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The Interpretation of Diffuse X-ray Reflexions from Single Crystals

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A description is given of the construction and use of a $\bar{\varrho}$, $\bar{\varphi}$-chart whereby the angular coordinates of any line in reciprocal space passing through a reciprocal point near to the sphere of reflexion can be found. An R-chart giving the distance from the same reciprocal point of the intersection of this line with the reflecting sphere is also given. Methods are described of using the Laue and also the Bragg reflexions to locate the charts correctly with respect to an enlarged drawing of the diffuse spot.

1. Introduction

Any departure from a truly periodic arrangement of the atoms in a crystal gives rise, in reciprocal space, to corresponding extensions of the points of the reciprocal lattice. These non-periodic atomic distributions may be due to heat motion or to structural anomalies such as, for instance, those which occur in diamond or cobalt or the age-hardening Al–Cu alloys. The extensions of the reciprocal points may take the form of a more or less spherical cloud surrounding the relp† or of a straight streak which decreases in intensity from the relp outwards.

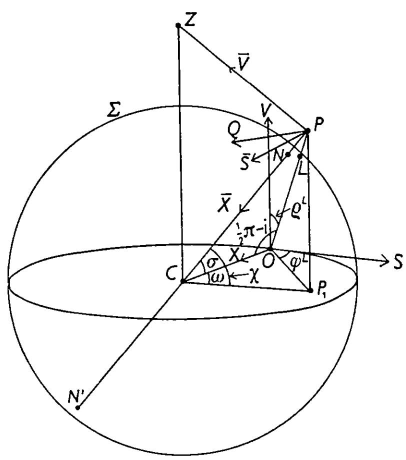

Fig. 1. Diagram showing the relation of the relp, P, to the Ewald sphere, Σ, and also the relation between the two sets of axes $X, S, V, \bar{X}, \bar{S}, \bar{V}$.

The usual way of studying a region in reciprocal space around a relp is to take a series of Laue photographs with settings of the crystal, say, 2°, 4°, etc. on one side or the other of the setting corresponding to the Bragg reflexion. On such photographs diffuse spots or streaks occur and the problem arises of relating a given position within a diffuse spot to the corresponding point in reciprocal space. The coordinates of any reciprocal point are usually defined in terms of the unit-cell vectors a^*, b^*, c^*, but in dealing with diffuse regions it is more convenient to use the angular coordinates of the rekha on which the point lies. In Fig. 1, Q represents the direction of any rekha drawn through the relp P. The angular coordinates of PQ will be denoted $\bar{\varrho}$, $\bar{\varphi}$, to distinguish them from ϱ, φ-symbols which are commonly used in the interpretation of diffraction photographs (Henry, Lipson & Wooster, 1951, p. 39).

2. The $\bar{\varrho}$, $\bar{\varphi}$-chart for a cylindrical camera

The ϱ, φ-chart has a fixed axial system X, S, V (Fig. 1) for all relps. These axes are chosen so that the incident X-rays travel in the direction XO, where O is the origin of the reciprocal lattice, OV is a direction perpendicular to OX and parallel to the axis of the cylindrical camera and OS is perpendicular to OX and OV. Unlike the ϱ, φ-chart, the $\bar{\varrho}$, $\bar{\varphi}$-chart has a different axial system for each relp. This axial system has its origin at the relp P and $P\bar{X}$ is directed along PC, the line joining the relp to the centre of the Ewald sphere Σ. $P\bar{V}$ is perpendicular to $P\bar{X}$ and lies in the vertical plane CPZ, and $P\bar{S}$ is horizontal and perpendicular to $P\bar{X}$ and $P\bar{V}$. A stereogram (Fig. 2) shows the relation between the two sets of axes. The relp P is supposed to lie outside the Ewald sphere and the line PO cuts the sphere in L (Fig. 1). Thus L corresponds to the point on Σ giving rise to the Laue spot. The direction OP is defined relative to the X, S, V axial system by the two angles ϱ^L, φ^L. Any arbitrary rekha PQ may be defined in relation to the axes $\bar{X}, \bar{S}, \bar{V}$ by the angles $\bar{\varrho}$, $\bar{\varphi}$ which bear the same relation to these axes as ϱ, φ bear to the axes X, S, V.

† Following Ramachandran & Wooster (1951), we use the terms 'relp' for 'reciprocal lattice point', 'rekha' for the straight line passing through an arbitrary point and the nearest relp, and 'rel-vector' for the vector joining the origin of the reciprocal lattice to the relp.

Although at first sight it may seem unduly complicated to change the axes of reference with the position of the relp, the convention adopted above makes it possible to use the same set of charts for any relp and any wave-length of X-rays. Any other system would require charts which changed progressively as the relp moved away from the origin.

An example of a $\bar{\varrho}$, $\bar{\varphi}$-chart is given in Fig. 3 from which it will be seen that it consists of two sets of curves which are approximately (*a*) vertical straight lines, and (*b*) hyperbolae having a common vertical

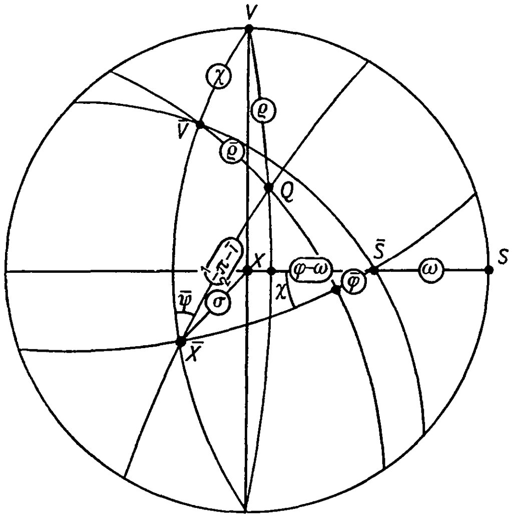

Fig. 2. Stereogram giving the angles between the direction of the rekha, Q, and the axes $X, S, V, \bar{X}, \bar{S}, \bar{V}$.

axis. The locus of all rekhas having a common $\bar{\varrho}$ value is a cone described about $\bar{V}$ with a semi-angle $\bar{\varrho}$. This cone cuts the Ewald sphere in a curve which is nearly an hyperbola, and this in turn is projected gnomonically from C on to the tangent plane passing through N, the point in which $P\bar{X}$ passes through Σ. The locus of all rekhas having a common $\bar{\varphi}$ value is a plane containing the axis $P\bar{V}$. This cuts the Ewald sphere in a small circle which after projection from C gives a nearly straight vertical line. The exact form of the line is obtained by the calculations given in the Appendix. The length NP will be denoted by R_0 and the radius of the Ewald sphere by G. The ratio $s = R_0/G$ is the quantity which determines the form of the $\bar{\varrho}$, $\bar{\varphi}$-curves. When P lies outside of Σ the sign of s is taken as positive and when P lies inside Σ it is negative. Charts for different values of s have been drawn, keeping the same value of R_0 throughout and adjusting the value of G according to the relation $G = R_0/s$. When s is small the charts do not differ greatly from one another, because the influence of the curvature of the sphere is not very large. It is therefore enough to draw the charts for a few values of s, say $\pm 0{\cdot}02$, $\pm 0{\cdot}05$ and $\pm 0{\cdot}10$. Fig. 3 shows the chart for $s = +0{\cdot}02$. In the drawings actually used in this work the value of R_0 was taken as 10 cm. The method of obtaining the value of s from the experimental quantities is given in § 5. When an actual value of s differs from the values chosen for the charts, the chart drawn for the nearest value of s may be used.

3. Method of using the $\bar{\varrho}$, $\bar{\varphi}$-charts

The whole region under study on the photograph may be only a few millimetres across and it is therefore necessary to make measurements of position as well as of intensity by means of a microphotometer. From these measurements a diagram is plotted so that the appropriate chart may be directly compared with it. In making this diagram of the diffuse spot it is necessary to make the correct enlargement. Unit distance on the film corresponds to k units on the diagram; for non-equatorial spots there are two values of k, denoted k' and k'', which apply to horizontal and vertical directions respectively on the photograph. The values of k' and k'' are as follows:

$$k' = (R_0/rs)/[1+(h/r)^2]^{\frac{1}{2}} \, ,$$

$$k'' = (R_0/rs)/[1+(h/r)^2] \, ,$$

where h is the distance of the point on the film from the equatorial line and r is the radius of the camera. The denominators in these expressions for k' and k'' are determined by the distance of the film from the crystal and by the inclination of the film to the reflected X-rays.

The location of the chart on the microphotometer diagram presents certain difficulties. The equatorial (horizontal) direction of the chart must correspond with the horizontal direction of the photograph. It is not at all evident, however, where the centre of the chart must be placed on the microphotometer diagram. It is possible to use the Laue spot for this purpose since the coordinates of the rekha PL (Fig. 1) with respect to $\bar{X}$, $\bar{S}$, $\bar{V}$, namely $\bar{\varrho}(L)$, $\bar{\varphi}(L)$, can be obtained as shown in § 6. When these coordinates are known, the position on the chart corresponding to one point on the microphotometer diagram is known and thus the relation between the two is fixed. A second method consists in oscillating the crystal so as to cause the point P to cut the Ewald sphere at a point P'; from the position of the Bragg spot and a knowledge of the coordinates $\bar{\varrho}(P')$, $\bar{\varphi}(P')$ of the rekha PP' the chart may be correctly related to the microphotometer diagram (Fig. 4).

The $\bar{\varrho}$, $\bar{\varphi}$-chart may be used for two purposes: (*a*) to find $\bar{\varrho}$, $\bar{\varphi}$ for any point within the diffuse spot, and (*b*), being given a certain rekha defined relative to the crystallographic axes, to find what point on the diffuse spot corresponds to it. Since the $\bar{X}$, $\bar{S}$, $\bar{V}$ axial system bears no simple relation to the X, S, V axes, it is necessary in interpreting the results to make a transformation of the $\bar{\varrho}$, $\bar{\varphi}$-coordinates to the X, S, V axes or to a set of crystallographic axes. This can be

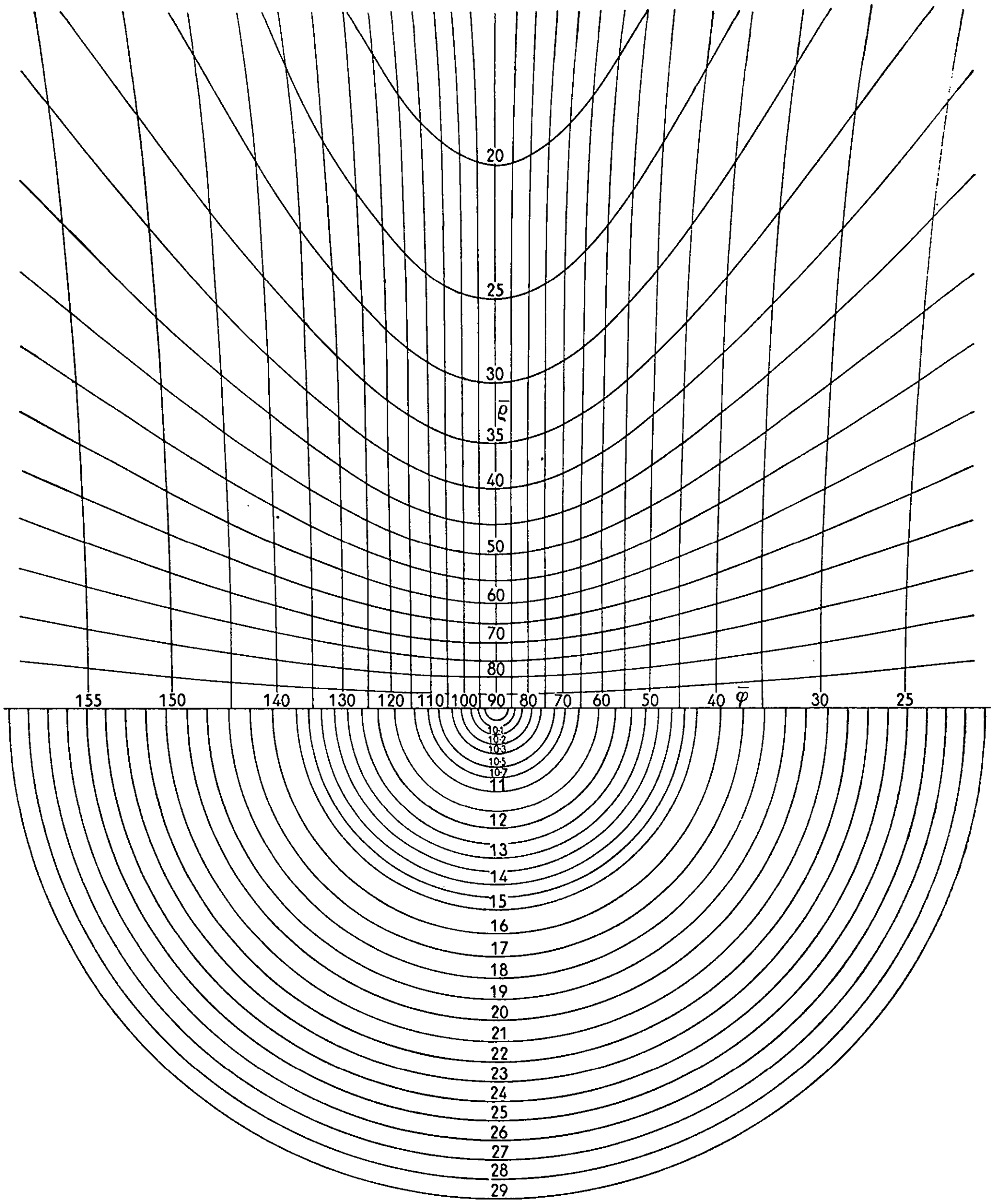

Fig. 3. A chart giving $\bar{\varrho}$, $\bar{\varphi}$ and R for a value of $s = +0{\cdot}02$.

done in the usual way from the direction cosines of the $\bar{X}$, $\bar{S}$, $\bar{V}$ axes relative to those of the X, S, V axes.

4. The *R*-chart

The locus of all points at a constant distance R from P intersects the Ewald sphere in a small circle about N. When projected from C on to the tangent plane at N this results in a circle. For each value of R greater than R_0 there is such a circle, and all these circles are concentric. In the lower half of Fig. 3 is shown such a set of circles corresponding to values of R for $s = +0{\cdot}02$. The values of R given in these circles may be converted into the usual units in reciprocal space (Å^{-1}) by multiplying by the factor $s/R_0\lambda$, where $R_0 = 10$ cm. and λ is expressed in Ångström units. The calculations necessary for constructing these circles are given in the Appendix.

5. The determination of *s*

The direction of the rel-vector OP (Fig. 1) is given by the angles i, ϱ^L and φ^L, and these can be found from the position on the photograph of the Laue spot. If the crystal is rotated through the Bragg setting for the relp P, the point P will intersect Σ at P' (Fig. 4).

The angles θ, ϱ^B and φ^B for the Bragg spot on the photograph may be read off. The relations between these angles are

$$\varrho^L = \varrho^B\,,$$
$$\sin i = \sin \varrho^L \sin \varphi^L\,,$$
$$\sin \theta = \sin \varrho^B \sin \varphi^B\,.$$

The ratio s may be evaluated from the relation

$$PN.PN' = PL.PO\,.$$

Dividing both sides of this equation by G^2 and substituting the values $PO/G = 2 \sin \theta$, $LO/G = 2 \sin i$, $PN/G = s$, we obtain

$$\begin{aligned} s(2+s) &= 4\,(\sin \theta - \sin i) \sin \theta \\ &= 4\,(\sin \theta - \sin \varrho^L \sin \varphi^L) \sin \theta\,. \end{aligned} \tag{1}$$

When $s \ll 1$ and P lies on the equator, this expression leads to

$$s \approx 2\,(\varphi^B - \varphi^L) \sin \theta \cos m\,,$$

where $m = \frac{1}{2}(\varphi^L + \varphi^B)$ and $(\varphi^B - \varphi^L)$ is the angle through which the crystal is turned in going from the Laue to the Bragg setting.

6. Use of the Laue spot to fix the position of the $\bar{\varrho}, \bar{\varphi}$-chart relative to the microphotometer diagram

To relate the systems of reference X, S, V and $\bar{X}, \bar{S}, \bar{V}$, the angles $\sigma = X\bar{X}$, $\omega = S\bar{S}$, $\chi = V\bar{V}$, are used (Figs. 1 and 2). From the triangles CPP_1 (Fig. 1) we obtain

$$\sin \chi = 2 \sin \theta \cos \varrho^L/(1+s)\,,$$

and from triangle CPO (Fig. 1)

$$\sin \sigma = 2 \sin \theta \cos i/(1+s)$$

or

$$\cos \sigma = \tfrac{1}{2}\{1+(1+s)^2 - 4 \sin^2 \theta\}/(1+s)\,.$$

The value of ω can be obtained from the right-sided spherical triangle $X\bar{X}\bar{S}$ of Fig. 2 by the relation

$$\cos \omega = \cos \sigma / \cos \chi\,.$$

Using these auxiliary angles and the known ϱ, φ-values for any rekha PQ, the required values of $\bar{\varrho}, \bar{\varphi}$ corresponding to the new axial system may be calculated from the equations

$$\left.\begin{aligned} \cos \bar{\varrho} &= \cos \chi \cos \varrho + \sin \chi \sin \varrho \sin (\varphi - \omega)\,, \\ \tan \bar{\varphi} &= \frac{-\sin \chi \cos \varrho + \cos \chi \sin \varrho \sin (\varphi - \omega)}{\sin \varrho \cos (\varphi - \omega)}\,. \end{aligned}\right\} \tag{2}$$

One particular rekha for which ϱ and φ are known is PL, corresponding to the Laue spot. For this rekha $\varrho = \pi - \varrho^L$ and $\varphi = \pi + \varphi^L$ and we calculate the corresponding $\bar{\varrho}$ and $\bar{\varphi}$ from the above formulae. From these values a particular point on the chart may be marked which corresponds with the Laue spot on the microphotometer diagram. This information, combined with the fact of the common equatorial direction of both chart and diagram, fixes their relation to one another.

7. Use of the Bragg spot to fix the position of the $\bar{\varrho}, \bar{\varphi}$-chart relative to the microphotometer diagram

The Bragg spot may be impressed on the photograph by rotating the crystal through the required angle from the Laue setting. The Bragg spot corresponds to the intersection with the Ewald sphere of the rekha PP' (Fig. 4). The coordinates of PP', $\varrho(P')$, $\varphi(P')$

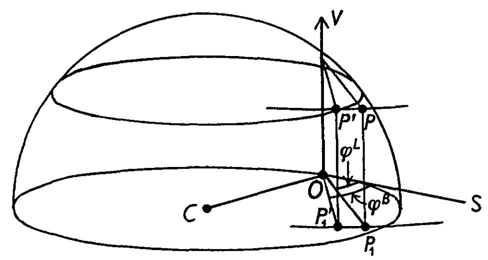

Fig. 4. Diagram showing the relation between the positions P, P' of the relp in the crystal settings corresponding to the diffuse and Bragg reflexions respectively.

relative to the axes X, S, V, are

$$\varrho(P') = \tfrac{1}{2}\pi,\ \varphi(P') = m + \tfrac{1}{2}\pi\,.$$

The values of $\bar{\varrho}(P')$ and $\bar{\varphi}(P')$ calculated from the equation (2) are as follows:

$$\left.\begin{aligned} \cos \bar{\varrho}(P') &= \sin \chi \cos (\omega - m)\,, \\ \tan \bar{\varphi}(P') &= \cos \chi \cot (\omega - m)\,. \end{aligned}\right\} \tag{3}$$

Where both the Bragg and Laue spots are registered on the film they may be used to check one another, but if strictly monochromatic radiation is used only the Bragg spot is available.

The determination of $\bar{\varrho}$ and $\bar{\varphi}$ for any rekha from the given values of ϱ and φ can be carried out graphically, as is indicated in Fig. 2. The accuracy may not be high enough and then the use of the equations in §§ 6 and 7 is preferable.

Where possible it is better to use equatorial spots because of the simplification of the formulae. The following equalities obtain for such spots:

$$k' = k'' = R_0/rs,\ \varrho^L = \varrho^B = \tfrac{1}{2}\pi,\ i = \varphi^L,\ \theta = \varphi^B,$$
$$\chi = 0,\ \omega = \sigma\,.$$

Often it is not possible to do what is required using only equatorial spots and it is more satisfactory to use the general expressions given here, rather than resort to special experimental devices for bringing all spots on to the equator in turn.

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APPENDIX

The construction of the $\bar{\varrho}$, $\bar{\varphi}$-chart

In Fig. 5 there is shown a central section of the Ewald sphere passing through the relp P, and containing the

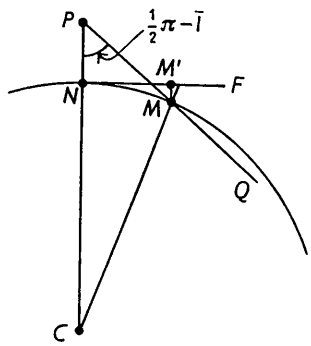

Fig. 5. Diagram showing the relation between the lengths $PM = R$, $PN = R_0$, $NM' = R'$ and $NC = G$.

rekha PQ. The angle CPQ is denoted $\frac{1}{2}\pi-\bar{\imath}$, and if PQ cuts Σ in M we have, from triangle CPM,

$$R^2-2R(G+R_0)\sin\bar{\imath}+R_0(2G+R_0) = 0\,. \qquad (4)$$

Thus, being given $\bar{\imath}$ and R_0/G, the value of R can be calculated. R_0 is taken for convenience in plotting as 10 cm.

The circle on the R-chart corresponding to a given value of R has a radius R', where

$$R' = R\cos\bar{\imath}\,. \qquad (5)$$

Thus R' corresponds to NM' in Fig. 5, where M' is the perpendicular projection of M on the tangent plane NF. Within the required accuracy, M' coincides with the projection of M from C on the tangent plane NF. To plot a point on the chart corresponding to particular value of $\bar{\varrho}$ and $\bar{\varphi}$ we first calculate $\bar{\imath}$ and an auxiliary angle $\bar{\psi}$ (Fig. 2) from the relations

$$\left.\begin{aligned}\sin\bar{\imath} &= \sin\bar{\varrho}\sin\bar{\varphi}\,,\\ \tan\bar{\psi} &= \tan\bar{\varrho}\cos\bar{\varphi}\,.\end{aligned}\right\} \qquad (6)$$

The polar coordinates of the required point are thus R', $\bar{\psi}$ and its Cartesian coordinates are $R'\sin\bar{\psi}$, $R'\cos\bar{\psi}$.

References

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The Symmetry of Real Periodic Two-Dimensional Functions

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The symmetry of real periodic functions is considered, taking into account reversal symmetry elements which relate one point to another where the function has the same magnitude but opposite sign. There are 46 reversal space groups in two dimensions, and 3 in one dimension, which contain one or more of such symmetry elements. The number in three dimensions is not yet known. Reversal space groups can be denoted by symbols analogous to those of the Hermann–Mauguin space-group notation.

1. Introduction

It is well known that a periodic function which can be represented by a Fourier series

$$f(x, y, z) = \sum_h\sum_k\sum_l F(hkl)\exp\left[-2\pi i(hx+ky+lz)\right] \quad (1)$$

can be represented in projection on a plane perpendicular to the z direction by

$$f_0(x, y) = \sum_h\sum_k F(hk0)\exp\left[-2\pi i(hx+ky)\right]\,. \quad (2)$$

In crystal-structure analysis, a number of investigators (Clews & Cochran, 1949; Dyer, 1951*a*, *b*; Raeuchle & Rundle, 1952) have made practical use of the properties of a related two-dimensional function,

$$f_L(x, y) = \sum_h\sum_k F(hkL)\exp\left[-2\pi i(hx+ky)\right]\,. \quad (3)$$