

*The shape of reflections on X-ray, single-crystal photographs.*

(With Plates X and XI.)

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*Introduction.*

IN the early days of X-ray crystallography the study of the atomic and molecular structure of crystals was of primary importance. It was more necessary to know the arrangement of the atoms in, say, rocksalt, quartz, diamond, or graphite, than to know the exact distances apart of the atoms, or the small deviations from the mean atomic structure which may result from heat movements, eccentricity of growth, mechanical distortion, and other factors.

Now, however, the range of problems is widening, and X-ray methods are being used as a research tool by many workers whose main interest is in other branches of science. It is necessary, therefore, to point out that the familiar Bragg law,  $n\lambda = 2d \sin \theta$ , which relates order of spectrum  $n$ , wave-length  $\lambda$ , crystal spacing  $d$ , and diffraction angle  $\theta$  in an ideal crystal, though still of course applicable, must be applied with some caution to crystals which are not ideal in either structure or texture, and which may be of irregular or eccentric shape. A case in point may be cited from recent scientific literature. R. S. Krishnan<sup>1</sup> found that the 111 reflection of an almost parallel beam of Cu  $K\alpha$  radiation from the oscillating octahedral plate surface of a particular diamond was recorded, on a photographic film some 40 cm. away from the specimen, as a wavy line. Applying the Bragg law directly, he interpreted this as meaning that there was a periodic variation in  $\theta$  from top to bottom of the plate and that therefore  $d$ , the lattice spacing, must similarly vary, by as much as 1 in 2000, from region to region in that diamond. The actual cause of the waviness of the reflection was much more probably a corrugation (and therefore an excentring of parts) of the crystal face. It will be shown later in this paper that apparent variations in  $\theta$  do not by any means necessarily signify a variation in spacing, and ways of finding out just what such variations do imply will be outlined.

In order to make the fullest use of the information given by a photograph, not only the position and intensity, but also the shape of the individual reflections must be studied, and the distribution of intensity within each reflection. There have been many papers<sup>2</sup> on this subject in connexion with precision measurements of lattice spacing using the powder method, and it has been shown that for a proper interpretation of results, certain experimental conditions must be fulfilled. The use of a powder is not always either convenient or expedient, however, even

<sup>1</sup> R. S. Krishnan, Proc. Indian Acad. Sci., Sect. A, 1944, vol. 19, p. 298. [M.A. 9-108.]

<sup>2</sup> A. J. Bradley and A. H. Jay, Proc. Physical Soc., 1932, vol. 44, p. 563 [M.A. 5-305]; 1933, vol. 45, p. 507. E. R. Jette and F. Foote, Journ. Chem. Physics, 1935, vol. 3, p. 605. G. W. Brindley and F. W. Spiers, Proc. Physical Soc., 1938, vol. 50, p. 17. A. J. C. Wilson and H. Lipson, *ibid.*, 1941, vol. 53, p. 245. A. Taylor and H. Sinclair, *ibid.*, 1945, vol. 57, pp. 108, 126.

for precision work; the crystal may be one which does not readily powder, or which does not readily form a uniform powder; it may be a single specimen too precious to destroy; it may be unstable, or soft and easily distorted. Moreover, the intensity of a line on a powder photograph is, generally speaking, small compared with that of the same reflection observed by means of single-crystal oscillation, and time of exposure may be an important factor, especially if the crystal has to be maintained at a particular temperature or pressure, if it is hygroscopic or volatile, and so on. Resolution of reflections is also sometimes impossible in powder photographs. Now precision work *can* be attempted using single crystals if the shape of, and distribution of intensity in, the observed reflections can be interpreted in relation to the shape and other properties of the crystal, to the divergence of, and distribution of intensity in, the incident X-ray beam, and to the actual apparatus and photographic method used. A study of the shapes of reflections is also useful in other respects. It may give information about those very features of the natural crystal which would be lost by powdering it, or even by cleaving, fracturing, or working it in such a way as to obtain a specimen of controlled shape. Or it may help to elucidate the actual effect of cleavage, grinding, temperature or pressure change, electrical or heat treatment, ageing, &c., on surface or internal structure.

If any investigation of this kind is to be carried out, however, it is essential that the research worker should be able to distinguish between:

- (a) effects due to experimental methods employed;
- (b) effects due to crystal shape or size;
- (c) effects due to divergence of, and distribution of intensity in, the incident beam;
- (d) effects due to absorption, extinction, and to distortion or imperfection which involves only a difference between the surface layers and the main body of the crystal;
- (e) effects due to distortion (either mechanical or incurred during growth) which has produced a comparatively large disorientation of the crystallites which make up the main body of the crystal;
- (f) effects which involve an actual change of structure without apparent change of shape (e.g. some kinds of temperature transformation);
- (g) effects which are due to an inherent lack of regularity in the atomic or molecular arrangement, whether the departure from regularity is of a static or a dynamic kind.

Now it is not possible, in the course of a short paper, to deal exhaustively with all these effects, but it is hoped that, by indicating the main principles involved, some guidance will be given for the avoidance of major pitfalls.

#### *Experimental methods.*

The various methods used in single-crystal work employ either a stationary crystal, or a moving crystal and a stationary film, or a moving crystal and a moving film. Each of these methods will influence the shapes of the reflections in a different way. For the sake of completeness, the methods themselves will be briefly outlined.

*The Laue method.*—In this method the crystal is held stationary in a particular position, and  $\theta$ , the angle between the incident beam (supposed strictly parallel)

and the normal to any particular set of crystal planes, is therefore invariable *if the planes are strictly parallel throughout the crystal*. The incident beam contains a range of wave-lengths varying from a minimum, which depends on the voltage applied to the X-ray tube, to an effective maximum, which depends upon the crystal itself (since  $\sin \theta = \lambda/2d$  must be less than unity, and therefore  $\lambda_{\text{effective maximum}}$  must be less than  $2d_{\text{max}}$ ). Each set of planes, of spacing  $d$ , orientation  $\theta_L$ , will selectively reflect, out of the polychromatic incident beam, a wave-length  $\lambda$  such that  $n\lambda = 2d \sin \theta_L$ . The positions of the spots on the photographic plate or film (e.g. pl. X, fig. 1) depend only on the crystal symmetry and setting, and the pattern changes markedly even for a small change in that setting. On the other hand, it follows that all cubic crystals, say, whatever their lattice constant may be, will give Laue pictures which, as far as the positions of the spots are concerned (but not the intensities), are identical for similar settings. Since, however, it is  $n\lambda$  and not  $\lambda$  alone that is fixed by  $d$  and  $\theta$ , a single spot on a Laue photograph may sometimes be given by two or even three different wave-lengths reflected in different orders.

If the X-ray beam is not parallel and the crystal is not small, or if the planes in the crystal deviate from strict parallelism for any reason whatever, then a Laue photograph will reveal the fact by a change of shape of the spots from the shape that would normally be expected according to a simple geometrical construction.

If, however, the crystal planes ( $hkl$ ) are irregularly spaced, but remain strictly parallel to each other, the Laue spot corresponding to those planes will show nothing unusual; the reflections from other sets of planes in such a crystal may, however, show abnormalities.

It will be realized that, in using the total X-ray output of any target, the distribution of intensity among the wave-lengths in the incident beam will be far from uniform, especially if the applied voltage is high enough to excite the  $K$  or  $L$  radiation characteristic of the target; but this does not matter, because the Laue method is not used for the determination of intensities of reflection, nor for the measurement of spacing, but mainly for the detection of crystal symmetry, twinning, or distortion, or for the determination of crystal orientation.

*The rotation method.*—In the rotation or oscillation method the crystal setting is continuously varied about a particular direction, usually a simple zone-axis, but, ideally at least, the incident beam is parallel and contains only one wave-length. (In practice, of course, even a single characteristic line such as the  $\text{Cu } K\alpha_1$  has a finite width.) Since  $\lambda$  is invariable, the angle of selective reflection  $\theta_B$  must depend upon the spacing  $d$ . The position of a reflection on the photographic plate or film will depend also on the orientation of the reflecting planes relative to the rotation axis, this fact giving rise to the characteristic layer-line arrangement (pl. X, figs. 2, 4, 6). The dependence of  $\theta_B$  upon  $d$  will be especially marked if  $d$  is small ( $2\theta_B \rightarrow 180^\circ$ ). *Any variation in crystal spacing, therefore, may be expected to produce big changes of position of the back reflections, or which  $2\theta_B$  approaches  $180^\circ$ .*

Disturbances in the parallelism of the crystal planes will, however, only affect the positions or shapes of the spots on the film, if the inclinations of the planes to the rotation axis are thereby affected. This assumes, of course, that the film is stationary.

*Moving plate or film methods.*—In the Weissenberg method, the crystal rotates about a zone-axis which is coincident in direction with the axis of a cylindrical film, and the film itself moves parallel with this axis, its speed and extent of translation being synchronized with the rotation of the crystal. In the Schiebold-Sauter method the plate or film, which is parallel to the rotation axis of the crystal and normal to the incident X-ray beam, rotates, synchronously with the crystal, about its own normal. There are also other methods involving translations or rotations of the film in other directions relative to the rotation axis of the crystal and the direction of the incident X-ray beam.<sup>1</sup>

Now an X-ray reflection does not take place instantaneously; it necessarily occupies an appreciable, though small, period of time, and during that time the film will move. This may result either in a spreading or in a focusing of the reflection, but it will certainly affect the shape in a way that bears a definite geometrical relationship to the experimental set-up.

Detailed consideration will not be given here to the interpretation of the results likely to be obtained from moving-film photographs of crystals of irregular shape, structure, or texture, but it will be realized that in some respects these results will be much more informative than those obtained from a simple rotation photograph. In a rotation photograph the position of a spot depends only on the spacing and the direction of the plane normal relative to the rotation axis, so that, for example, spiralling of the planes *about that axis* would not be detectable by the simple rotation method. In a method involving translation or rotation of the film, however, the *time* at which the reflection takes place is a crucial factor. This time will vary for sets of planes which, though equally inclined to the rotation axis and of equal spacing, are not parallel to each other, and the result of spiral distortion about the rotation axis, for example, would be a change of length of the reflections in the direction of translation of the film. Any *accidental* crystal movement will of course also affect spot shapes.

*Focusing methods. Intensification.*—Various methods have been devised for focusing the reflections from a crystal. These include the use of bent crystal monochromators, and cameras in which the specimen is placed on the circumference instead of at the centre of the cylindrical film. Here again, it is the experimental arrangements that principally decide the shape of the X-ray reflection. Similarly, photographic intensification causes a loss of definition which should be avoided in any study of shape.

*Effect of crystal shape upon the shape of X-ray reflections  
in the Laue and rotation methods.*

It often happens that crystals grow in the shape of needles or plates and must be examined in that form, since they cannot be cut without distortion. This means that the spots on the film will be of varying shapes. If the incident beam is parallel and crystal absorption is negligible, the shape of the spot, whether in the Laue or the rotation method, will be given by the projection of the crystal shape on to the film, along the direction of the particular reflected beam, over the period during which the reflection is taking place (fig. 1). Pl. XI, fig. 4, shows the shape of the spots obtained by Laue reflection from the surface of a

<sup>1</sup> International tables for the determination of crystal structures. Berlin, 1935, vol. 2, p. 676. [M.A. 6-145.]

large (distorted) diamond plate. Even allowing for the distortion, the irregular shape of the surface is quite obvious.

For a disk-shaped crystal, some spots will be disk-shaped, others needle-shaped (pl. XI, fig. 2). When the Laue method is used, the shape of the spot is decided (for a parallel beam and non-absorbent crystal only) by the orientation of the crystal relative to the film and the incident beam, because the crystal is reflecting

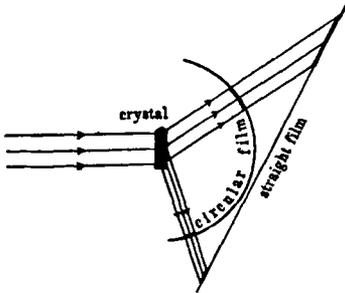


FIG. 1.  
Effect of crystal shape  
on shape of spots.

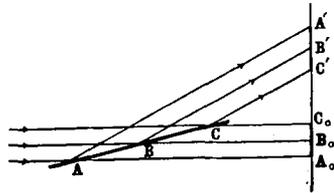


FIG. 2.  
Differences in point of  
origin for angle  $\theta$ .

all the time. When the rotation method is used, the shape of the spot will be dependent upon the crystal orientation *at the time of reflection* and upon the spacing, which controls the reflecting angle. Spots that are disk-shaped in the one method may quite well be needle-shaped in the other.

One simple point that must never be lost sight of in making observations on photographs of a crystal of finite size, using a beam of finite section, is that the origin from which  $\theta$  is to be measured varies from point to point in the crystal

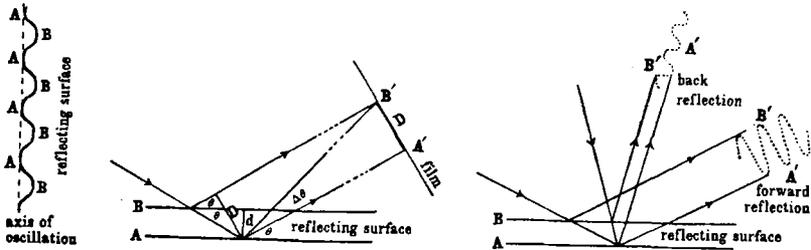


FIG. 3. X-ray reflections from a corrugated surface.

fig. 2). The point  $A$  will reflect to  $A'$ , the point  $B$  to  $B'$ , and the point  $C$  to  $C'$ . The angle of deviation of the ray  $AA'$  is  $A'AA_0$ , not  $A'BB_0$ , although  $B$  may be the true axis of rotation and  $B_0$  the true centre of the photograph. This is obvious in the case illustrated, but it is not so obvious in the case of, say, a surface which is uneven or spherical, when the true centre of rotation is difficult to locate and is not, perhaps, at the centre of the reflecting region. In the case of the diamond surface used by R. S. Krishnan, for example, a vertical corrugation (fig. 3) involving an excentring of parts  $B$  of the surface by 0.004 cm.

would cause an apparent variation in  $\theta_{\text{III}}$  of the order found ( $\sim 0.7'$ ), since if  $d$  is the amount of excentring and  $\Delta\theta$  the apparent change of  $\theta$ ,

$$\frac{d}{\sin \theta} = \frac{D}{\sin 2\theta} = \frac{L \cdot \Delta\theta}{\sin 2\theta} \quad (\theta = 22^\circ, L = 40 \text{ cm.}).$$

It will be seen from the formula, or from the diagram, however, that for the high-order reflections ( $\theta \rightarrow 90^\circ$ ) the variation in  $\theta$  caused by the same amount of corrugation would be *less*, since  $\sin 2\theta/\sin \theta$  is a maximum for  $\theta \rightarrow 0$  and a minimum for  $\theta \rightarrow 90^\circ$ . This is in direct contrast to the *greater* variation in  $\theta$  for high-order reflections that would result from a variation in spacing.

The *broadening* of the reflections that is the consequence of extreme smallness of the crystallites ( $10^{-6}$  cm. or less linear dimensions) is more often met with in powder or fibre diagrams than in single-crystal work, although it may occur, and the shape of the crystallites (spherical, acicular, or disk-like) will influence the broadening, which may, for crystallites of anisotropic shape, be very different for different reflections.<sup>1</sup> The broadening due to this cause is always much greater for back reflections, if the crystallites are spherical.

*Divergency of the incident beam, and shape of focal spot.*

If the incident beam is not quite parallel (and it never is) the actual dimensions of the spot will depend on the crystal  $\rightarrow$  film distance. On Laue photographs taken at any distance a focusing of some spots (usually those for which  $\theta$  is small) and a spreading of others will result. This is well shown on pl. X, fig. 1, which is a Laue photograph of a large undistorted crystal of urea oxalate placed with its longest dimension vertical and parallel to the film.

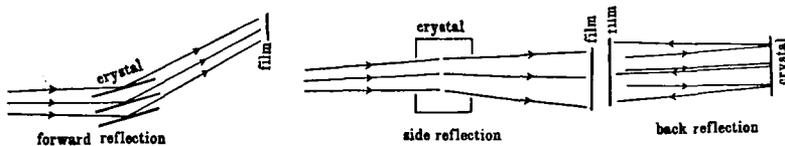


FIG. 4. Laue method, showing broadening of side and back reflections.

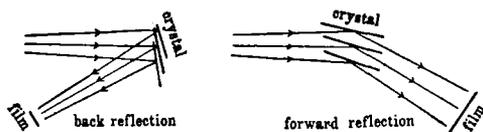


FIG. 5. Rotation method, showing focusing of back reflections.

A simple sketch shows that the tendency of a divergent beam is to broaden the back reflections in a Laue photograph (fig. 4), while in a rotation photograph the back reflections are focused and the forward reflections are broadened or distorted (fig. 5).

If the crystal is large enough to cover the whole of the divergent beam, then

<sup>1</sup> P. P. Ewald, Proc. Physical Soc., 1940, vol. 52, p. 167 [M.A. 8-133]. M. von Laue, Ann. Physik, 1936, ser. 5, vol. 26, p. 55.

the spots on Laue or on rotation photographs may not have very sharp edges, because the X-rays at the edge of the beam will be less concentrated than those in the properly collimated middle (pl. XI, fig. 4).

It is frequently found that, in Laue photographs taken with a slightly divergent beam, a sharp intense spot of well-defined shape (sometimes a doublet) is superimposed, not necessarily centrally, upon a bigger, fainter, and perhaps more diffuse spot (pl. X, fig. 3; pl. XI, fig. 1).

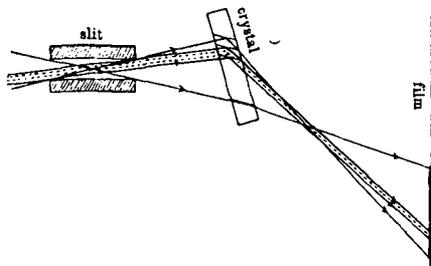


FIG. 6. Characteristic reflection superimposed on reflection of general radiation, in Laue photograph.

perhaps in another order (such that  $n_1/n_2 = \lambda_2/\lambda_1$ ), over the range  $\theta + \Delta\theta$  to  $\theta - \Delta\theta$ . This coincident spot will probably be much fainter. A small movement of the crystal either way will usually cause the partial or complete disappearance of the sharp 'characteristic spot', although the spot that remains will still be given by wave-lengths reflected in different orders (pl. XI, fig. 1).

If the slit system is not fully collimating, the shape of the focal spot on the target of the X-ray tube is a very important factor in deciding the shape of the reflections. Pl. XI, fig. 3, shows the comparative photographs given by four different X-ray tubes of a small benzil prism (height about  $1\frac{1}{2}$  times width) rotating about its longest dimension. In (a) the tube had a horizontal line focus which was at right angles to the height of the prism, and the effect of crystal shape is, to a large degree, cancelled. In (b) the tube had a vertical line focus, parallel to the height of the prism, and the effect of anisotropy of crystal shape is accentuated. In (c) the focus was circular but ill-defined, whereas in (d) it was circular and fairly sharp. The same slit system was used in all four experiments; only the X-ray tube was changed. The same effect can be demonstrated using a tube with a line focus, and turning the crystal itself through  $90^\circ$  about the direction of the X-ray beam. Pl. X, figs. 3 and 5, are Laue photographs of the same needle of urea oxalate placed with its length vertical and horizontal respectively, and parallel to the film in each case. If the focus were circular or the slit system correctly collimating, the photographs should be identical if one is turned through  $90^\circ$ .

The three factors considered so far, that is, the particular X-ray method used, the shape of the crystal, and the shape of the incident beam, are not usually studied for their own intrinsic interest. But it may be necessary to take them very seriously into account, before the shapes of the reflections can be used to give information about the remaining factors, which are more important from a crystallographic point of view.

*Absorption, extinction, and surface effects.*

The effect of absorption must, of course, be considered as much in the case of single crystals as for a powder, or even rather more, since added to the ordinary absorption there will be the 'extinction' (primary and secondary) which depends on the state of perfection of the crystal.<sup>1</sup> A perfect crystal will reflect only a fraction, say one-thirtieth, of the intensity reflected by a crystal mosaic, and this 'extinction', although difficult to estimate or to measure,<sup>2</sup> is not difficult to observe. It is frequently found that spots on Laue or on rotation photographs are doubled. Such doubling may be the result of ordinary absorption and path differences (fig. 7). In that case it is usually found for long rather than for short wave-lengths. Quite frequently it is observed for the 'characteristic spots' mentioned in the last section, although the high-order, short wave-length spots on which they are superimposed do not show it (pl. XI, fig. 1).

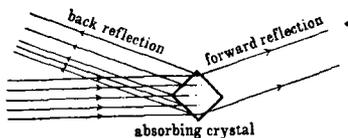


FIG. 7. Doubling of spots due to absorption.

The doubling, however, is quite often due to the fact that the surface of a crystal is more mosaic, less perfect, and therefore a much better reflector than the inside.

It is reported that if a quartz crystal is subjected to standing supersonic waves, the disturbance of the atoms at the antinodes causes the crystal to become more mosaic and to reflect better at these points, and the double spots previously observed on Laue photographs become multiple spots, the number of components varying with the mode of vibration.<sup>3</sup>

If the crystal surface is not only a mosaic but is subject also to strain, other effects will be observed that are considered in a later section.

*Crystal distortion, with special reference to 'spiral structures'.*

It has already been mentioned that if the individual crystallites of which the crystal is ordinarily composed are sufficiently small, a broadening of the reflections will occur. A similar broadening might also occur if the crystal were a mixture of larger grains of different lattice parameters or if there were actual structural distortions (uneven expansions and contractions, warping or curving of planes) in the individual grains.<sup>4</sup>

If, however, there is a *regular* distortion of the crystal, such as the 'spiralling' described by Bernauer as characteristic of many single crystals of organic compounds, and observed by him by means of the polarizing microscope,<sup>5</sup> then some

<sup>1</sup> P. P. Ewald and M. Renninger, *The solid state of matter*. Internat. Conf. Physics, London, 1934, vol. 2, p. 57.

<sup>2</sup> R. W. James, *Zeits. Krist.*, 1934, vol. 89, p. 295. Summary of earlier work, with references.

<sup>3</sup> S. Nishikawa, Y. Sakisaka, and I. Sumoto, *Physical Rev.*, 1933, vol. 43, p. 363; M. Y. Colby and S. Harris, *ibid.*, 1934, vol. 46, p. 445. F. Klauer, *Physikal. Zeits.*, 1935, vol. 36, p. 208.

<sup>4</sup> E. Orowan and K. J. Pascoe, *Nature*, London, 1941, vol. 148, p. 467. E. Orowan, *ibid.*, 1942, vol. 149, p. 643. A. R. Stokes and A. J. C. Wilson, *Proc. Physical Soc.*, 1944, vol. 56, p. 174.

<sup>5</sup> F. Bernauer, *Zeits. Krist.*, 1926, vol. 64, p. 505; *Fortschr. Min. Krist. Petr.*, 1927, vol. 11, p. 293. L. J. Spencer, *Curvature in crystals*. *Min. Mag.*, 1921, vol. 19, p. 263.

most peculiar and unmistakable effects will be found on Laue photographs, even when rotation photographs show little or nothing out of the ordinary. Since these effects have not been discussed previously, they will be described here in some detail. They sometimes indicate a spiralling which has occurred during growth, and sometimes a spiral distortion due to cleavage. Crystals of urea oxalate  $2\text{CO}(\text{NH}_2)_2 \cdot \text{C}_2\text{H}_2\text{O}_4$ , provide a good example of the latter. They are monoclinic,  $a$  7.02,  $b$  12.42,  $c$  5.08 Å.,  $\beta$   $97^\circ 30'$ , space-group  $P2_1/a$ , two molecules in the unit cell. The atoms are arranged in layers parallel to the (201) plane, which is in consequence an excellent cleavage plane. The crystals are platy in habit, with the large natural face parallel to (010), and it is quite easy to obtain cleavage needles, the length of which is parallel to the zone-axis [102]. If the needles are sufficiently thin, the cleavage produces a slight spiralling about this [102] axis. The result on a Laue photograph taken with the X-rays parallel to the symmetry plane and perpendicular to the spiral axis is shown in pl. X, fig. 3. Here the spiral axis and the plane of symmetry are both vertical. It will be seen that although the spots on the left-hand side of the photograph are in positions which are the mirror-image of those on the right-hand side, there is a marked asymmetry of shape. All the spots, in fact, are either focused or are tilted through various angles in an anti-clockwise direction from their normal mirror-image orientations. This rotation of the spots is observed no matter which plane in the [102] zone is parallel to the X-ray beam (pl. X, figs. 3, 8), and its amount and direction vary in different crystals. By considering only the reflections from planes in the [102] zone, it is possible to calculate the pitch of the screw. It will

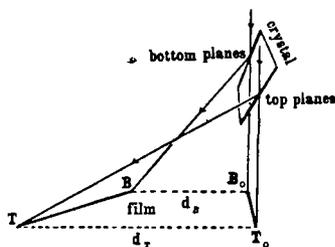


FIG. 8. Effect due to a spiral structure in the crystal.

8). The portion  $T$  of the Laue spot which is due to the planes at the top of the crystal will be at a certain distance  $d_T$  from the origin  $T_0$  (trace of central beam which has passed through the top of the crystal), and this will differ from the distance  $d_B$  corresponding to the same planes at the bottom of the crystal. If  $D$  is the crystal  $\rightarrow$  film distance, then the angle through which the plane normal has twisted from top to bottom will be  $\frac{1}{2}(\tan^{-1}d_T/D - \tan^{-1}d_B/D)$ . The urea oxalate cleavage needle giving pl. X, figs. 3, 5, 7, was found to be spiralling about [102] in a left-handed screw direction by about 16 minutes per millimetre.

A comparison of Laue photographs taken with a particularly long needle with the [102] spiral axis placed horizontally ( $a$ ) parallel to the film and ( $b$ ) parallel to the X-rays and therefore perpendicular to the film, shows a remarkable difference in the two cases (pl. X, figs. 5, 7). In the case ( $a$ ) the size of the collimator pin-holes limits the size of the reflecting portion of the crystal, and

be remembered that the position (distance and direction) of any part of a Laue spot, relative to its corresponding origin on the film, gives the direction-cosines of the normal to the reflecting planes in the corresponding part of the crystal, due allowance being made for size and divergence of the incident beam. Since the planes are spiralling slightly about [102], the plane normals at the top and bottom (say) of the needle whose vertical length is parallel to [102] will be differently orientated relative to the incident beam (fig.

the spots, although showing the individual distortion that has been described in connexion with pl. X, fig. 3, do not give anything like the impression of over-all distortion that is gained from (b), where the whole crystal is reflecting. One would hardly believe that it is the same crystal giving these two photographs, and that all that has been done is to turn the crystal through  $90^\circ$  about a vertical axis. When the spiral axis is parallel to the incident X-ray beam, the effect is to superimpose a screw motion of the whole pattern on whatever symmetry would normally have been present. It must also be remembered that, quite apart from any distortion effect, the pattern from the part *A* of the needle nearest to the source of incident X-rays will be appreciably larger than that from the part *B* nearest to the film, owing to the variation in effective crystal  $\rightarrow$  film distance from *AO* to *BO* (fig. 9).

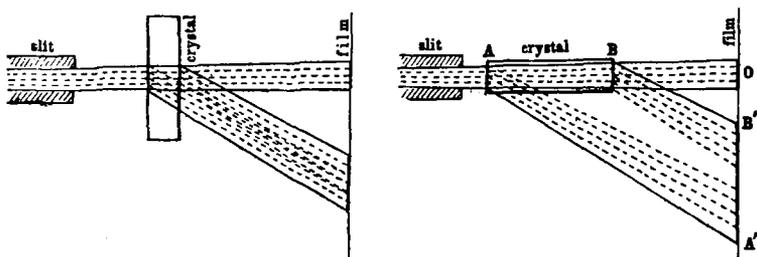


FIG. 9. Crystal with spiral structure: (a) parallel to the photographic film, (b) parallel to the X-ray beam.

Of course, it will be realized that any kind of angular distortion, such as curving or kinking of the crystals (Orowan and Pascoe, *loc. cit.*), will be similarly revealed by means of Laue photographs.

Rotation photographs can give the same information, but they give it in a different way. When a spirally distorted crystal, such as urea oxalate, is rotated about the spiral axis, the rotation photograph obtained on a stationary plate or film is a perfectly normal one, showing no apparent distortion at all (pl. X, fig. 2) except perhaps that due to the combination of a vertical needle and a slightly divergent beam. If the film were moving parallel to the axis of rotation (as in the Weissenberg method) some reflections would be lengthened and some shortened, but without any variation of the Bragg angle  $\theta$ . When the needle axis is tilted to the vertical, the rotation photograph shows variously tilted spots (best resolved when the rotation axis is not quite coincident with a zone-axis), where shapes are distorted in different ways by the superimposed spiralling (pl. X, fig. 4). This distortion of the shapes of the rotation spots is most marked when the spiral axis is perpendicular to the axis of rotation; and in this case (pl. X, fig. 6) some spots may occasionally be found to show angular spreading over quite a considerable range.

Orowan and Pascoe (*loc. cit.*) have shown that it is possible, by means of rotation photographs, to distinguish between lattice curvature and fragmentation into disorientated crystallites. If the curvature is continuous, reflected rays from one side of the crystal will converge, and from the other side they will diverge, giving very differently shaped spots in different quadrants of the photograph.

A purely random disorientation of the crystallites through a small range of

angles will cause a spreading of rotation spots along 'powder' circles. Pl. XI, fig. 8, shows such a spreading found in the case of a very small crystal of bröggerite. The extension of the spots is least for Bragg angles near to  $45^\circ$ . On Laue photographs a small random disorientation of this kind leads to 'asterism', a radial elongation of the reflections, which are drawn out into ellipses whose major axis is perhaps several times longer than the minor. If the Bragg angle is  $\theta$  radians, the ratio of major to minor axis is approximately  $1/\theta$ .<sup>1</sup> This means that the spots nearest to the central spot are drawn out the most. Pl. XI, fig. 7, shows the asterism effect for the very small crystal of bröggerite, in which, however, there is also a slight tendency to spiral.

Pl. XI, fig. 6, is a Laue photograph of diamond which at first appears to show asterism. In fact, however, it is seen that the spreading of the spots is greater for larger angles of  $\theta$ , an effect which is clearly due to crystal shape (the diamond was a plate placed nearly parallel to the incident rays) and to the divergency of the X-rays used. In general, the distortion seen in rotation or oscillation photographs is not so easy to interpret, nor so informative as that observed by the Laue method. The rotation and oscillation methods are particularly useful for the observation of small changes of lattice dimensions or structure which involve little or no change of crystal shape.

*Effect of change of structure without change of crystal shape.*

Some recent observations by Ubbelohde and Woodward<sup>2</sup> provide an excellent example of this effect. They have found that X-ray rotation photographs of such crystals as Rochelle salt and potassium dihydrogen ortho-phosphate show a splitting of some reflections when the temperature lies within the Curie region for the particular crystal, although the same crystal gives single reflections at temperatures both above and below that range. The crystal, outwardly at least, is not broken up, and certainly recovers from any sub-crystalline breaking-up that may temporarily occur within the region. Now a splitting of Laue spots might be explained by absorption or by a variation of the texture of the crystal, as has been pointed out earlier in this paper, and a splitting of rotation spots could be due to the same effect, the outer parts of the crystal being less absorbing or better reflecting than the middle. But in that case the forward reflections would show the splitting rather than the back reflections (fig. 7). In Ubbelohde's and Woodward's photographs the splitting is most marked in the back reflections, showing that a real variation of spacing is involved; and it is only shown by some planes. Others remain unaltered or are split to a much less degree. It is found that the results are explained by assuming that the structure, orthogonal above and below the Curie region, changes within that region to a sub-crystalline combination of two less symmetrical forms which are, however, only slightly different from the original in lattice angles and parameters. In Rochelle salt, for example, a change of the angle between the  $b$  and  $c$  axes from  $90^\circ$  to  $90^\circ 2'$  or  $89^\circ 58'$ , without any change of length of the axes themselves, accounts quite rigorously for the observed splitting of the reflections.

Similarly, the changes of spacing corresponding to thermal expansion, isotope

<sup>1</sup> W. H. Bragg and W. L. Bragg, *The crystalline state*. London, 1933, vol. 1, p. 202. [M.A. 5-385.]

<sup>2</sup> A. R. Ubbelohde and I. Woodward, *Nature*, London, 1945, vol. 155, p. 170.

substitution, elastic strain, and so on, can be measured by means of rotation photographs, but not by the Laue method. Such changes are always observed by means of back reflections ( $2\theta \rightarrow 180^\circ$ ) for which the percentage change of position is greatest and the apparent variation in  $\theta$  due to divergency of beam or imperfection of the single crystal is usually least. These changes of spacing do not involve a noticeable change of shape.

There are many cases of crystals which are composed of crystallites having one crystallographic direction only in common. Examples of these, which include drawn aluminium wire and fibre photographs, are given in Bragg's book 'The crystalline state'. Such crystals give photographs which are similar to rotation photographs, but usually with somewhat extended and diffuse spots. They cannot, of course, be regarded as single crystals, but the transition from such orientated crystal agglomerates to true single crystals is a gradual one, depending upon the amount of disorientation of the remaining crystal directions.

#### *Lack of regularity in single-crystal structure.*

The atoms in all crystals are vibrating about their mean positions with a frequency that is small compared with the frequency of X-rays. Any such vibration can therefore be regarded, from the point of view of the X-rays, as a set of instantaneous *displacements* of the atoms from their mean positions. In the case of thermal vibrations, the displacements are dependent upon the elastic forces in the lattice, and of course upon the temperature. There are many other factors, however, which may lead to the displacement, either permanent or transient, of the atoms from their mean positions. A system of permanent displacements, due for example to strain, is sometimes referred to as a 'frozen heat motion'.<sup>1</sup> Any such displacement, whether static or dynamic, can be formally considered as due to a pattern of stationary waves in the crystal and will give rise, therefore, to a non-Laue scattering of X-rays (pl. X, figs. 3, 7). Thermal vibrations give very typical diffuse background effects which are most easily observable on Laue photographs taken with an incident X-ray beam which has either been monochromatized or includes an intense characteristic component.<sup>2</sup> These effects are often seen as quite strong *diffuse* spots in the near neighbourhood of a *sharp* Laue spot. Pl. X, fig. 8, shows the diffuse spots corresponding to the diffraction of Cu  $K\alpha$  and Cu  $K\beta$  radiation by waves modifying the structure of the  $(\bar{2}01)$  'layer' plane in urea oxalate. It is very clear that the diffuse spots are hardly distorted at all by the spiralling of the structure, although they are probably slightly enlarged. The contrast in their shape and that of the  $(\bar{2}01)$  Laue spot lying between them is quite striking. The standing waves giving rise to these diffuse spots correspond to an oscillation of the individual atoms and therefore, in a sense, to an apparent oscillation of the whole crystal,<sup>3</sup> the superposition of a small spiralling in any direction will have little more effect upon the shape of the diffuse spots than upon that of the spots of a rotation photograph when the axes of rotation and of spiralling coincide.

<sup>1</sup> G. W. Brindley, Proc. Physical Soc., 1940, vol. 52, p. 117.

<sup>2</sup> K. Lonsdale, Reports on Progress in Physics (Physical Soc.), 1943, vol. 9 (for 1942-3), p. 256.

<sup>3</sup> K. Lonsdale and H. Smith, Proc. Roy. Soc. London, Ser. A, 1941, vol. 179, pp. 14-15. [M.A. 8-209.]

Any strain or distortion involving a breakdown of crystal periodicity may also give 'extra' spots on Laue photographs, but as a rule spots due to surface distortion are sharp, not diffuse, and they are not temperature-sensitive. C. R. Bose<sup>1</sup> has described the most interesting case of a crystal, phloroglucine dihydrate, in which there is a breakdown of the periodicity along the *c*-axis *in the outer parts only of the crystal*, with the result that the 'extra' spots found are all hollow. The inside of the crystal does not give the non-Laue scattering. The partial breakdown of *c*-axis periodicity results also in the appearance of weak continuous lines connecting the spots in some zones found on the Laue photographs.

E. Aruja<sup>2</sup> has described photographs of chrysotile, a fibrous mineral of the asbestos group, which show a drawing-out of spots *along the layer-lines*; this indicates a perfect periodicity along the fibre length, but a partial breakdown of periodicity normal to that direction.

The presence of foreign atoms in any structure will cause local disturbance, and a solid solution of one kind of atom in the lattice of another may give sufficient disorder to lead to diffuse spot effects very much like those characteristic of thermal vibrations. The occurrence of 'holes' in the structure, if sufficiently frequent, should have a similar effect. The segregation of the solute atoms, or some of them, as a separate phase may be characterized, in its initial stages, by the appearance of 'ghosts', streaks, and diffuse spots, which have received special attention in connexion with the effects of heat-treatment of alloys.<sup>3</sup>

Certain substances, such as cobalt, can crystallize in either of two closely-related modifications, which may coexist over a certain range of temperature. Edwards and Lipson<sup>4</sup> have found that in the hexagonal form of cobalt, which is stable at room-temperatures, 'mistakes' occur at random intervals along the hexagonal axis because there are two different ways in which one close-packed layer of atoms can be fitted on to another and the structure occasionally goes the wrong way. This causes a diffuse broadening of some of the lines on powder photographs, but on single-crystal oscillation photographs there is a spreading-out of some spots along definite lines.

All cases of structural irregularity in crystals are most easily investigated by the use of reciprocal lattice methods of interpretation (James, loc. cit.), but to consider these in any detail would bring us far beyond the range of this paper.

*Summary.*—The shapes of the spots observed on X-ray photographs of single crystals are influenced by the experimental method used, the properties of the incident beam, and the shape, absorption, structure, and texture of the crystal examined. If the first three factors can be allowed for, it is possible to obtain useful and interesting information concerning the sub-crystalline structure and the departures from regularity of the atomic or molecular arrangement. The limitations of the particular X-ray method used are illustrated by Laue and rotation photographs of a spirally distorted crystal of urea oxalate, and spiral and asterism effects in diamond and bröggerite photographs are also shown.

<sup>1</sup> C. R. Bose, Proc. Nat. Inst. Sci. India, 1944, vol. 10, p. 201.

<sup>2</sup> X-ray analysis in industry. Nature, London, 1944, vol. 153, p. 534.

<sup>3</sup> A. Guinier, Compt. Rend. Acad. Sci. Paris, 1938, vol. 206, p. 1972; 1943, vol. 217, p. 22. G. D. Preston, Proc. Physical Soc., 1940, vol. 52, p. 77. V. Daniel and H. Lipson, Proc. Roy. Soc. London, Ser. A, 1943, vol. 181, p. 368.

<sup>4</sup> O. S. Edwards and H. Lipson, Proc. Roy. Soc. London, 1942, vol. 180, p. 268. [M.A. 8-284, 362.]

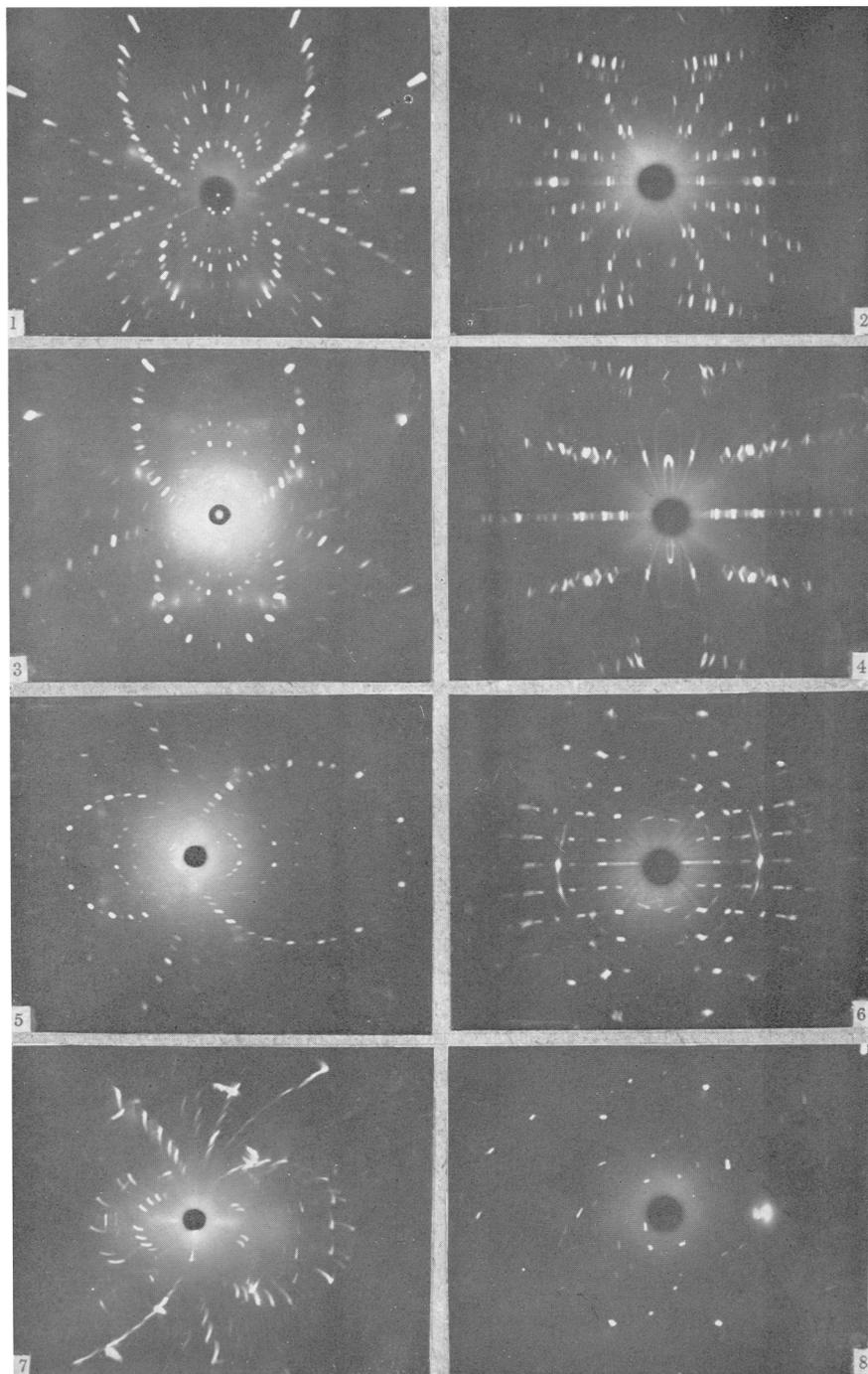
## EXPLANATION OF PLATES X AND XI.

PLATE X consists entirely of photographs of urea oxalate.

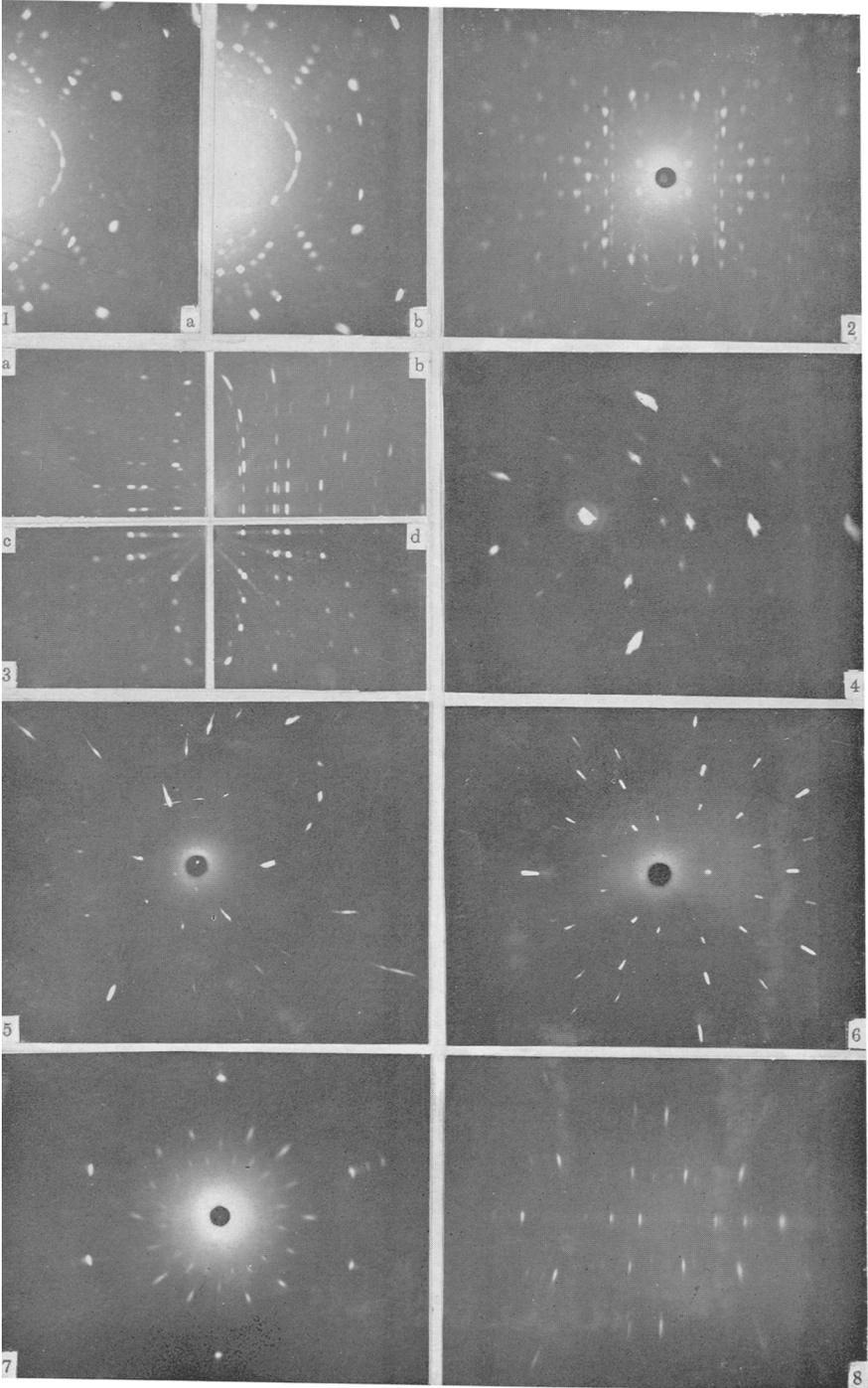
- FIG. 1. Laue photograph of undistorted plate, length [102] vertical, large face (010) parallel to incident X-ray beam, small face ( $\bar{2}01$ ) parallel to photographic film. Shows effects due to beam divergence and crystal shape.
- FIG. 2. Rotation photograph of needle, spirally distorted about [102] axis, which is parallel to the length of needle, and about which rotation takes place. Shows effects due to beam divergence and crystal shape only.
- FIG. 3. Laue photograph of needle, spirally distorted about [102] axis, which is parallel to length of needle. Placed as for fig. 1, showing effects due to beam divergence, crystal shape, spiral distortion, atomic displacements due to strain and thermal vibration. Also shows Laue spots given in *different orders* by general and characteristic radiation.
- FIG. 4. Rotation photograph about [001] vertical, length of needle tilted to vertical, showing effects due to beam divergence, crystal shape and excentring due to tilt, and spiral distortion.
- FIG. 5. Laue photograph of same crystal as in fig. 3, turned through  $90^\circ$  about incident beam direction. Showing effects due to beam divergence, crystal shape, shape of X-ray tube focus, spiral distortion, atomic displacements due to strain and thermal vibration.
- FIG. 6. Rotation photograph about [010] vertical, spiral axis [102] horizontal, showing pronounced distortion of spots due to spiral distortion of crystal, and spreading of ( $\bar{2}01$ ) reflections in particular.
- FIG. 7. Laue photograph of same crystal as in fig. 5, turned through  $90^\circ$  about vertical direction. Length of needle now parallel to incident X-ray beam. Shows effect of crystal shape and distortion, and also strong non-Laue reflections due to strain.
- FIG. 8. Laue photograph of distorted needle, [102] vertical, placed so that ( $\bar{2}01$ ) plane is reflecting at an angle between the Bragg angles corresponding to Cu  $K\alpha$  and Cu  $K\beta$ . Showing effect due to crystal distortion and crystal shape, but showing little or no effect on the 'thermal' spots which bracket the  $\bar{2}01$  Laue reflection.

PLATE XI shows a variety of effects, using other crystals.

- FIG. 1. Laue photographs of beryl at settings  $1^\circ$  apart, showing transitory appearance of split reflections due to characteristic radiation, superimposed on reflections of general radiation in a different order.
- FIG. 2. Rotation photograph of beryl, showing narrow and broad reflections obtained from a thin plate as it rotates. In some instances, spots of different shapes are superimposed on each other, owing to the lack of resolution in this method.
- FIG. 3. Rotation photographs of benzil (small prism, height vertical,  $1.5 \times$  width) showing effect of non-collimation of incident X-ray beams from targets of various shapes and definitions.
- FIG. 4. Laue photograph of large distorted diamond plate (D 19 in Phil. Trans. Roy. Soc., Ser. A, 1934, vol. 232, p. 469) placed for Bragg reflection from (111) face; showing effect of crystal shape and distortion.
- FIG. 5. Laue photograph of small piece of diamond chipped off corner of specimen D 19, showing asterism and orientated distortion (cf. pl. X, figs. 3 and 5).
- FIG. 6. Laue photograph of square diamond plate, showing effect of crystal shape and beam divergence. Spots near to undeviated incident beam are small, whereas asterism involves a maximum distortion of spots for which  $\theta$  is small.
- FIG. 7. Laue photograph of very small crystal of bröggerite, cube axis parallel to incident X-ray beam, showing effect of partial disorientation of crystallites (asterism and very slight spiralling); also showing sharper spots due to characteristic radiation.
- FIG. 8. Rotation photograph of same crystal as in fig. 7, cube axis vertical, photograph film parallel to X-ray beam, showing spreading of reflections (especially back reflections) circularly about forward and back directions of incident beam, due to partial disorientation of crystallites.



K. LONSDALE: SHAPES OF X-RAY SPOTS



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