to be due to a 100 reflection. Aluminium, however, is face-centered cubic, and there is no 100 reflection from such a lattice, since *hkl* must be unmixed for diffraction to occur. In this case, spot 5, is due to overlapping diffracted beans from second, fourth, sixth, etc. orders of 100 diffraction. But these Bragg planes are all parallel and are represented on the stereographic projection by one pole, which is conventionally designated as {100}. The corresponding diffraction spot is also called, conventionally but loosely, the 100 spot.

45° from each, must be a {110} pole. Next consider zone C; the distance between pole 6′ and either pole 5′ or P_E is also 45°. But reference to a standard projection, such as Fig. 2-40, shows that there is no important pole located midway on the great circle between {100}, identified with 5′, and {110}, identified with P_E. The original assumption is therefore wrong. A second assumption is required which is consistent with the angles measured so far, namely that 5′ is a {100} pole, as before, but that P_A and P_B are {110} poles. P_E must then be a {100} pole and 6′ a {110} pole. This assumption is checked by measuring the angles in the triangle a - b - 5′. Both a and b are found to be 55° from 5′, and 71° from each other, which conclusively identifies a and b as {111} poles. Note also, from a standard projection, that a {111} pole must lie on a great circle between {100} and {110}, which agrees with the fact that a, for example, lies on the great circle between 5′, assumed to be {100}, and P_B, assumed to be {110}. The second assumption is therefore shown to be consistent with the data.

Figure 16-7 shows the stereographic projection in a more complete form, with all poles of the type {100}, {110}, and {111} located and identified. Note that it was not

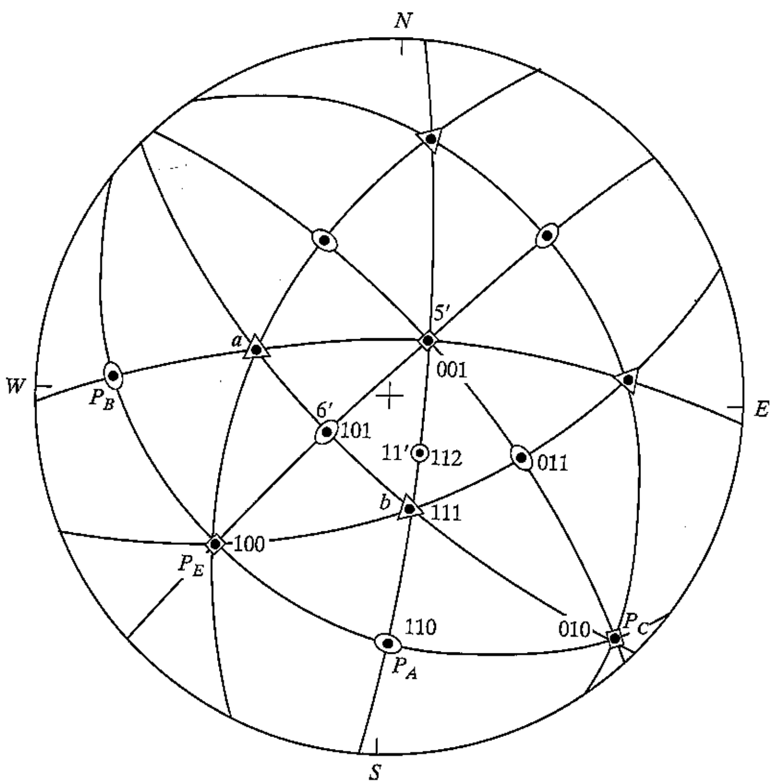


Figure 16-7 Stereographic projection of Fig. 16-6 with poles identified.

necessary to index all the observed diffraction spots in order to determine the crystal orientation, which is specified completely, in fact, by the locations of any two {100} poles on the projection. The information given in Fig. 16-7 is therefore all that is commonly required. Occasionally, however, it may be necessary to determine the Miller indices of a particular diffraction spot on the film, spot 11 for example. To find these indices, note that pole 11′ is located 35° from (001) on the great circle passing through (001) and (111). Reference to a standard projection and a table of interplanar angles shows that its indices are (112).

As mentioned above, the stereographic projection of Fig. 16-7 is a complete description of the orientation of the crystal. Other methods of description are also possible. The crystal to which Fig. 16-7 refers had the form of a square plate and was mounted with its plane parallel to the plane of the film (and the projection) and its edges parallel to the film edges, which are in turn parallel to the *NS* and *EW* axes of the projection. Since the (001) pole is near the center of the projection, which corresponds to the specimen normal, and the (010) pole near the edge of the projection and approximately midway between the *E* and *S* poles, a rough description of the crystal orientation is as follows: one set of cube planes is approximately parallel to the surface of the plate while another set passes diagonally through the plate and approximately at right angles to its surface.

Another method of description may be used when only one direction in the crystal is of physical significance, such as the plate normal in the present case. For example, a compression test of this crystal may be required with the axis of compression normal to the plate surface. The interest is then in the orientation of the crystal relative to the compression axis (plate normal) or, stated inversely, in the orientation of the compression axis relative to certain directions of low indices in the crystal. Now inspection of a standard projection such as Fig. 2-39(a) shows that each half of the reference sphere is covered by 24 similar and equivalent spherical triangles, each having {100}, {110}, and {111} as its vertices. The plate normal, i.e., the direction along which the polychromatic bean was incident on the crystal, will fall in one of these triangles and it is necessary to draw only one of them in order to describe the precise location of the normal. In Fig. 16-7, the plate normal lies in the (001)-(101)-(111) triangle which is redrawn in Fig. 16-8 in the conventional orientation, as though it formed part of a (001) standard projection. To locate the plate normal on this new drawing, measure the angles between the center of the projection in Fig. 16-7 and the three adjacent 001, 101, and 111 poles. Let these angles be ρ_{001}, ρ_{101}, and ρ_{111}. These angles are then used to determine the three arcs shown in Fig. 16-8. These are circle arcs, but they are *not* centered, in general, on the corresponding poles; rather, each one is the locus of points located at an equal *angular* distance from the pole involved and their intersection therefore locates the desired point. Another method of arriving at Fig. 16-8 from Fig. 16-7 consists simply in rotating the whole projection, poles and plate normal together, from the orientation shown in Fig. 16-7 to that of a standard (001) projection.

Similarly, the orientation of a single-crystal wire or rod may be described in terms of the location of its axis in the unit stereographic triangle. Note that this

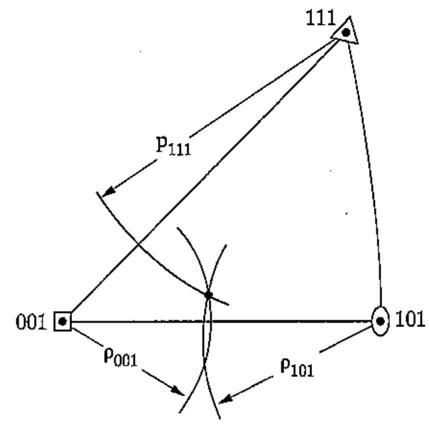


Figure 16-8 Use of the unit stereographic triangle to describe crystal orientation. The point inside the triangle is the normal to the single crystal plate whose orientation is shown in Fig. 16-7.

method does not completely describe the orientation of the crystal, since it allows one rotational degree of freedom about the specimen axis. This is of no consequence, however, if only the value of some measured physical or mechanical property is needed along a particular direction in the crystal.

There are other ways of manipulating both the Greninger chart and the stereographic projection, and the particular method used is purely a matter of personal preference. For example, the individual spots on the film may be ignored, and the various hyperbolae on which they lie may be used. The spots on one hyperbola are due to diffracted beams from planes of one zone and, by means of the Greninger chart, the axis of this zone can be plotted directly without plotting the poles of any of the planes belonging to it. The procedure is illustrated in Fig. 16-9. Keeping the centers of film and chart coincident, rotate the film about this center until a particular hyperbola of spots coincides with a curve of constant γ on the chart, as in (a). The amount of rotation required is read from the intersection of a vertical pencil line, previously ruled through the center of the film and parallel to one edge, with the protractor of the Greninger chart. Suppose this angle is ε. Then the projection is rotated by the same angle ε with respect to the underlying Wulff net and the zone axis is plotted on the vertical axis of the projection at an angle γ from the *circumference*, as in (b).[2] Note that zone A itself is represented by the great circle located at an angle γ above the *center* of the projection. Many investigators use only the zone axes in solving the orientation of the crystal; they will ordinarily not plot the zone (great) circle. Others prefer to plot all zone circles and to use the intersections of multiple circles as additional information. In either case, once all the zone axes or great circles of the important zones are plotted, analysis focuses on the most important poles, i.e., those poles at the intersection of a number of hyperbolas and

[2] Note that, when a hyperbola of spots is lined up with a horizontal hyperbola on the chart as in [Fig. 16-9(a)], the vertical hyperbolae can be used to measure the difference in angle δ for any two spots and that this angle is equal to the angle between the planes causing those spots, just as the angle between two poles lying on a meridian of a Wulff net is given by their difference in latitude.

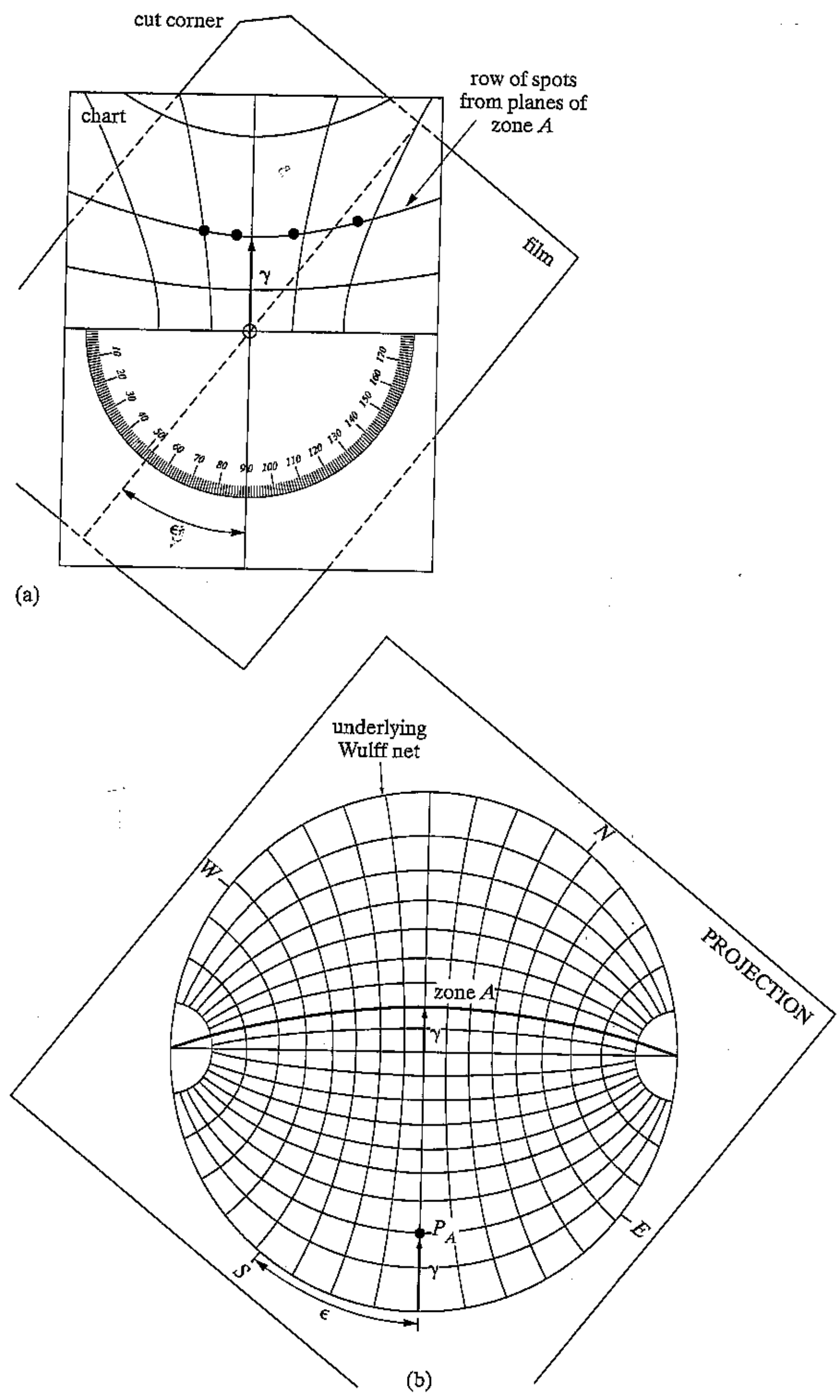


Figure 16-9 Use of the Greninger chart to plot the axis of a zone of planes on the stereographic projection. P_A is the axis of zone A.

which are well-separated from neighboring diffracted beams are always of low indices and can usually be indexed without difficulty.

An experienced investigator working with a familiar material can often recognize the symmetry of Laue patterns from low-index or near-low-index directions, and compilations of Laue patterns from specific directions [G.40] or commercially available computer simulation programs are very handy in this context (e.g., [16.2]). Figure 16-10a was traced from film (note the "UR" labeled the upper right of the original film is now flipped), and the pattern of spots exhibits mirror symmetry across the row of spots labeled with "1" at each end (of course some distortion appears since the incident beam is slightly off zone 1). Mirror-related pairs of hyperbolas are indicated in Fig. 16-10b and include zones 3 and 4, 5 and 6, 7 and 8, 9 and 10, and 11 and 12. Prominent hyperbola intersections are outlined by circles in Fig. 16-10a, and important intersections are labeled A-G in Fig. 16-10b. The pair of intersections C and D are mirror related as are E and F. The intersection matching G lies off the film. Use of sets of symmetry related and crystallographically equivalent zones can speed identification of symmetry related zone intersections greatly since these must necessarily be the same type of *hkl*.

Measurement of the angles between intersections A-G (directly with the Greninger chart or after transfer to the stereographic projection) reveals A and B correspond to 111 and 110 type reflections, respectively, while the pair C and D are 210 type reflections, the pair E and F are 211 reflections and G is a 311 type reflection. Inspection of the calculated 441 and 331 Laue patterns shown in Fig. 16-10c and d, respectively, confirms the identification given above. Note that the intensities of the symmetry-related spots may vary for different crystallographically equivalent zones due to the tilt of the crystal, and hyperbolae may not appear to be identical due to such differences in intensity or to distortions produced by incident beams along high index directions (e.g., 2 mm symmetry is associated with Laue pattern recorded with the incident beam along 110 and this is far from apparent at B in Fig. 16-10a). For patterns recorded with the beam along a low index direction such as 100 or 111, several parallel, closely-spaced hyperbolas may be visible and care is required when selecting symmetry related sets.

Another method of indexing plotted poles depends on having available a set of detailed standard projections in a number of orientations, such as {100}, {110}, and {111} for cubic crystals. It is also a trial and error method and may be illustrated with reference to Fig. 16-6. First, a prominent zone is selected and an assumption is made as to its indices: for example, assume that zone *B* is a $\langle 100 \rangle$ zone i.e., its zone axis P_B is $\langle 100 \rangle$. This assumption is then tested by (a) rotating the projection about its center until P_B lies on the equator of the Wulff net and the ends of the zone circle coincide with the *N* and *S* poles of the net, and (b) rotating all the important points on the projection about the *NS*-axis of the net until P_B lies at the center and the zone circle at the circumference. The new projection is then superimposed on a {100} standard projection and rotated about the center until all points on the projection coincide with those on the standard. If no such coincidence is obtained, P_B is unlikely to be $\langle 100 \rangle$, and another standard projection should be tried. For the par-

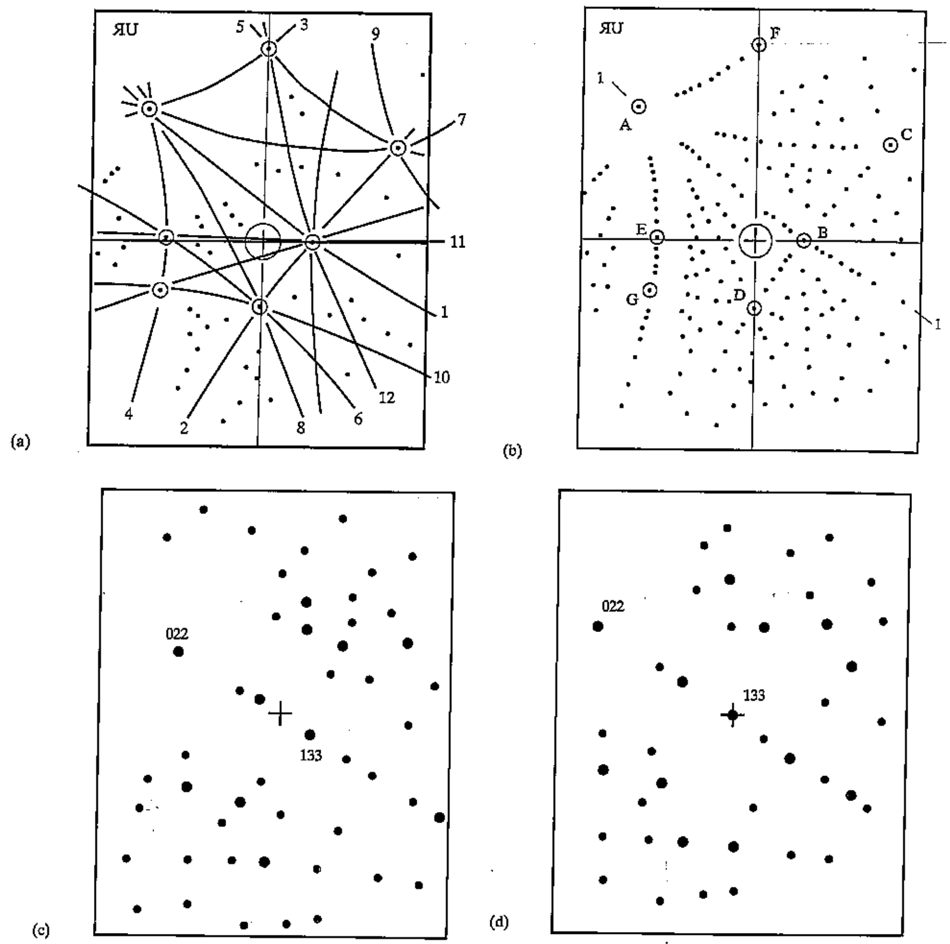


Figure 16-10 Back reflection Laue patterns for analysis by consideration of symmetry. (a) Pattern traced from the originial. (b) Zones indicated on the pattern. (c) Simulation of 144 pattern and (d) Simulation of 133 pattern (after G.P.). The larger filled circles represent more intense diffracted beams in the simulations.

ticular case of Fig. 16-6, a coincidence would be obtained only on a {110} standard, since P_B is actually a {110} pole. Once a match has been found, the indices of the unknown poles are given simply by the indices of the poles on the standard with which they coincide.

In the absence of a Greninger chart, the pole corresponding to any observed Laue spot may be plotted by means of an easily constructed "stereographic ruler." The construction of the ruler is based on the relations shown in Fig. 16-11. This drawing is a section through the incident beam OC and any diffracted beam CS. Here it is convenient to use the plane normal CN' rather than CN and to make the

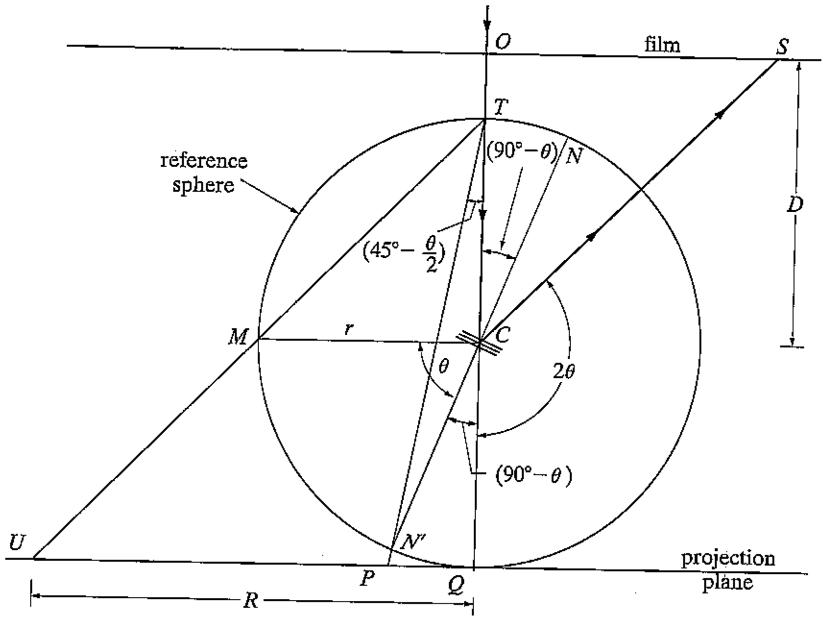


Figure 16-11 Relation between diffraction spot S and stereographic projection P of the plane causing the spot, for back reflection.

projection from T, the intersection of the reference sphere with the incident beam. The projection of the pole N' is therefore at P. From the measured distance OS of the diffraction spot from the center of the film,

$$OS = OC \tan(180° - 2\theta) = D \tan(180° - 2\theta), \tag{16-4}$$

the distance PQ of the projected pole from the center of the projection is

$$PQ = TQ \tan\left(45° - \frac{\theta}{2}\right) = 2r \tan\left(45° - \frac{\theta}{2}\right), \tag{16-5}$$

where D is the specimen-film distance and r the radius of the reference sphere. The value of r is fixed by the radius R of the Wulff net used, since the latter equals the radius of the basic circle of the projection. If the pole of the plane were in its extreme position at M, then its projection would be at U. The point U therefore lies on the basic circle of the projection, and UQ is the radius R of the basic circle. Because the triangles TUQ and TMC are similar, $R = 2r$ and

$$PQ = R \tan\left(45° - \frac{\theta}{2}\right). \tag{16-6}$$

The ruler is constructed by marking off, from a central point, a scale of centimeters by which the distance *OS* may be measured. The distance *PQ* corresponding to each distance *OS* is then calculated from Eqs. (16-4) and (16-6), and marked off from the center of the ruler in the opposite direction. Corresponding graduations are given the same number and the result is the ruler shown in Fig. 16-12, which also illustrates the method of using it. [Calculation of the various distances *PQ* can be avoided by use of the Wulff net itself. Figure 16-11 shows that the pole of the reflecting plane is located at an angle θ from the edge of the projection, and θ is given for each distance *OS* by Eq. (16-13). The ruler is laid along the equator of the Wulff net, its center coinciding with the net center, and the distance *PQ* corresponding to each angle θ is marked off with the help of the angular scale on the equator.]

From the choice of plane normal made in Fig. 16-11, it is apparent that the projection must be viewed from the side opposite the x-ray source. This requires that the film be read from that side also, i.e., with its cut corner in the upper right-hand position. The projection is then placed over the film, illuminated from below, as shown in Fig. 16-12. With the center of the ruler coinciding with the center of the projection, the ruler is rotated until its edge passes through a particular diffraction spot. The distance *OS* is noted and the corresponding pole plotted as shown, on the other side of center and at the corresponding distance *PQ*. This procedure is repeated for each important diffraction spot, after which the projection is transferred to a Wulff net and the poles indexed by either of the methods previously described. Note that this procedure gives a projection of the crystal from the side opposite the x-ray source, whereas the Greninger chart gives a projection of the crystal as seen from the x-ray source. A crystal orientation can, of course, be described just as well from one side as the other, and either projection can be made

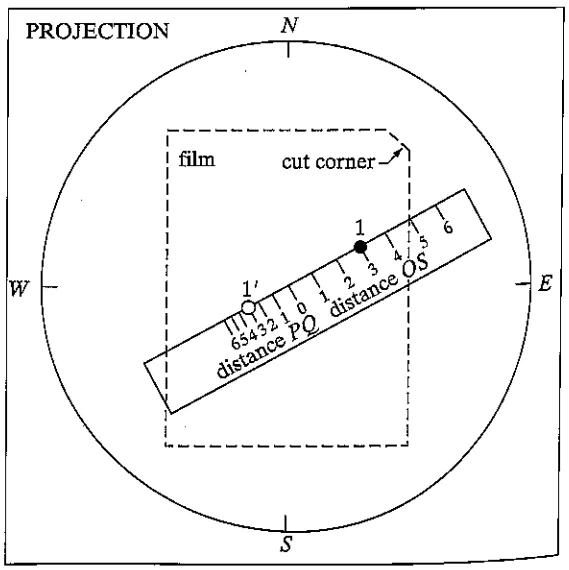


Figure 16-12 Use of a stereographic ruler to plot the pole of a reflecting plane on a stereographic projection in the back-reflection Laue method. Pole 1′ is the pole of the plane causing diffraction spot 1.

to coincide with the other by a 180° rotation of the projection about its *EW*-axis. Although simple to use and construct, the stereographic ruler is not as accurate as the Greninger chart in the solution of back-reflection patterns.

The methods of determining and describing crystal orientation have been presented here exclusively in terms of cubic crystals, because these are the simplest kind to consider and the most frequently encountered. These methods are quite general, however, and can be applied to a crystal of any system as long as its interplanar angles are known.

However, a noncubic crystal may have such low symmetry and/or be so oriented that the Laue pattern shows only one spot, or none at all, from a low-index plane. Plane indexing can then be difficult. Methods of coping with this problem include the following:

1. The crystal is re-oriented, in a manner suggested by the Laue pattern, and examined in a diffractometer. See Sec. 16-5.
2. A set of simulated Laue patterns, covering the unit stereographic triangle of the crystal, is generated by a computer [16.2]. The simulated pattern which most nearly matches the unknown yields tentative (*hkl*) indices for three prominent spots. Measurements on the film of the angles between these spots and the film center (incident x-ray beam) yield tentative indices for the crystal plane normal to the incident beam. A simulated pattern is then generated for this special orientation and compared with the unknown pattern to verify the plane indexing.

Specialized books on the Laue methods are those of Amoros *et al.* [G.31] and Preuss *et al.* [G.40]. The latter contains a catalog of back-reflection patterns, many generated by a computer.

16-3 TRANSMISSION LAUE METHOD

Given a specimen of sufficiently low absorption, a transmission Laue pattern can be obtained and used, in much the same way as a back-reflection Laue pattern, to reveal the orientation of the crystal.

In either Laue method, the diffraction spots on the film, due to the planes of a single zone in the crystal, always lie on a curve which is some kind of conic section. When the film is in the transmission position, this curve is a complete ellipse for sufficiently small values of ϕ, the angle between the zone axis and the transmitted beam (Fig. 16-13). For somewhat larger values of ϕ, the ellipse is incomplete because of the finite size of the film. When $\phi = 45°$, the curve becomes a parabola; when ϕ exceeds 45°, a hyperbola; and when $\phi = 90°$, a straight line. In all cases, the curve passes through the central spot formed by the transmitted beam.

The angular relationships involved in the transmission Laue method are illustrated in Fig. 16-14. Here a reference sphere is described about the crystal at *C*, the incident beam entering the sphere at *I* and the transmitted beam leaving at *O*. The

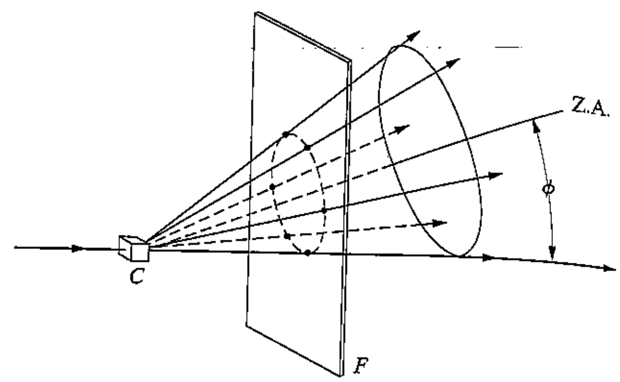


Figure 16-13 Intersection of a conical array of diffracted beams with a film placed in the transmission position. C = crystal, F = film, Z.A. = zone axis.

film is placed tangent to the sphere at O, and its upper right-hand corner, viewed from the crystal, is cut off for identification of its position during the x-ray exposure. The beam diffracted as plane shown strikes the film at R, and the normal to this diffraction plane intersects the sphere at P.

Consider diffraction from planes of a zone whose axis lies in the yz-plane at an angle ϕ to the transmitted (or incident) beam. If a single plane of this zone is

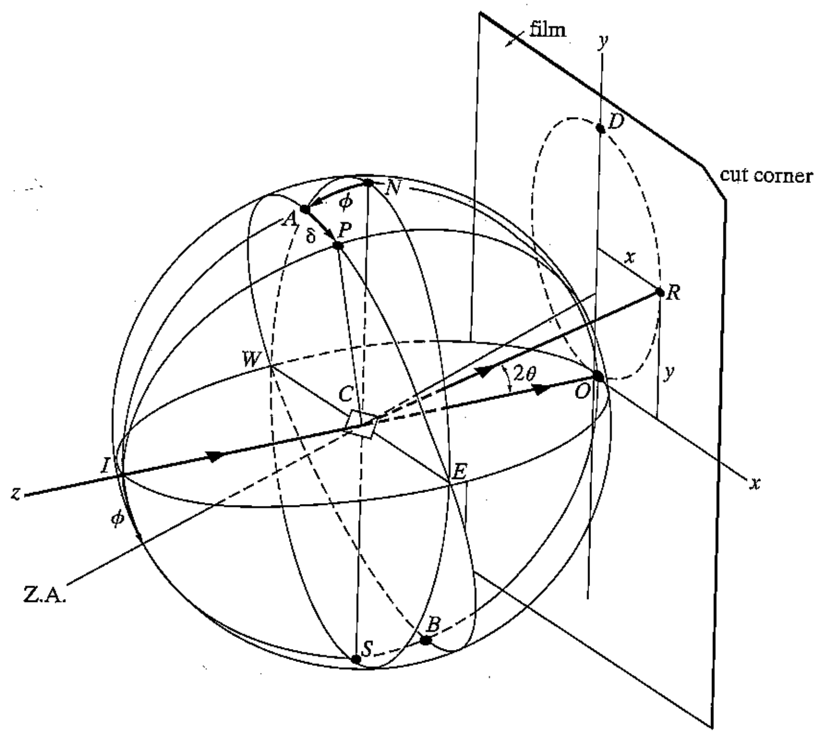


Figure 16-14 Relation between plane normal orientation and diffraction spot position in the transmission Laue method.

rotated so that its pole, initially at A, travels along the great circle $APEBWA$, then it will pass through all the orientations in which planes of this zone might occur in an actual crystal. During this rotation, the diffraction spot on the film, initially at D, would travel along the elliptical path $DROD$ shown by the dashed line.

Any particular orientation of the plane, such as the one shown in the drawing, is characterized by particular values of ϕ and δ, the angular coordinates of its pole. These coordinates in turn, for a given crystal-film distance D (= CO), determine the x,y coordinates of the diffraction spot R on the film. The plane orientation follows from the spot position, and one way of proceeding is by means of the Leonhardt chart shown in Fig. 16-15.

This chart is exactly analogous to the Greninger chart for solving back-reflection patterns and is used in precisely the same way. It consists of a grid composed of two sets of lines: the lines of one set are lines of constant ϕ and correspond to the

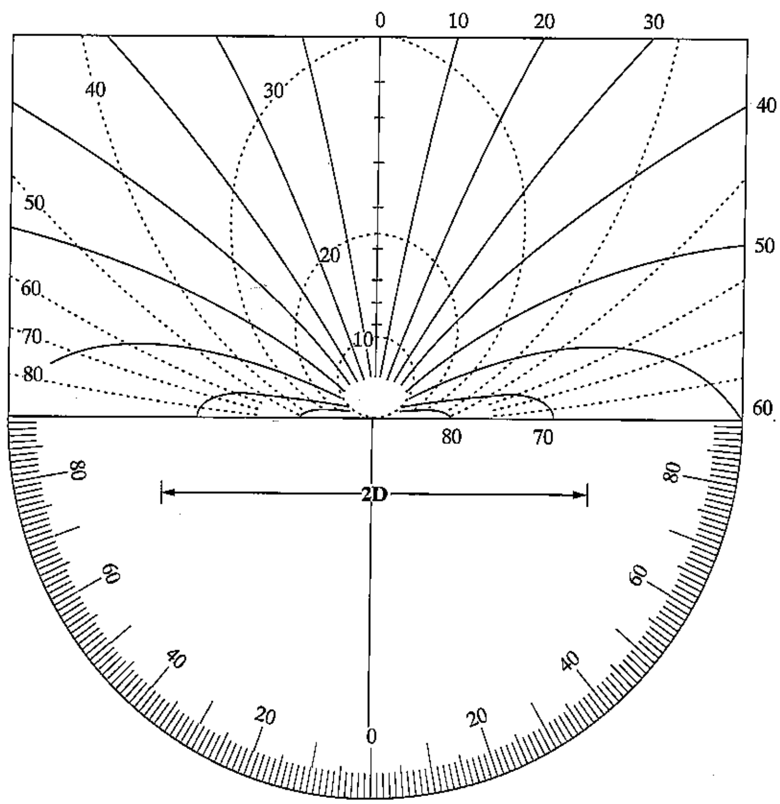


Figure 16-15 Leonhardt chart for the solution of transmission Laue patterns, reproduced in the correct size for a specimen-to-film distance of 3 cm. The dashed lines are lines of constant ϕ, and the solid lines are lines of constant δ. (Courtesy of C. G. Dunn [16.3].)

meridians on a Wulff net, and the lines of the other are lines of constant δ and correspond to latitude lines. By means of this chart, the pole of a plane causing any particular diffraction spot may be plotted stereographically. The projection plane is tangent to the sphere at the point I of Fig. 16-14, and the projection is made from the point O. This requires that the film be read from the side facing the crystal, i.e., with the cut corner at the upper right. Figure 16-16 shows how the pole corresponding to a particular spot is plotted when the film and chart are in the parallel position. An alternate way of using the chart is to rotate it about its center until a line of constant ϕ coincides with a row of spots from planes of a single zone, as shown in Fig. 16-17; knowing ϕ and the rotation angle ε, allows the axis of the zone to be plotted directly.

A stereographic ruler may be constructed for the transmission method and will give greater plotting accuracy than the Leonhardt chart, particularly when the angle ϕ approaches 90°. Figure 16-18, which is a section through the incident beam and any diffracted beam, shows that the distance of the diffraction spot from the center of the film is given by

$$OS = D \tan 2\theta. \tag{16-7}$$

The distance of the pole of the diffraction plane from the center of the projection is given by

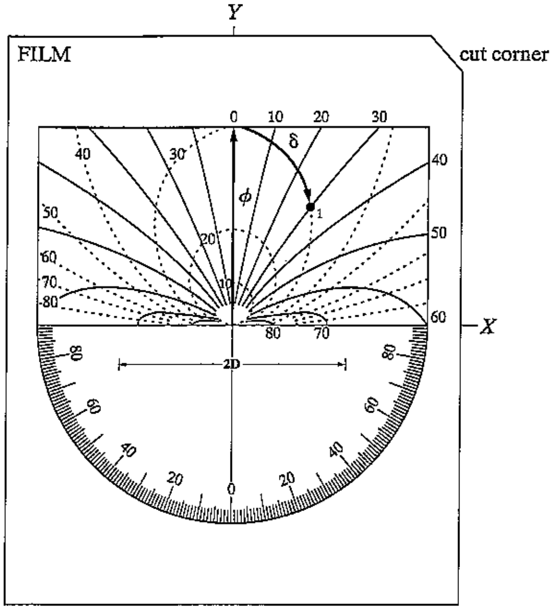
$$PQ = R \tan\left(45^\circ - \frac{\theta}{2}\right). \tag{16-8}$$

Figure 16-19 illustrates the use of a ruler constructed according to these equations. In this case, the projection is made on a plane located on the same side of the crystal as the film and, accordingly, the film must be read with its cut corner in the upper left-hand position.

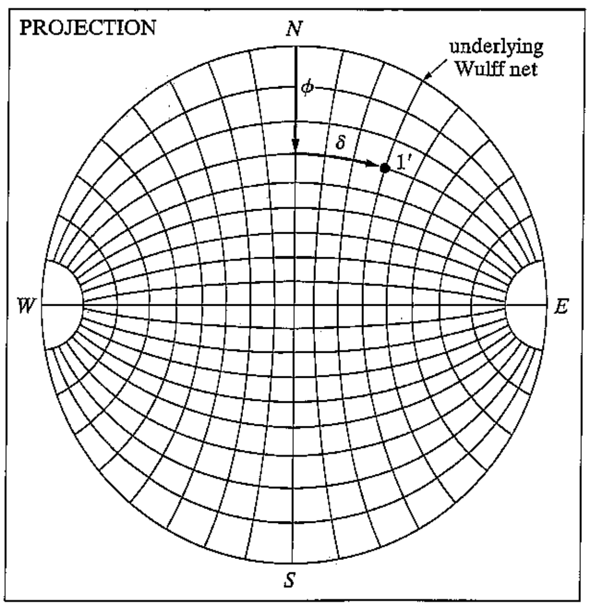
Whether the chart or the ruler is used to plot the poles of diffraction planes, they are indexed in the same way as back-reflection patterns. The location of the projected poles is quite different for the two x-ray methods. The poles of planes responsible for observed spots on a transmission film are all located near the edge of the projection, since such planes must necessarily be inclined at small angles to the incident beam. The reverse is true of back reflection patterns.

16-4 DIFFRACTOMETER METHOD

Still another method of determining crystal orientation involves the use of the diffractometer and a procedure radically different from that of either Laue method. With the essentially monochromatic radiation used in the diffractometer, a single crystal will diffract only when its orientation is such that a certain set of diffraction planes is inclined to the incident beam at an angle θ which satisfies Bragg's law for that set of planes and the characteristic radiation employed. But when the detector, fixed in position at the corresponding angle 2θ, discloses that diffraction *is*



(a)



(b)

Figure 16-16 Use of the Leonhardt chart to plot the pole of a plane on a stereographic projection. Pole 1' in (b) is the pole of the plane causing diffraction spot 1 in (a).

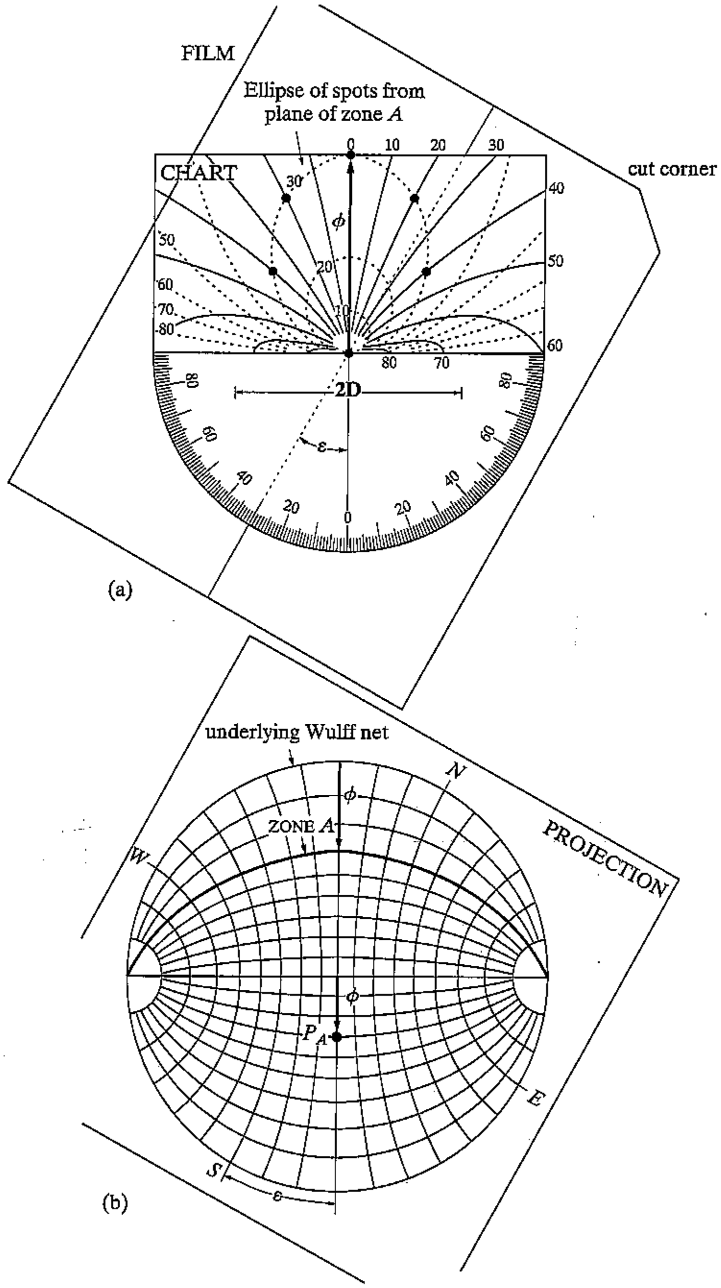


Figure 16-17 Use of the Leonhardt chart to plot the axis of a zone of planes on the projection. P_A is the axis of zone A.

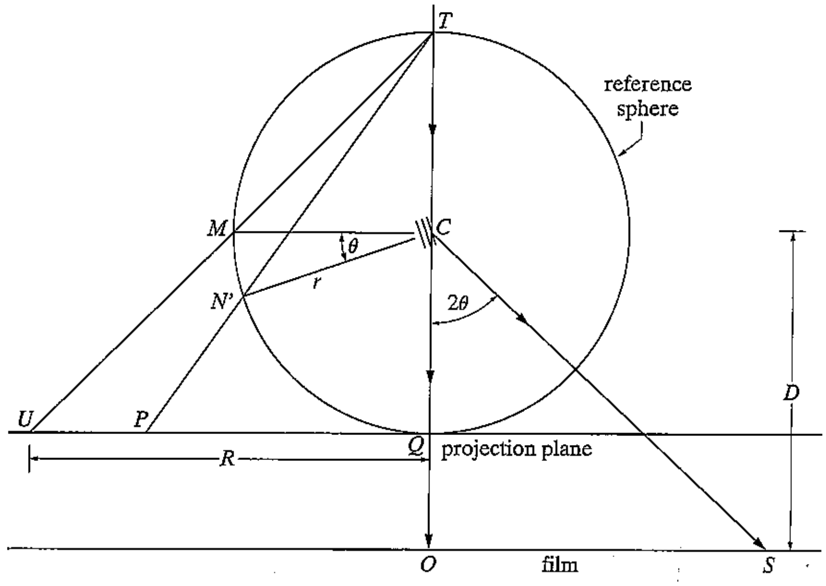


Figure 16-18 Relation between diffraction spot S and stereographic projection P of the plane causing the spot, in transmission.

produced, then the inclination of the diffraction plane relative to any chosen line or plane on the crystal surface is known from the position of the crystal. Two kinds of operation are required:

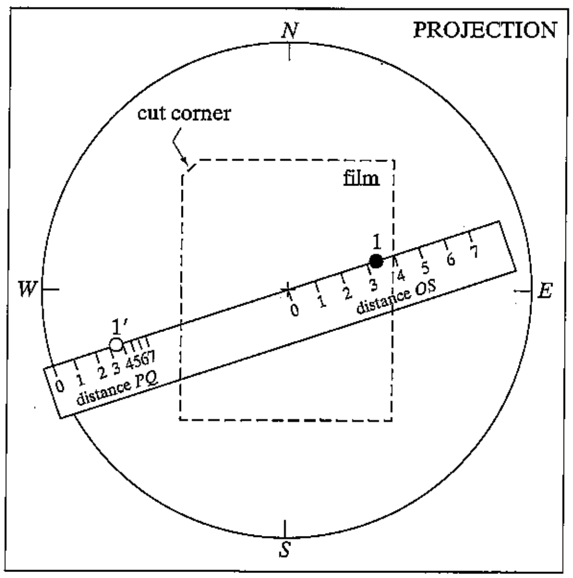


Figure 16-19 Use of a stereographic ruler to plot the pole of a diffracting plane on a stereographic projection in the transmission Laue method. Pole 1' is the pole of the plane causing diffraction spot 1.

ection. P_A is the

1. rotation of the crystal about various axes until an angular position is found for which diffraction occurs.
2. location of the pole of the diffraction plane diffraction on a stereographic projection from the known angles of rotation.

The diffractometer method has many variations, depending on the particular kind of goniometer used to hold and rotate the specimen. Only one of these variations will be described here, that involving the goniometer used in the reflection method of determining preferred orientation, since that is the kind most generally available in materials laboratories. This specimen holder, described in detail in Sec. 14-9, needs very little modification for use with single crystals, the chief one being an increase in the width of the primary beam slits in a direction parallel to the diffractometer axis in order to increase the diffracted intensity. This type of holder provides the three possible rotation axes shown in Fig. 16-20: one coincides with the diffractometer axis, the second (*AA'*) lies in the plane of the incident beam *I* and diffracted beam *D* and tangent to the specimen surface, shown here as a flat plate, while the third (*BB'*) is normal to the specimen surface.

Suppose the orientation of a cubic crystal is to be determined. For such crystals it is convenient to use {111}: there are four sets of these and their diffracting power is usually high. First, the 2θ value for the 111 reflection (or, if desired, the 222 reflection) is computed from the known spacing of the {111} planes and the known wavelength of the radiation used. The detector is then fixed in this 2θ position. The specimen holder is now rotated about the diffractometer axis until its surface, and the rotation axis *AA'*, is equally inclined to the incident beam and the diffracted beam, or rather, to the line from crystal to detector with which the diffracted beam, when formed, will coincide. The specimen holder is then fixed in this position, no further rotation about the diffractometer axis being required. Then, by rotation about the axis *BB'*, one edge of the specimen, or a line drawn on it is made parallel to the diffractometer axis. This is the initial position illustrated in Fig. 16-20.

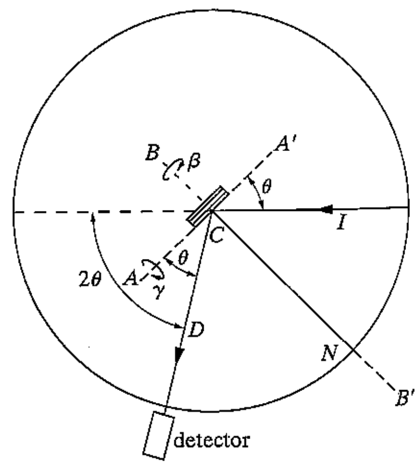


Figure 16-20 Crystal rotation axes for the diffractometer method of determining orientation

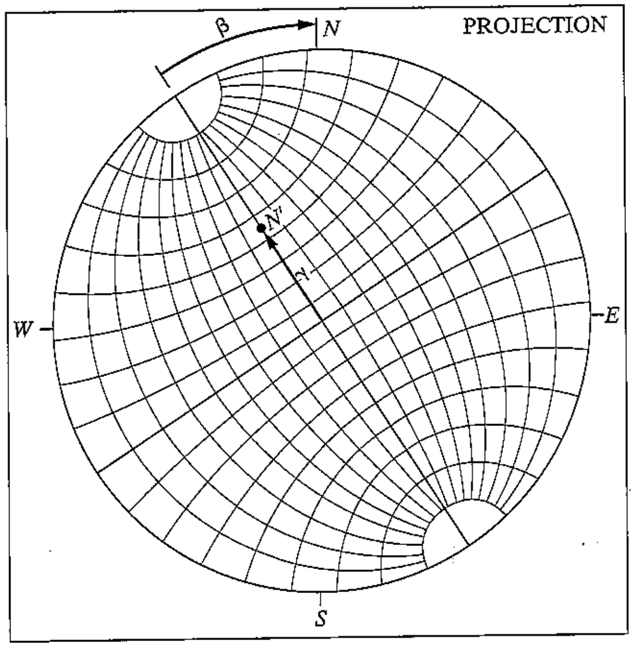


Figure 16-21 Plotting method used when determining crystal orientation with the diffractometer. (The directions of the rotations shown here correspond to the directions of the arrows in Fig.16-20.)

The crystal is then slowly rotated about the axes *AA'* and *BB'* until an indication of a reflection is observed on the rate meter. Computerized diffractometers allow this search to be automated; the computer systematically checks different combinations of notations about axes AA' and BB' until a peak is found, whereupon the search ends and the computer awaits further instructions. The increases in productivity which result from the ability to align crystals while the operator is elsewhere should not be underestimated.

Once the position of the crystal for diffraction has been found, the normal to one set of {111} planes coincides with the line *CN*, that is, lies in the plane of the diffractometer circle and bisects the angle between incident and diffracted beams. The pole of these diffracting planes may now be plotted stereographically, as shown in Fig. 16-21. The projection is made on a plane parallel to the specimen surface, and with the *NS*-axis of the projection parallel to the reference edge or line mentioned above. When the crystal is rotated β degrees about *BB'* from its initial position, the projection is also rotated β degrees about its center. The direction *CN*, which might be called the normal to "potential" diffraction planes, is represented by the pole N', which is initially at the center of the projection but which moves γ degrees along a radius when the crystal is rotated γ degrees about AA'.

The object is to make N' coincide with a {111} pole and so disclose the location of the latter on the projection. The search may be made by varying γ continuously for fixed values of β 4 or 5° apart; the projection is then covered point by point along a series of radii. It is enough to examine one quadrant in this way since there will always be at least one {111} pole in any one quadrant. Once one pole has been located, the search for the second is aided by the knowledge that it must be 70.5° from the first. Although two {111} poles are enough to fix the orientation of the crystal, a third should be located as a check.

Parenthetically, it should be noted that the positioning of the crystal surface and the axis AA' at equal angles to the incident and diffracted beams is done only for convenience in plotting the stereographic projection. There is no question of focusing when monochromatic radiation is diffracted from an undeformed single crystal, and the ideal incident beam for the determination of crystal orientation is a parallel beam, not a divergent one.

In the hands of an experienced operator, the diffractometer method is faster than either Laue method. Furthermore, it can yield results of greater accuracy if narrow slits are used to reduce the divergence of the incident beam, although the use of extramely narrow slits will make it more difficult to locate the diffracting positions of the crystal. On the other hand, the diffractometer method furnishes no permanent record of the orientation determination, whereas Laue patterns may be filed away for future reference. This is true even with most computer automated systems for diffractometer-based crystal orientation. But what is more important, the diffractometer method does not readily disclose the state of perfection of the crystal, whereas a Laue pattern yields this kind of information at a glance (see Sec. 17-2) and in many investigations the relative perfection of a single crystal is of as much interest as its orientation.

All things considered the Laue methods are preferable when only occasional orientation determinations are required, or when there is any doubt about the quality of the crystal. When the orientations of large numbers of crystals have to be determined in a routine manner, the diffractometer method is superior. In fact, this method was developed largely for just such an application during World War II, when the orientation of large numbers of quartz crystals had to be determined. These crystals were used in radio transmitters to control, through their natural frequency of vibration, the frequency of the transmitted signal. For this purpose quartz wafers had to be cut with faces accurately parallel to certain crystallographic planes, and the diffractometer was used to determine the orientations of these planes in the crystal.

16-5 SETTING A CRYSTAL IN A REQUIRED ORIENTATION

After the orientation of a crystal is found by x-rays, it is often necessary to rotate it into some special orientation, such as one with $\langle 100 \rangle$ along the incident beam, for the purpose of either (a) subsequent x-ray examination in the special orientation, or (b) subsequent cutting along some selected plane. To obtain this orientation, the crystal is mounted in a three-circle goniometer like that shown in Fig. 8-7, whose arcs have been set at zero, and its orientation is determined by, for example, the back-reflection Laue method. A projection of the crystal is then made, and from this projection the goniometer rotations which will bring the crystal into the required orientation are determined.

For example, suppose it is required to rotate the crystal whose orientation is given by Fig. 16-7 into a position where [011] points along the incident beam and [100] points horizontally to the left, i.e., into the standard (011) orientation shown by Fig. 2-39(b) if the latter were rotated 90° about the center. The initial orientation (Position 1) is shown in Fig. 16-22 by the open symbols, referred to *NSEW*-axes. Since (011) is to be brought to the center of the projection and (100) to the left side, (010) will lie on the vertical axis of the projection when the crystal is in its final position. The first step therefore is to locate a point 90° away from (011) on the great circle joining (010) to (011), because this point must coincide with the north pole of the final projection. This is simply a construction point; in the present case it happens to coincide with the (0$\bar{1}$1) pole, but generally it is of no crystallographic significance. The projection is then rotated 22° clockwise about the incident-beam axis to bring this point onto the vertical axis of the underlying Wulff net. (In Fig. 16-22, the latitude and longitude lines of this net have been omitted for clarity.) The crystal is now in Position 2, shown by open symbols referred to *N′S′E′W′*-axes. The next

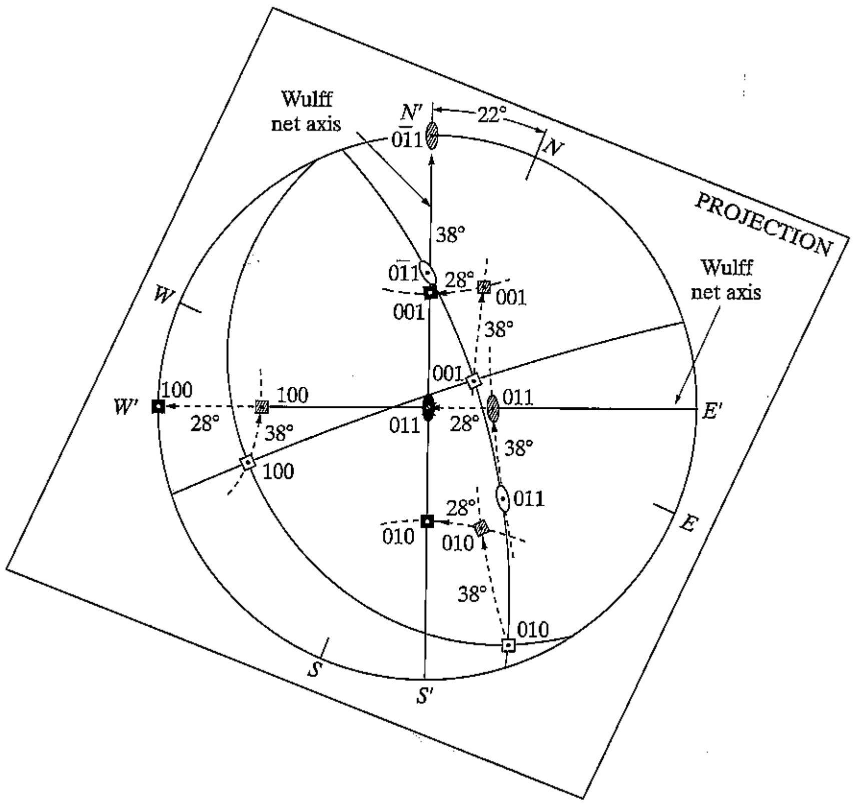


Figure 16-22 Crystal rotation to produce specified orientation. Position 1 is shown in Fig 16-7, position 2 is indicated by open symbols, position 3 by shaded symbols, and position 4 by solid symbols.

rotation is performed about the $E'W'$-axis, which requires that the underlying Wulff net be arranged with its equator vertical so that the latitude lines will run from top to bottom. This rotation, of 38°, moves all poles along latitude lines, shown as dashed small circles, and brings $(0\bar{1}1)$ to the N'-pole, and (100) and (011) to the $E'W'$-axis of the projection, as indicated by the shaded symbols (Position 3). The final orientation is obtained by a 28° rotation about the $N'S'$-axis, with the equator of the underlying Wulff net now horizontal; the poles move to the positions shown by solid symbols (Position 4).

The necessity for selecting a construction point 90° from (011) should now be evident. If this point, which here happens to be $(0\bar{1}1)$, is brought to the N'-pole, then (011) and (100) must of necessity lie on the $E'W'$-axis; the final rotation about $N'S'$ will then move the latter to their required positions without disturbing the position of the $(0\bar{1}1)$ pole, since $(0\bar{1}1)$ coincides with the $N'S'$-axis.

The order of these three rotations is not arbitrary. The sterographic rotations correspond to physical rotations on the goniometer and must be made in such a way that one rotation does not physically alter the position of any axis about which a subsequent rotation is to be made. The goniometer used here was initially set with the axis of its uppermost arc horizontal and coincident with the primary beam, and with the axis of the next arc horizontal and at right angles to the incident beam. The first rotation about the beam axis therefore did not disturb the position of the second axis (the $E'W'$-axis), and neither of the first two rotations disturbed the position of the third axis (the vertical $N'S'$-axis). Whether or not the stereographic orientations are performed in the correct order makes a great difference in the rotation angles found, but once the right angles are determined by the correct stereographic procedure, the actual physical rotations on the goniometer may be performed in any sequence.

The back-reflection Laue pattern of an aluminum crystal rotated into the orientation described above is shown in Fig. 16-23. Note that the arrangement of spots has 2-fold rotational symmetry about the primary beam, corresponding to the 2-fold rotational symmetry of cubic crystals about their $\langle 110 \rangle$ axes. (Conversely, the observed symmetry of the Laue pattern of a crystal of unknown structure is an indication of the kind of symmetry possessed by that crystal. Thus the Laue method can be used as an aid in the determination of crystal structure.)

The crystal-setting procedure illustrated in Fig. 16-22 can be carried out whether or not the indices of the various poles are known. If the Laue pattern of a crystal is difficult to solve, any spot on it can be indexed by using a Laue camera and a diffractometer in sequence [16.4]. In addition, a goniometer is required that fits both instruments. The procedure is as follows:

1. Make a Laue pattern and a stereographic projections of the poles corresponding to a few important spots.
2. By the procedure of Fig. 16-22, rotate the pole to be indexed to the center of the projection. The corresponding rotation on the goniometer will make the unknown plane (*hkl*) normal to the incident beam of the Laue camera.

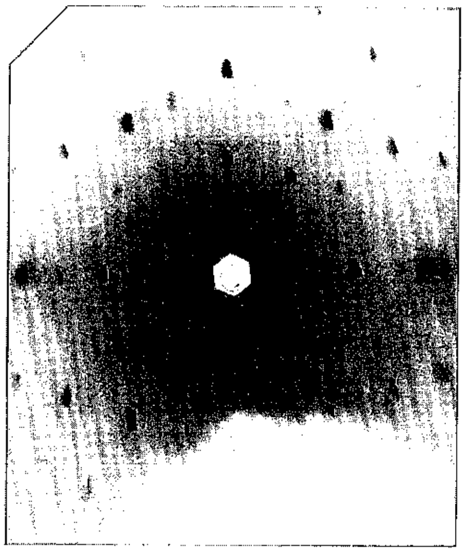


Figure 16-23 Back-reflection Laue pattern of an aluminum crystal. The incident beam is parallel to [011], points vertically upward, and [100] points horizontally to the left. Tungsten radiation, 30 kV, 19 mA, 40 min exposure, 5 cm specimen-to-film distance. (The light shadow at the bottom is that of the goniometer which holds the specimen.)

3. Transfer the goniometer and crystal to the diffractometer, in such a way that the *(hkl)* plane normal bisects the angle between the incident and (potential) diffracted beams.
4. Make a diffractometer scan to find the angle 2θ at which diffraction occurs from the *(hkl)* planes. [Higher-order reflections may also be observed, i.e., diffraction from *(nh nk nl)* planes.]
5. Calculate the spacing d of the *(hkl)* planes from 2θ and the known value of λ.
6. From this value of d determine *(hkl)* by calculation from the known crystal structure or by examining a list of known d spacings for the substance involved (Sec. 9-3).

There is another method of setting a crystal in a standard orientation, which does not require either photographic registration of the diffraction pattern or stereographic manipulation of the data. This involves real-time observation of the Laue pattern: the diffracted beams formed in the transmission Laue method are so intense, for a crystal of the proper thickness that the spots they form on a fluorescent screen are readily visible in a dark room. The observer merely rotates the crystal about the various arcs of the goniometer until the pattern corresponding to the required orientation appears on the screen. Obviously, this pattern must be recognized when it appears, but a little study of a few Laue photographs made of crystals in standard orientations provides enough experience.

Various area detectors are available (see below) and would be employed if the job of crystal setting occurs frequently enough to justify the expense. An alternative is the construction of a light-and x-ray-tight viewing box. This box encloses the fluorescent screen which the observer views through a binocular eyepiece set in the wall of the box, either directly along the direction of the transmitted beam, or indirectly in a direction at right angles by means of a mirror or a right-angle prism. For x-ray protection, the optical system should include lead glass, and the observer's hands should be shielded during manipulation of the crystal if the goniometer axes cannot be controlled remotely. Direct manipulation of the goniometer head is very undesirable while the x-ray tube is energized (even if "reliable" shutters are closed during manipulation): there is too great a risk of operator carelessness. Even without motorized axes controlled outside the radiation enclosure, flexible cables can be attached to the knobs of the goniometer allowing remote rotation.

More elaborate apparatus permits electronic amplification of transmission Laue spots formed on a fluorescent screen. An image of the spot pattern on the screen can be projected by a lens on to the front (input) face of an image-intensifier tube. The intensified image appears on the rear (output) face of the tube and is bright enough to be observed directly or photographed in 1/220 second [16.5-16.7]. This large gain in image intensity permits photography, by a motion picture or television camera, of rapid changes in a Laue pattern caused, for example, by a phase change in the crystal. (The image-intensifier tube has also made it possible to obtain a transmission Laue photograph with a single 30-nanosecond pulse from a high-power pulsed x-ray tube [16.8].) Multiple wire area detectors can be used to record Laue patterns as can charge-coupled-device (CCD) detectors coupled to fluorescent screens; an additional advantage of these systems is that the data is recorded in digital form, ready for further analysis on a computer.

PROBLEMS

***16-1** A back-reflection Laue photograph is made of an aluminum crystal with a crystal- to-film distance of 3 cm. When viewed from the x-ray source, the Laue spots have the following *x, y* coordinates, measured (in inches) from the center of the film, see table at the top of the next page. Plot these spots on a sheet of graph paper graduated in inches. By means of a Greninger chart, determine the orientation of the crystal, plot all poles of the form {100}, {110}, and {111}, and give the coordinates of the {100} poles in terms of latitude and longitude measured from the center of the projection.

16-2 A transmission Laue photograph is made of an aluminum crystal with a crystal-to-film distance of 5 cm. To an observer looking through the film toward the x-ray source, the spots have the following *x, y* coordinates (in inches):

x	y	x	y
+0.26	+0.09	−0.44	+1.24
+0.45	+0.70	−1.10	+1.80
+1.25	+1.80	−1.21	+0.40
+1.32	+0.40	−1.70	+1.19
+0.13	−1.61	−0.76	−1.41
+0.28	−1.21	−0.79	−0.95
+0.51	−0.69	−0.92	−0.26
+0.74	−0.31		

x	y	x	y
+0.66	+0.88	−0.10	+0.79
+0.94	+2.44	−0.45	+2.35
+1.24	+0.64	−0.77	+1.89
+1.36	+0.05	−0.90	+1.00
+1.39	+1.10	−1.27	+0.50
+0.89	−1.62	−1.75	+1.55
+1.02	−0.95	−1.95	+0.80
+1.66	−1.10	−0.21	−0.58
		−0.59	−0.28
		−0.85	−1.31
		−1.40	−1.03
		−1.55	−0.36

Proceed as in Prob. 16-1, but use a stereographic ruler to plot the poles of diffraction planes.

***16-3** Determine the necessary angular rotations about (a) the incident beam axis, (b) the east-west axis, and (c) the north-south axis to bring the crystal of Prob. 16-2 into the "cube orientation," i.e., that shown by Fig. 2-39 (a).