6

THE LAUE METHOD

The Laue method is the oldest of the x-ray diffraction methods. A collimated beam of continuous spectrum falls upon a fixed single crystal. For each set of planes *hkl*, the spacing $d(hkl)$ and the Bragg angle $\theta(hkl)$ are fixed. A reflected beam will be produced if the correct wavelength which satisfies the Bragg law is contained in the continuous spectrum. The different reflected beams have different wavelengths and hence a Laue pattern is "colored." Since the intensity of the continuous spectrum increases with the target atomic number Z, it is preferable to use a tungsten target tube, but the unfiltered radiation from a copper target tube running at, say, 35 kv is often used for Laue patterns.

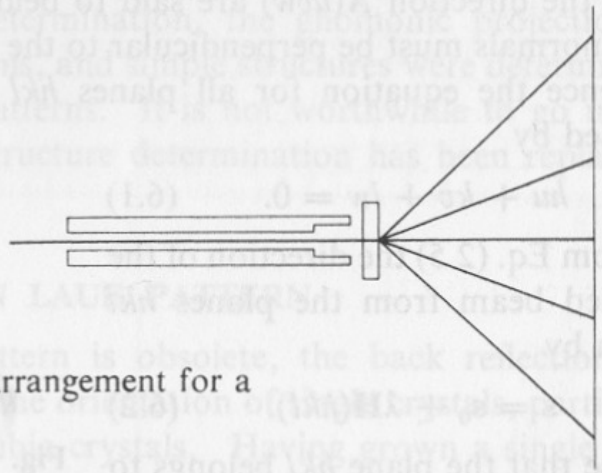

Fig. 6.1 The experimental arrangement for a transmission Laue pattern.

6.1 THE TRANSMISSION LAUE PATTERN

The experimental arrangement for a transmission Laue pattern is illustrated by Fig. 6.1. The collimated continuous spectrum passes through a thin slip of single crystal. The diffracted beams are registered on a film placed perpendicular to the primary beam at a distance of, say, 5 cm from the crystal. If the crystal is symmetrically oriented with respect to the primary beam, the Laue pattern may show a very high symmetry. Figure 6.2 shows the transmission Laue pattern of Quartz taken with the primary beam parallel to the *c*-axis. The 3-fold symmetry of the crystal is readily seen in the Laue pattern.

It is evident that the diffraction spots of Fig. 6.2 fall on sets of ellipses which pass through the central spot. This is true whether or not the crystal has a symmetrical orientation. All spots falling on an ellipse are due to

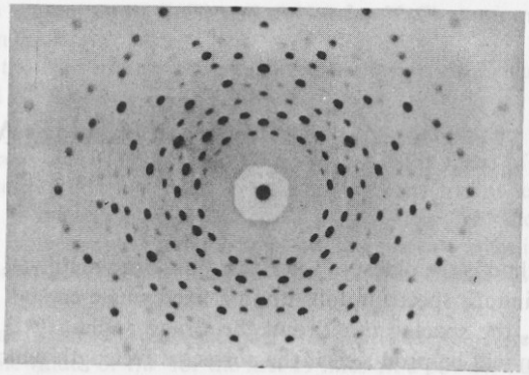

Fig. 6.2 Transmission Laue pattern of Quartz, made with the primary beam parallel to the hexagonal *c*-axis, and *D*-5.0 cm. This reproduction is half size.

planes *hkl* which belong to a particular zone *uvw*. We define a zone axis $\mathbf{A}(uvw) = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$, where *uvw* are integers. All planes *hkl* containing the direction $\mathbf{A}(uvw)$ are said to belong to the zone *uvw*. Since the planar normals must be perpendicular to the zone axis, $\mathbf{H}(hkl) \cdot \mathbf{A}(uvw) = 0$ and hence the equation for all planes *hkl* belonging to the zone *uvw* is expressed by

$$hu + kv + lw = 0. \qquad (6.1)$$

From Eq. (2.5) the direction of the diffracted beam from the planes *hkl* is given by

$$\mathbf{s} = \mathbf{s}_0 + \lambda\mathbf{H}(hkl). \qquad (6.2)$$

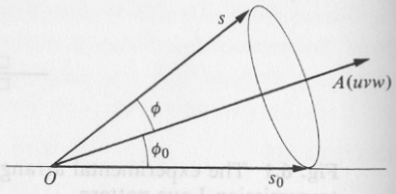

Fig. 6.3 The cone with axis $\mathbf{A}(uvw)$ whose surface contains the directions of all reflected beams *hkl* which belong to the zone *uvw*.

Suppose that the plane *hkl* belongs to the zone *uvw*. Forming the scalar product with $\mathbf{A}(uvw)$ on both sides of Eq. (6.2), we obtain

$$\mathbf{s} \cdot \mathbf{A}(uvw) = \mathbf{s}_0 \cdot \mathbf{A}(uvw) + \lambda\mathbf{H}(hkl) \cdot \mathbf{A}(uvw).$$

But since $\mathbf{H}(hkl) \cdot \mathbf{A}(uvw) = 0$ for all planes *hkl* belonging to the zone *uvw*, we obtain $\phi = \phi_0$, where ϕ_0 is the angle between the primary beam and the zone axis $\mathbf{A}(uvw)$, and ϕ is the angle between $\mathbf{A}(uvw)$ and the reflected beam from any plane *hkl* belonging to the zone *uvw*. As illustrated by Fig. 6.3, the reflected beams for all planes belonging to the zone *uvw* form the elements of a cone which contains the primary beam as one element and has the zone axis $\mathbf{A}(uvw)$ as the cone axis. The intersection of this cone with a film normal to the primary beam gives the ellipses observed on a transmission Laue pattern.

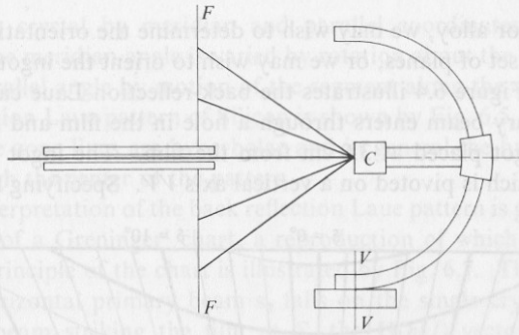

Fig. 6.4 Schematic representation of the back reflection Laue camera.

The positions of the diffraction spots give the directions of the various diffracted beams, and the corresponding planar normals $\mathbf{H}(hkl)$ are readily constructed. The intersections of these planar normals with the plane of the film gives the gnomonic projection of the Laue pattern. This gnomonic projection is readily interpreted as a projection of the reciprocal lattice. In the early days of structure determination, the gnomonic projection was much used to index Laue patterns, and simple structures were determined by means of transmission Laue patterns. It is not worthwhile to go into the details, since this method of structure determination has been replaced by other more powerful methods.

6.2 THE BACK REFLECTION LAUE PATTERN

Although the transmission pattern is obsolete, the back reflection Laue pattern is much used today for the orientation of single crystals, particularly for the orientation of single cubic crystals. Having grown a single crystal

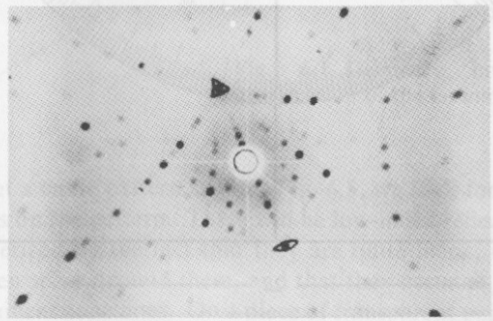

Fig. 6.5 Back reflection Laue pattern of Silicon, as seen from the sample $D = 3.0$ cm.

ingot of a metal or alloy, we may wish to determine the orientation of some principal axis or set of planes, or we may wish to orient the ingot for cutting a desired face. Figure 6.4 illustrates the back-reflection Laue camera. The collimated primary beam enters through a hole in the film and falls on the single crystal ingot placed at 3.0 cm from the film. The ingot mount is a vertical circle which is pivoted on a vertical axis VV. Specifying the orientation of the crystal by meridian and parallel coordinates (longitude and latitude), the meridian angle is varied by rotation about the vertical axis VV, and the parallel angle by motion of the segment along the vertical circle. A back-reflection Laue pattern of Silicon is shown by Fig. 6.5. For this type of pattern, the zone lines are hyperbolae and in general the hyperbolae do not pass through the center of the pattern.

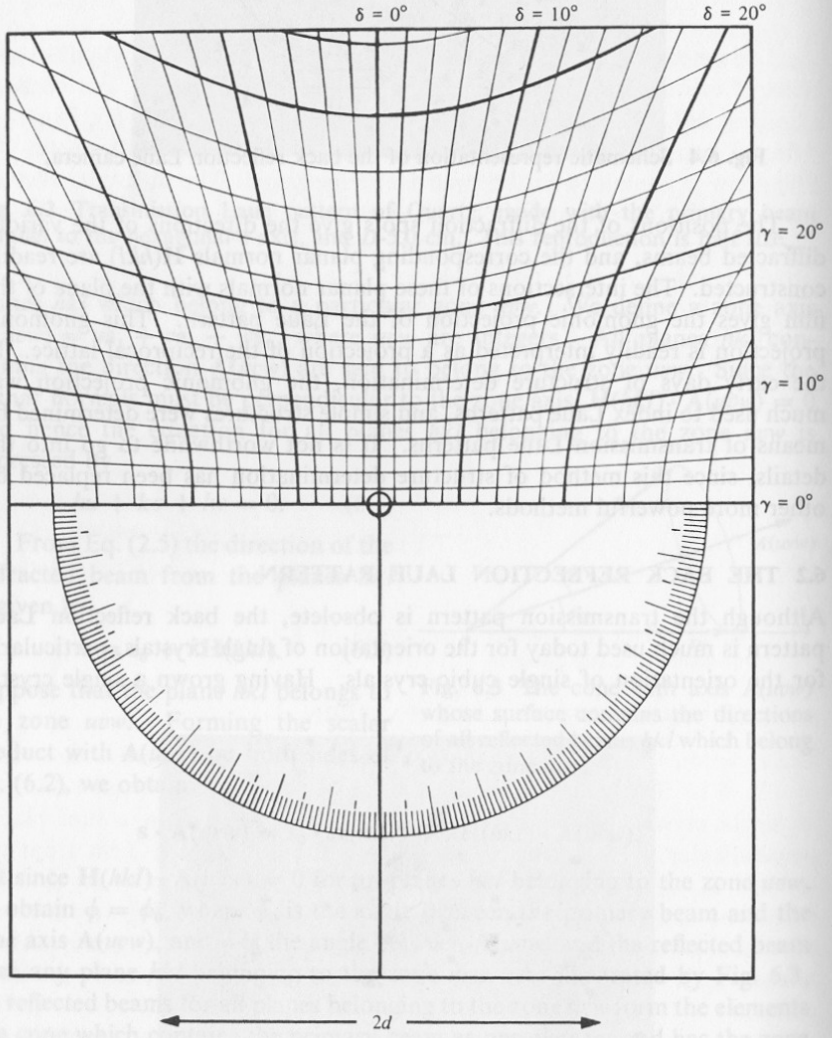

Fig. 6.6 Greninger chart for the solution of back reflection Laue patterns, reproduced in the correct size for a specimen to film distance D of 3.00 cm. Lines of constant meridian are horizontal, and lines of constant parallel are vertical; the intervals are 2°.

The interpretation of the back reflection Laue pattern is greatly facilitated by the use of a Greninger[1] chart, a reproduction of which is given by Fig. 6.6. The principle of the chart is illustrated by Fig. 6.7. The film is vertical and the horizontal primary beam $\mathbf{s}_0$ falls on the single crystal C. For the diffracted beam striking the film at S, the $\mathbf{H}(hkl)$ vector normal to the diffracting planes bisects the angle between $\mathbf{s}$ and $-\mathbf{s}_0$. The intersection at point H on the film is the gnomonic projection of the planes hkl producing the spot S. We now label position S with the meridian and parallel coordinates *of point H*. If this is done for a large number of points S, we can draw curves of constant meridian and constant parallel. On the Greninger net, the North-South axis is taken horizontal, so that the horizontal curves are lines of constant meridian (longitude) and the vertical curves are lines of constant parallel (latitude). In terms of this net, the position of any diffraction spot S gives the meridian and parallel coordinates of the *corresponding planar normal H*.

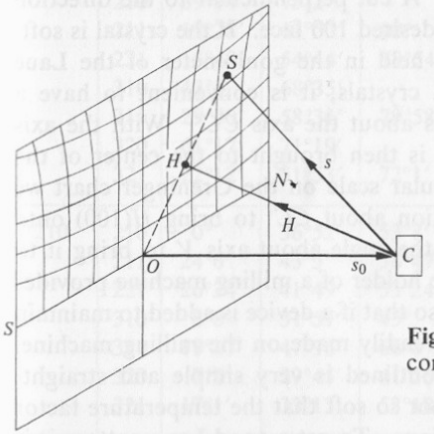

Fig. 6.7 Geometry involved in the construction of the Greninger chart.

To interpret a cubic pattern such as Fig. 6.5, we look for the three most important spots on the pattern. These will be low-index reflections, and they will be characterized by the fact that they are quite black, that there is an appreciable open space around them, and that they occur at the intersection of several prominent zone lines. On a piece of transparent paper we mark the three important spots, trace the three connecting zone lines, and indicate the center of the pattern as well as the vertical and horizontal directions. With a 9 cm × 12 cm film and the standard crystal to film distance D = 3.0 cm,

the pattern of a cubic crystal will always contain at least one of the three important reflections 100, 110, or 111. Since multiple orders superimpose on a Laue pattern, when we speak of the reflection 100 we mean the superposition of 100, 200, 300, 400, etc. Keeping the center of the tracing on the center of the Greninger chart, and rotating to bring two of the important reflection spots on a line of constant meridian, the difference in parallel readings gives directly the angle between the two planar normals H. Repeating for the other two pairs of diffraction spots, we obtain the three angles between the three planar normals $\mathbf{H}(hkl)$. The hkl-indices of the three principal spots are then readily obtained from Table 6.1, which gives the angles between planar normals in a cubic crystal. The angles can be read from the chart to better than 0.5° and in general two of the measured angles will suffice to index all three planes, with the third measured angle serving as a check.

Suppose that we wish to cut a 100 face. If 100 was not among the three reflections indexed, we can change the orientation of the crystal and make another pattern on which the 100 reflection appears. With the Greninger Chart we then measure the meridian and parallel coordinates of $H(100)$. In doing this we rotate the chart 90° so that the meridian and parallel coordinates of the chart correspond to the meridian and parallel scales of the Laue camera. The settings of the Laue camera are then changed to bring $H(100)$ parallel to the primary beam. A cut perpendicular to the direction of the primary beam will produce the desired 100 face. If the crystal is soft, the cut may be made with the ingot held in the goniometer of the Laue camera. To be able to handle hard crystals, it is convenient to have a graduated circle which reads rotations about the axis CC'. With the axis CC' horizontal, the $H(100)$ direction is then brought to the center of the diagram in two steps. From the circular scale on the Greninger chart we read off the angle necessary for rotation about CC' to bring $H(100)$ onto the equator of the diagram, and then the angle about axis V to bring it to the center of the diagram. The sample holder of a milling machine provides directly the rotation about the axis V, so that if a device is added to maintain the orientation about CC', the cut is readily made on the milling machine.

The procedure which has been outlined is very simple and straightforward for cubic crystals which are not so soft that the temperature factor $\exp(-2M)$ kills the high-angle reflections. To get a good Laue pattern it is generally necessary to clean and etch that part of the surface of the ingot which is being studied. Except for materials whose fluorescence radiation will be absorbed in the air, it is advisible to cover the film with a thin aluminum sheet. For crystals of lower than cubic symmetry, orientations are usually best found by making a series of Laue patterns with regular variations in the orientation of the sample. Symmetry in the pattern can usually be recognized even when the sample is still several degrees from a simple setting.

Table 6.1

ANGLES BETWEEN PLANAR NORMALS IN THE CUBIC SYSTEM*

100	100	0°	90°					
	110	45°	90°					
	111	54°44′						
	210	26°34′	63°26′	90°				
	211	35°16′	65°54′					
	221	48°11′	70°32′					
	310	18°26′	71°34′	90°				
	311	25°14′	72°27′					
	320	33°41′	56°19′	90°				
	321	36°43′	57°42′	74°30′				
110	110	0°	60°	90°				
	111	35°16′	90°					
	210	18°26′	50°46′	71°34′				
	211	30°	54°44′	73°13′	90°			
	221	19°28′	45°	76°22′	90°			
	310	26°34′	47°52′	63°26′	77°5′			
	311	31°29′	64°46′	90°				
	320	11°19′	53°58′	66°54′	78°41′			
	321	19°6′	40°54′	55°28′	67°48′	79°6′		
111	111	0°	70°32′					
	210	39°14′	75°2′					
	211	19°28′	61°52′	90°				
	221	15°48′	54°44′	78°54′				
	310	43°5′	68°35′					
	311	29°30′	58°31′	79°58′				
	320	61°17′	71°19′					
	321	22°12′	51°53′	72°1′	90°			
210	210	0°	36°52′	53°8′	66°25′	78°28′	90°	
	211	24°6′	43°5′	56°47′	79°29′	90°		
	221	26°34′	41°49′	53°24′	63°26′	72°39′	90°	
	310	8°8′	31°57′	45°	64°54′	73°34′	81°52′	
	311	19°17′	47°36′	66°8′	82°15′			
	320	7°7′	29°45′	41°55′	60°15′	68°9′	75°38′	82°53′
	321	17°1′	33°13′	53°18′	61°26′	70°13′	83°8′	90°
211	211	0°	33°33′	48°11′	60°	70°32′	80°24′	
	221	17°43′	35°16′	47°7′	65°54′	74°12′	82°12′	
	310	25°21′	49°48′	58°55′	75°2′	82°35′		
	311	10°2′	42°24′	60°30′	75°45′	90°		
	320	25°9′	37°37′	55°33′	63°5′	83°30′		
	321	10°54′	29°12′	40°12′	49°6′	56°56′		
		70°54′	77°24′	83°44′	90°			

(continued)

Table 6.1 (*continued*)

221	221	0°	27°16′	38°57′	63°37′	83°37′	90°	
	310	32°31′	42°27′	58°12′	65°4′	83°57′		
	311	25°14′	45°17′	59°50′	72°27′	84°14′		
	320	22°24′	42°18′	49°40′	68°18′	79°21′	84°42′	
	321	11°29′	27°1′	36°42′	57°41′	63°33′	74°30′	
		79°44′	84°53′					
310	310	0°	25°51′	36°52′	53°8′	72°33′	84°16′	
	311	17°33′	40°17′	55°6′	67°35′	79°1′	90°	
	320	15°15′	37°52′	52°8′	74°45′	84°58′		
	321	21°37′	32°19′	40°29′	47°28′	53°44′	59°32′	
		65°	75°19′	85°9′	90°			
311	311	0°	35°6′	50°29′	62°58′	84°47′		
	320	23°6′	41°11′	54°10′	65°17′	75°28′	85°12′	
	321	14°46′	36°19′	49°52′	61°5′	71°12′	80°44′	
320	320	0°	22°37′	46°11′	62°31′	67°23′	72°5′	90°
	321	15°30′	27°11′	35°23′	48°9′	53°37′	58°45′	63°36′
		72°45′	77°9′	85°45′	90°			
321	321	0°	21°47′	31°	38°13′	44°25′	50°	60°
		64°37′	69°4′	73°24′	81°47′	85°54′		

* From R. M. Bozorth, *Phys. Rev.* **26,** 390 (1925).

The sphere of reflection construction for the back-reflection Laue pattern is shown by Fig. 6.8. The direction of the primary beam is represented by the vector s_0/λ whose terminal point is at O, the origin of the reciprocal lattice. For each wavelength in the beam there is a sphere of radius $1/\lambda$. The largest sphere has a radius $1/\lambda_{SWL}$, where λ_{SWL} is the short wave limit of the continuous spectrum. The smallest sphere has a radius $1/\lambda_M$, where λ_M is the somewhat indefinite longest wavelength which is not drastically absorbed before reaching the film. For convenience assume that the film is a disk of radius R. The maximum value of the angle $2\phi = 180 - 2\theta$ for reflections which can be recorded on the film is given by

$$\tan 2\phi_m = R/D.$$

All reflections appearing on the Laue pattern are then represented by the reciprocal lattice points in the volume which is shown on Fig. 6.8 by the section $ABCDE$, where the sphere OAE has the radius $1/\lambda_M$ and the sphere $OBCD$ has the radius $1/\lambda_{SLW}$. This volume divided by v_b, the volume per

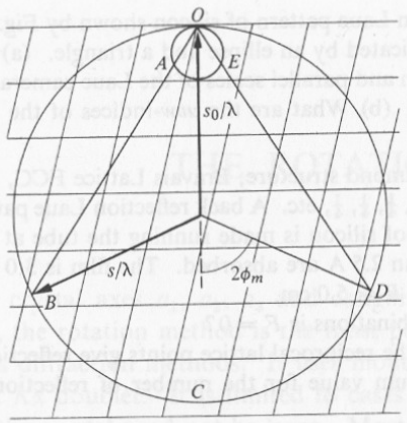

Fig. 6.8 Sphere of reflection construction for the back reflection Laue pattern.

point in reciprocal space, gives the maximum number of reflections which can appear on the Laue pattern:

$$n = \frac{4\pi}{3v_b} \sin^2 \phi_m (1 + \cos^2 \phi_m) \left(\frac{1}{\lambda^3_{SWL}} - \frac{1}{\lambda^3_M} \right). \tag{6.3}$$

The number of spots which will be observed on the Laue pattern may be much smaller than this computed n since the structure factor may be small or zero for many of the reciprocal lattice points, and some of the allowed reflections will be multiple orders which superimpose as a single diffraction spot.

REFERENCES

1. A. B. GRENINGER, *Zeit. für Krist.* **A91,** 424 (1935).

PROBLEMS

6.1 The transmission Laue pattern of quartz shown by Fig. 6.2 was made with the x-ray beam parallel to c and a distance $D = 5.0$ cm. The closest spots are at $s = 17$ mm from the center of the pattern. For quartz, $a = 4.90$ A and $c = 5.39$ A. Applying the third Laue equation, compute an approximate value for the voltage on the x-ray tube.

6.2 Suppose that the transmission Laue pattern of quartz shown by Fig. 6.2 had been recorded on a disk-shaped film of radius $R = 6.0$ cm, with the tube running at 45 kv. For quartz, $a = 4.90$ A, $c = 5.39$ A. The distance $D = 5.0$ cm. By a sphere of reflection construction analogous to that of Fig. 6.8, compute an upper limit to the number of reflections which could appear on the Laue pattern.

6.3 The back reflection Laue pattern of silicon shown by Fig. 6.5 contains the 110 and 111 reflections indicated by an ellipse and a triangle. (a) What should be the changes in the meridian and parallel scales of the Laue camera to bring 110 parallel to the primary beam? (b) What are the *uvw*-indices of the zone line connecting 110 and 111?

6.4 Silicon has the diamond structure, Bravais Lattice FCC, $a = 5.43$ A, 8 atoms per cell, positions 0 0 0, $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, etc. A back reflection Laue pattern of an arbitrarily oriented single crystal of silicon is made running the tube at 35 kv. Assume that wavelengths longer than 2.5 A are absorbed. The film is 3.0 cm from the crystal and is a disk of radius $R = 5.0$ cm.

a) For what *hkl* combinations is $F = 0$?
b) What fraction of the reciprocal lattice points give reflections?
c) What is a maximum value for the number of reflection spots on the Laue pattern?
d) Compare with Fig. 6.5.

6.5 Germanium has the diamond structure FCC, $a = 5.66$ A. A back-reflection Laue pattern is made with the tube operating at 25 kv and a crystal to film distance $D = 3.0$ cm.

a) For what classes of reflections *hkl* is $F = 0$?
b) If the $n(100)$ reflection (multiples of 100) is near the center of the pattern, what is approximately the distance from this spot to the nearest spot on the film?
c) Suppose the orientation of the crystal is such that both the $n(100)$ and $n(110)$ reflections are on the film and the midpoint of the connecting zone line is near the center of the film. By constructing the appropriate section of the reciprocal lattice, determine an approximate upper limit for the number of spots on the zone line between $n(100)$ and $n(110)$.

6.6 Derive Eq. (6.3).