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On the X-ray Diffraction Patterns of Polymer Films

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Equations are derived which relate the angular spread of arcs in X-ray diagrams of oriented polymer films to the dispersion of the crystallites. A simple graphical method of measuring the dispersion is indicated, and the use of the equations in indexing reflexions and in checking the self-consistency of the interpretation of the X-ray diagram is pointed out.

1. Introduction

Polymer films usually show some degree of uniplanar orientation, i.e. the molecules tend to lie with their fibre axes in the planes of the films. In some cases stretched films have high uniplanar orientation, and also considerable orientation about the direction of stretching; such a film, when examined by X-rays with the beam parallel to the plane of the film, frequently gives a diffraction photograph in which the apparent orientation is better than can be readily obtained with fibre specimens of the same polymer. It is clear, however, that these X-ray photographs differ in several respects from rotation or fibre photographs, and a geometrical investigation is necessary before they can be fully interpreted. Such an investigation is attempted here. The angular position of a reflexion with reference to the equator of the diagram is first calculated for a single crystallite in terms of parameters which define the orientation of the crystallite and the polymer film. The reflexions in an X-ray photograph of a film or fibre are in general not spots, but are drawn out into arcs as a result of the imperfect orientation of the crystallites. We derive equations connecting the angular spread of these arcs with the dispersion of orientation.

The equations obtained may be used to calculate the dispersion of the crystallites from measurements of the lengths of equatorial arcs, and also to deduce ξ and ζ values from the reflexions. Comparison of the measured lengths of the various arcs with the values calculated from the dispersion gives a useful check on the self-consistency of the interpretation of the X-ray diagram, and may enable a decision to be made as to whether all the reflexions originate from the same crystalline phase.

Throughout this paper we shall assume that a flat photographic plate, perpendicular to the primary beam is used. The results could easily be extended to cylindrical or conical films.

2. Specification of orientation

Consider a plane through the 'fibre axis' of any crystallite, perpendicular to the polymer film. The angle φ between this plane and the direction of orientation (i.e. of rolling or stretching) is defined as the 'in plane' disorientation of the particular crystallite. The 'out of plane' disorientation, ψ, is the angle between the plane of the film, and a plane through the fibre axis which intersects the film in a straight line perpendicular to the direction of orientation. In this way φ, ψ are defined symmetrically, and equations derived for the diagram obtained with the beam passing through the edge of the film may be transformed into relations which hold for the beam normal to the film by interchanging φ and ψ (with an appropriate change of sign). To define the signs of φ and ψ we consider the film edge-on to the beam, with the direction of orientation vertical. We count φ and ψ positive if the upper half of a crystallite is nearer the X-ray plate, and if it is to the right of the film looking along the primary beam.

For some purposes it is convenient to consider the X-ray diagrams of films which have been rotated about a vertical axis. The angle between the primary beam and the plane of the film will be called μ, which will be positive if the rotation appears clockwise from above. We shall also have occasion to consider reflexions from films which are tilted about a horizontal axis perpendicular to the primary beam. The angle of tilt will be called ν, and will be subject to the same sign convention as φ.

The position of a spot in the X-ray diagram is specified (for given θ) by the angle χ which the line joining it to the primary spot makes with the right-hand side of the equator. In the following pages χ will be calculated as a function of φ, ψ for different positions of the film. Unless otherwise stated, the direction of orientation will be assumed vertical.

3. Equatorial reflexions

(a) *Film edge-on to X-ray beam* ($\mu = 0$, $\nu = 0$), *and* $\psi = 0$.

Fig. 1 shows the sphere of reflexion in reciprocal space, centre M, radius unity. The primary beam

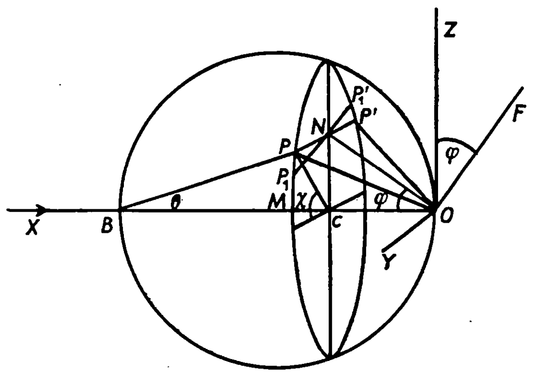

Fig. 1. Sphere of reflexion, $\mu = \nu = 0$; equatorial reflexions.

enters the sphere at B and emerges at O, the origin of the reciprocal lattice. OF is the axis of rotation of the reciprocal lattice of a crystallite corresponding to rotation about its fibre axis, and the plane $PP'O$, normal to OF, is the zero layer of the lattice. We consider one lattice point P, which lies in the plane $PP'O$ and would therefore give an equatorial reflexion in a perfectly oriented specimen. If P is in a reflecting position it must lie on the sphere of reflexion, with $OP = \lambda/d = 2\sin\theta$. The locus of P is therefore a circle $PP_1P'P_1'$, centre C, formed by intersection of the sphere with the plane through P normal to MO. P, P' are two reflecting positions of a lattice point of a crystallite with an in-plane disorientation φ; CN is normal to PP', and obviously $N\hat{O}C = \varphi$.

Since $P\hat{B}O = \theta$ and $B\hat{P}O = \frac{1}{2}\pi$, $BP = 2\cos\theta$, $BC = 2\cos^2\theta$ and $OC = 2\sin^2\theta$; also $CP = 2\sin\theta\cos\theta$. Now $CN = OC\tan\varphi = CP\sin\chi$, hence $2\sin^2\theta\tan\varphi = 2\sin\theta\cos\theta\sin\chi$, or

$$\sin\chi = \tan\theta\tan\varphi\,. \tag{1}$$

This is the required relation between χ and θ, φ.

(b) *General case for film edge-on to beam* ($\mu = 0$, $\nu = 0$)

The problem is to calculate χ, or in other words the positions of P, $P'(P_1, P_1')$, when the crystallite is given an out-of-plane disorientation ψ. It is convenient to take a set of rectangular Cartesian axes with the incident beam as the negative direction of OX, and with OZ in the direction of stretching. The plane through BO containing OF will make an angle ψ with OZ, consequently the plane through O normal to OF cuts the plane OYZ in a line which will make an angle ψ with OY. The points P_1, P_1' lie in this plane. The equation of the plane $PP'O$ is obviously $z = x\tan\varphi$, and that of plane $P_1P_1'O$ is therefore

$$z = x\tan\varphi - y\tan\psi\,. \tag{2}$$

Now the coordinates of P_1 are OC, $CP\cos\chi$, $CP\sin\chi$ or

$$2\sin^2\theta,\ 2\sin\theta\cos\theta\cos\chi,\ 2\sin\theta\cos\theta\sin\chi\,. \tag{3}$$

Substitution of these into (2) gives

$$\sin\chi + \cos\chi\tan\psi = \tan\theta\tan\varphi\,, \tag{4}$$

from which we obtain

$$\chi = \sin^{-1}(\tan\theta\tan\varphi\cos\psi) - \psi\,. \tag{5}$$

The two values of χ found from (5) refer to the reflexions on the right and left of the diagram.

(c) *General case when the film has been rotated about a vertical axis*

This case is of possible practical importance because, as will be shown later, rotation of the specimen about a vertical axis can shorten the equatorial reflexions of specimens with imperfect orientation. It is most simply considered by allowing the sphere of reflexion to rotate through $-\mu$ about OZ. We require to calculate the points of intersection P_2, P_2' of the circle, centre C, in the new position with the plane (2). The coordinates of C will be $2\sin^2\theta\cos\mu$, $2\sin^2\theta\sin\mu$, 0, hence those of P_2 will be given by

$$\left.\begin{aligned} x &= 2\sin^2\theta\cos\mu - 2\sin\theta\cos\theta\sin\mu\cos\chi\,,\\ y &= 2\sin^2\theta\sin\mu + 2\sin\theta\cos\theta\cos\mu\cos\chi\,,\\ z &= 2\sin\theta\cos\theta\sin\chi\,. \end{aligned}\right\} \tag{6}$$

Substitution of these into (2) yields the equation

$$\sin\chi + u\cos\chi = v\tan\theta\,, \tag{7}$$

where

$$\left.\begin{aligned} u &= \tan\varphi \sin\mu + \tan\psi \cos\mu\,, \\ v &= \tan\varphi \cos\mu - \tan\psi \sin\mu\,. \end{aligned}\right\} \tag{8}$$

The solution of (7) is

$$\sin\chi = \frac{v\tan\theta \pm u(1+u^2-v^2\tan^2\theta)^{\frac{1}{2}}}{1+u^2}\,, \tag{9}$$

which gives χ as a function of $\varphi, \psi, \mu, \theta$. We may note that if $\mu = 0$, then $u = \tan\psi$ and $v = \tan\varphi$, and equation (9) reduces to (5). It is obvious that (7) and (9) have real solutions if, and only if,

$$1+u^2 \geqslant v^2 \tan^2\theta\,. \tag{10}$$

If this does not hold there will be no reflexion from the set of planes under consideration in this particular orientation.

4. Discussion and application of results for equatorial reflexions

The previous results may be useful in practice for at least two distinct purposes: they may be used to find the most advantageous position of the specimen for resolving near equatorial reflexions—this entails calculating the values of μ for which the spread of the arcs is a minimum—and they permit calculation of the dispersion of the orientation of the crystallites in the film.

(a) The most advantageous position of the specimen

We consider two cases: φ and ψ may take all values between $\pm\varphi_0$ and $\pm\psi_0$ respectively, or the fibre axis may take up all positions within an elliptical cone with greatest in-plane and out-of-plane disorientations φ_0 and ψ_0 respectively. We begin by considering the first case.

Equating to zero $(\partial\chi/\partial\varphi)_{\psi,\theta,\mu}$, obtained by partial differentiation of (7), gives

$$\cos\chi = \tan\theta \cot\mu\,, \tag{11}$$

from which, by substitution into (7), we obtain

$$\cos\psi \sin\mu = \sin\theta\,. \tag{12}$$

Hence for given μ, θ and ψ, χ is a monotonic function of φ, since in general ψ, μ, θ will not satisfy (12); if they do satisfy (12) in any special case, χ is independent of φ. As a consequence of (12) there exists for given ψ, θ a value of μ at which the reflexions arising from all values of φ coincide. For $\psi = 0$ this value is $\mu = \theta$, and the arc corresponding to this value of θ contracts to a spot on the equator. Similar considerations apply to χ as a function of ψ for given μ, θ, φ; χ becomes independent of ψ at a value of μ given by

$$\cos\varphi \cos\mu = \sin\theta\,, \tag{13}$$

and is determined from

$$-\cos\chi = \tan\theta \tan\mu\,. \tag{14}$$

Equation (14) shows that μ is negative in this case for the right-hand reflexion. A comparison of (11) and (14) reveals that these equations cannot be satisfied simultaneously, since $\theta \neq 0$; it follows that there is no value of μ at which both $\partial\chi/\partial\varphi = 0$ and $\partial\chi/\partial\psi = 0$ are satisfied simultaneously. These considerations show that the length of the arc in the X-ray diagram is determined by two of the positions $\pm\varphi_0$, $\pm\psi_0$. For values of μ between those given by (12) and (13) (with φ, ψ replaced by φ_0, ψ_0) the extremities of the arc correspond to $\varphi_0, -\psi_0$, and $-\varphi_0, \psi_0$, and outside this range of μ to φ_0, ψ_0, and $-\varphi_0, -\psi_0$. The semi-angle subtended by the arc may therefore be calculated from (7), (8) or (9) with values of φ_0, ψ_0 of the appropriate sign inserted. These points are illustrated by Fig. 2, in which χ is plotted as a function

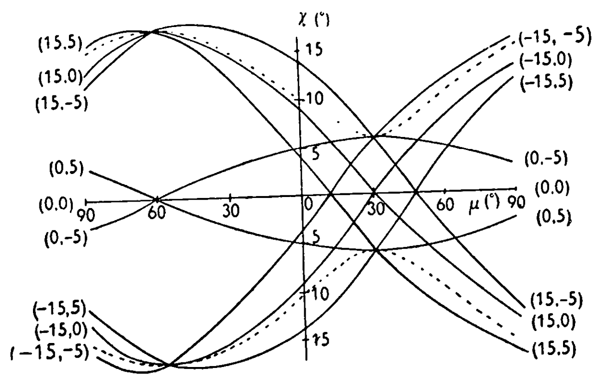

Fig. 2. Variation of χ with μ for $\theta = 30°$ and values of (φ, ψ) indicated. Broken line: $\chi_{\text{ell.}}$.

of μ for $\theta = 30°$, and $\varphi = 0°$ or $\pm 15°$, $\psi = 0°$ or $\pm 5°$. We see for example that if $\psi_0 = 5°$ the equatorial reflexion has a minimum spread ($2\chi = 11°\,40'$) for $\mu = 30°\,8'$.

In the case of the elliptical distribution of the directions of the fibre axes, the extreme positions can be written as follows:

$$\left.\begin{aligned} \tan\varphi &= \tan\varphi_0 \cos\eta\,, \\ \tan\psi &= \tan\psi_0 \sin\eta\,. \end{aligned}\right\} \tag{15}$$

We require to determine the value of η which makes χ a maximum. We consider in detail $\mu = 0$. Substituting the values of $\tan\varphi$ and $\tan\psi$ from (15) into (4), and equating to zero $(\partial\chi/\partial\eta)_{\varphi_0,\psi_0,\theta}$ obtained by partial differentiation of the resulting equation, we obtain

$$\tan\eta = -\frac{\tan\psi_0 \cos\chi}{\tan\varphi_0 \tan\theta}\,. \tag{16}$$

Using this value of η, we get from (4)

$$\sin^2\chi_{\text{ell.}} = \tan^2\theta \tan^2\varphi_0 \cos^2\psi_0 + \sin^2\psi_0 \tag{17}$$

in which $\chi_{\text{ell.}}$ is the required semi-angle subtended by the arc. If $\mu \neq 0$, a similar argument leads to the equation

$$\begin{aligned} \sin^2\chi_{\text{ell.}} = {} & \tan^2\varphi_0 (\cos\mu \tan\theta - \sin\mu \cos\chi_{\text{ell.}})^2 \\ & + \tan^2\psi_0 (\sin\mu \tan\theta + \cos\mu \cos\chi_{\text{ell.}})^2\,. \end{aligned} \tag{18}$$

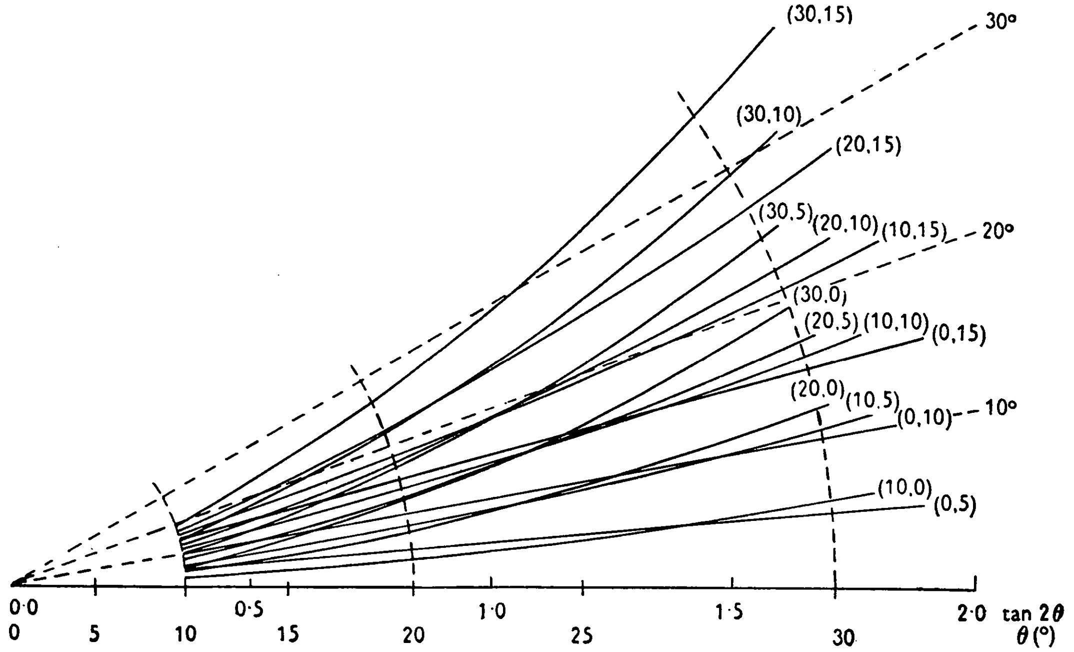

Fig. 3. Angular spread of equatorial reflexions for values of (φ_0, ψ_0) indicated. Rectangular distribution, $\mu = 0$.

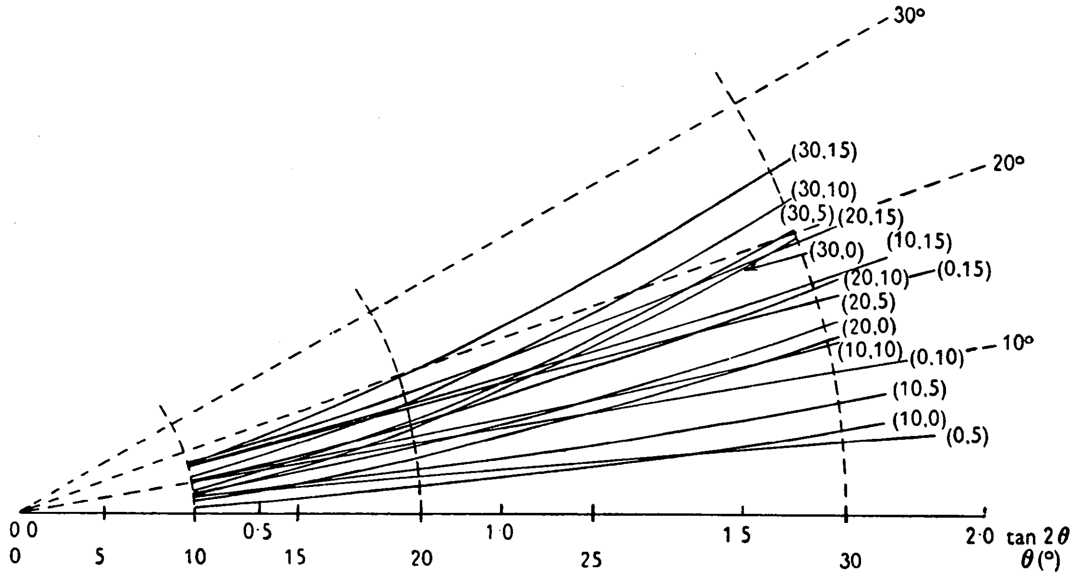

Fig. 4. Angular spread of equatorial reflexions for values of (φ_0, ψ_0) indicated. Elliptical distribution, $\mu = 0$.

The extreme values of $\chi_{\text{ell.}}$ as μ is varied are obtained by equating to zero $(\partial\chi_{\text{ell.}}/\partial\mu)_{\varphi_0,\psi_0,\theta}$, derived from (18). The resulting equation has two solutions, which are those of equations (12) and (13) with φ, ψ replaced by φ_0, ψ_0, and the corresponding values of $\chi_{\text{ell.}}$ are given by (11) and (14). The minimum value of $\chi_{\text{ell.}}$ is given by (11) if $\varphi_0 > \psi_0$ and by (14) if $\varphi_0 < \psi_0$. For $\varphi_0 = \psi_0$, $\chi_{\text{ell.}}$ is obviously independent of μ.

Values of $\chi_{\text{ell.}}$ for $\varphi_0 = 15°$, $\psi_0 = 5°$ are also plotted against μ in Fig. 2 (broken line).

(b) *Calculation of dispersion of crystallites*

In principle it is possible to calculate φ_0, ψ_0 from the values χ', χ'' for two equatorial reflexions, θ', θ''. For $\mu = 0$, we have from (4) (remembering that for the 'rectangular' distribution the extremes of the arc correspond to φ_0, $-\psi_0$)

$$\left.\begin{aligned} \tan\varphi_0 &= \frac{\sin(\chi'-\chi'')}{\tan\theta'\cos\chi''-\tan\theta''\cos\chi'}, \\ \tan\psi_0 &= \frac{\tan\theta'\sin\chi''-\tan\theta''\sin\chi'}{\tan\theta'\cos\chi''-\tan\theta''\cos\chi'}. \end{aligned}\right\} \tag{19}$$

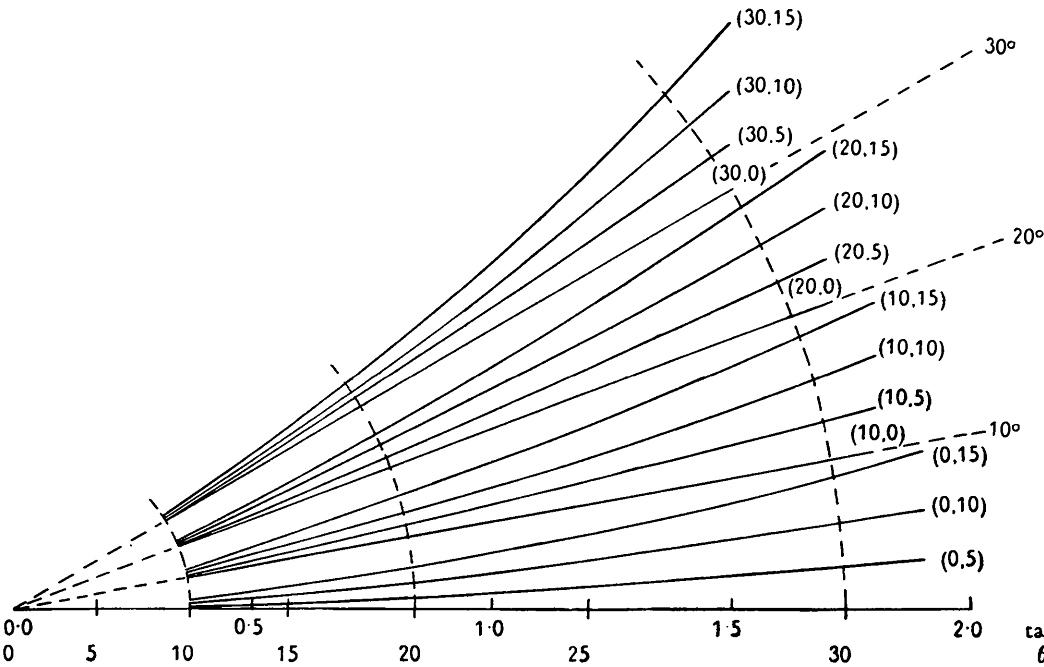

Fig. 5. Angular spread of equatorial reflexions for values of (φ_0, ψ_0) indicated. Rectangular distribution, $\mu = \frac{1}{2}\pi$

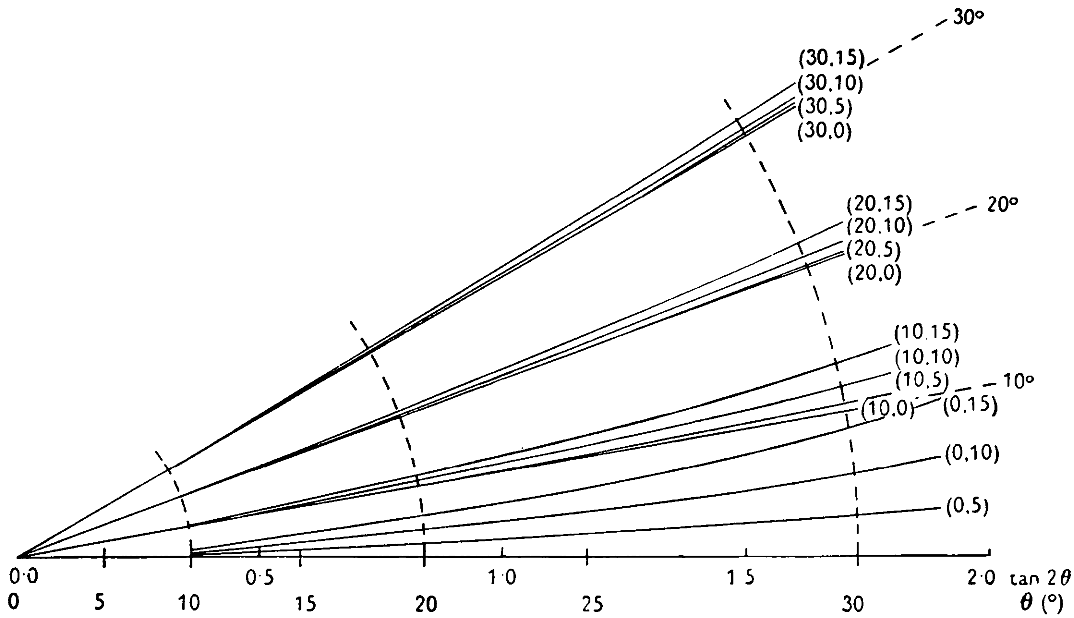

Fig. 6. Angular spread of equatorial reflexions for values of (φ_0, ψ_0) indicated. Elliptical distribution, $\mu = \frac{1}{2}\pi$.

For the elliptical distribution the corresponding equations are

$$\tan^2\varphi_0 = \frac{\cos^2\chi'' - \cos^2\chi'}{\tan^2\theta' \cos^2\chi'' - \tan^2\theta'' \cos^2\chi'},$$
$$\tan^2\psi_0 = \frac{\tan^2\theta' \sin^2\chi'' - \tan^2\theta'' \sin^2\chi'}{\tan^2\theta' \cos^2\chi'' - \tan^2\theta'' \cos^2\chi'}. \tag{20}$$

In well oriented films ψ_0 may be quite small. In such cases it will be advantageous to determine φ_0 by observations with the beam normal to the film, i.e. with $\mu = \frac{1}{2}\pi$. If ψ_0 is sufficiently small it follows from (9) or (18) that $\chi = \varphi_0$, from which φ_0 is found immediately. Returning now to the edge-on position, we see from equation (5) that for small ψ_0 and the rectangular distribution

$$\psi_0 = \chi - \sin^{-1}(\tan\theta \tan\varphi_0). \tag{21}$$

For the elliptical distribution we have, with the same approximation, from (17)

$$\sin^2 \psi_0 = \sin^2 \chi_{\text{ell.}} - \tan^2 \theta \tan^2 \varphi_0 . \qquad (22)$$

Even for values of ψ_0 as large as 15°, the error in χ introduced by the use of the approximate equations (21), (22) is less than 1° for values of φ_0, θ up to 30°.

Values of φ_0, ψ_0 may also be found from the equations relating these quantities with χ, θ, μ by graphical methods. Figs. 3 and 4 show the spread of equatorial reflexions as functions of θ for a number of φ_0, ψ_0 combinations, and $\mu = 0$. A circle described with the origin as centre, and of radius $\tan 2\theta$ cuts the relevant curve at a point which shows the limit of the arc. In other words the line joining this point to the origin makes an angle χ with the horizontal. These graphs if reproduced on transparent paper on a suitable scale can be superimposed on an X-ray diagram, and the values of φ_0, ψ_0 which give the best fit with the equatorial reflexions read off directly. Since certain combinations of φ_0, ψ_0 may be difficult to distinguish, it is advantageous to use also a second X-ray diagram taken with $\mu = \frac{1}{2}\pi$. The corresponding graphs for this case are given in Figs. 5, 6. A glance at these diagrams shows that combinations of φ_0, ψ_0 which are not resolved with $\mu = 0$, are easily distinguished when $\mu = \frac{1}{2}\pi$ and vice versa.

5. (*hkl*) reflexions

In general the line joining the reciprocal-lattice point P to the origin will not be perpendicular to the fibre axis, but will make an angle Δ with the latter. This angle may be calculated from the general expression

$$\frac{c^2}{l^2} \cos^2 \Delta \left[\Sigma \frac{h^2}{a^2} \sin^2 \alpha - 2 \Sigma \frac{hk}{ab} (\cos \gamma - \cos \alpha \cos \beta) \right] = 1 - \Sigma \cos^2 \alpha + 2 \cos \alpha \cos \beta \cos \gamma , \qquad (23)$$

in which α, β, γ, are the angles of the unit cell, and the fibre axis is assumed to be the c axis. Fig. 7 shows

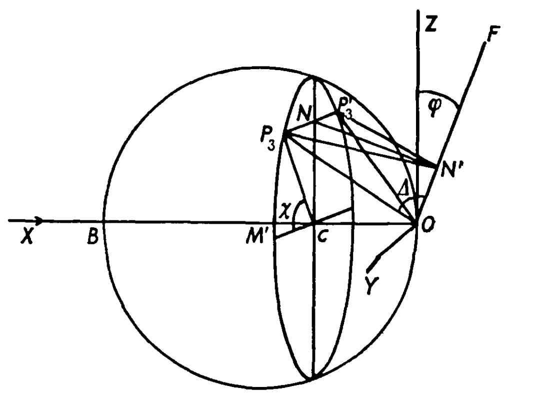

Fig. 7. Sphere of reflexion, $\mu = \nu = 0$; (*hkl*) reflexions.

the case for which $\psi = 0$ and $\mu = 0$; P_3, P_3' are reflecting positions of P, and P_3N', NN', $P_3'N'$ are perpendiculars from P_3, N, P_3' respectively to the 'fibre axis' OF. For all positions of P, ON' $(= \zeta) = 2 \sin \theta \cos \Delta$. Thus the plane $P_3P_3'N'$ is always parallel to the plane $PP'O$ of Fig. 1; if $\psi \neq 0$ the corresponding plane will be parallel to $P_1P_1'O$ (Fig. 1) whatever the values of φ, ψ may be. The distance between the two planes is always $2 \sin \theta \cos \Delta$. The plane $PP'O$ is given by equation (2), hence the parallel plane through N' is

$$\frac{z - x \tan \varphi + y \tan \psi}{(1 + \tan^2 \varphi + \tan^2 \psi)^{\frac{1}{2}}} = 2 \sin \theta \cos \Delta . \qquad (24)$$

In the general case, in which the sphere is rotated about OZ through $-\mu$, the coordinates of P_4 (the reflecting position of P) will be given by (6). Substitution of these into (24) again gives equation (7), but with

$$u = \tan \varphi \sin \mu + \tan \psi \cos \mu ,$$
$$v = \tan \varphi \cos \mu - \tan \psi \sin \mu + \frac{\cos \Delta}{\sin \theta} (1 + \tan^2 \varphi + \tan^2 \psi)^{\frac{1}{2}} . \qquad (25)$$

Thus χ is again given by equation (9), with the above definitions of u, v. We may note that u has the same value as in (8) but v contains an additional term, which of course vanishes when $\Delta = \frac{1}{2}\pi$, in which case the equations reduce to those of § 3.

By an argument similar to that leading to equations (11), (12) we may show that χ is not necessarily a monotonic function of φ and ψ. Thus the extremities of the arc need not correspond to the extreme positions of the fibre axis; the general equations for the extent of the arc are unmanageably complicated.

However we can show that for small ψ_0 and $\mu = 0$, useful expressions for the limits of the arc can still be obtained, and we shall only consider this case.

In the first place if $\psi_0 = 0$

$$\sin \chi = \tan \theta \tan \varphi + \cos \Delta / (\cos \theta \cos \varphi) , \qquad (26)$$

and χ determined from this equation has a minimum for a value of φ given by

$$\sin \varphi = -\sin \theta / \cos \Delta . \qquad (27)$$

Two cases arise, therefore, according to whether φ_0 is greater or less than $|\varphi|$ determined from (27). If φ_0 is less than this value, then χ is a monotonic function of φ, and the arc extends between χ values corresponding to $\pm\varphi_0$. In the other case the upper extremity of the arc (assuming that the latter does not extend to the meridian) still corresponds to $+\varphi_0$, but the lower extremity is determined by the crystallite for which φ is given by (27). The corresponding value of χ is $\cos^{-1} (\sin \Delta / \cos \theta)$.

For small ψ, when $\cos \psi$ may be taken as unity, we have from (7) and (25)

$$\sin (\chi + \psi) = \tan \theta \tan \varphi + \cos \Delta / (\cos \theta \cos \varphi) . \qquad (28)$$

It can be shown that the crystallite giving the minimum value of χ has a φ value still determined by (27) with an error of the order of ψ^2. The same two cases will therefore arise as for $\psi_0 = 0$, and it follows from (28) that the effect of a finite ψ_0 is to lengthen the arc by ψ_0 at each end.

If the indexing of a reflexion is uncertain the above equations may be used to calculate its ζ value. Since

$$\zeta = 2 \sin \theta \cos \Delta\,, \tag{29}$$

χ may readily be expressed in terms of ζ from the appropriate equations given above. Thus ζ may be evaluated from measurements of the positions of the extremities of the arcs. In practice it is of course desirable that these should be well defined, and the limitation on the value of ψ_0 mentioned above must be remembered.

We now consider the case in which a reflexion extends to the meridian. The general condition for this to occur is, from (7),

$$v \tan \theta = 1\,. \tag{30}$$

For $\mu = 0$ and $\psi_0 = 0$, this reduces to

$$\varphi = \Delta - \theta\,; \tag{31}$$

if $\Delta > \theta$ the value of φ obtained from this equation gives the minimum value of φ_0 which will allow the arc to touch the meridian. For small ψ_0 the corresponding value of φ_0 differs from that given in (31) only by quantities of order ψ_0^2. In the general case for the rectangular distribution (and $\mu = 0$) it follows from (25) and (30) that (hkl) reflexions will touch at the meridian or overlap if

$$\cos \Delta (1+\cos^2 \varphi_0 \tan^2 \psi_0)^{\frac{1}{2}} \geqslant \cos(\theta+\varphi_0)\,. \tag{32}$$

From (10) the condition that there should be a reflexion from the planes under consideration is

$$\cos \Delta (1+\cos^2 \varphi_0 \tan^2 \psi_0)^{\frac{1}{2}} \leqslant \cos \theta \cos \varphi_0 \cos \psi_0 + \sin \theta \sin \psi_0\,. \tag{33}$$

If $\psi_0 = 0$, this equation gives, for the least value of Δ which will give a reflexion for a given φ_0,

$$\Delta = \theta - \varphi_0\,. \tag{34}$$

This is identical with (31) with $\varphi = -\varphi_0$; hence the reflexion corresponding to the minimum value of Δ will be a meridional spot. It is easily shown that this is also true for $\psi_0 \neq 0$.

For the elliptical case the equations corresponding to (32) and (33) are identical with the latter with $\psi_0 = 0$, so long as $\varphi_0 > \psi_0$.

6. Meridional (00*l*) reflexions and polar arcs

It is easily shown from the equations of the preceding section that for planes with $\Delta = 0$

$$\tan \chi = 1/u\,. \tag{35}$$

Thus when $\mu = 0$ we have the physically obvious simple relation

$$\chi = \tfrac{1}{2}\pi - \psi\,. \tag{36}$$

For positions of the fibre axis between $\pm\varphi_0$, $\pm\psi_0$ the spread of the meridional reflexion is $2\psi_0$; from equation (5) we see that the spread of the equatorial reflexion is $2[\psi_0 + \sin^{-1}(\tan \theta \tan \varphi_0 \cos \psi_0)]$, and is therefore greater than that of the meridional arc, except for the trivial cases $\varphi_0 = 0$, $\theta = 0$, $\psi_0 = \frac{1}{2}\pi$. If ψ_0 has been determined by one of the methods described earlier, measurement of the spread of a 'meridional' reflexion obviously provides an effective check that the latter is a genuine meridional reflexion.

If a polar arc has a greater spread than would be expected from the spread of the equatorial reflexions, it may not be a true single $(00l)$ reflexion. In this case resolution into two or more spots may be possible by tilting the film through an angle ν about a horizontal axis perpendicular to the primary beam. By methods similar to those employed in § 5 it may be shown that the resulting value of χ corresponding to given φ, ψ, ν is still given by equation (7), if, for $\mu = 0$, u, v are defined by (37):

$$\left.\begin{aligned} u &= \tan \psi \cos \varphi / \cos(\varphi+\nu)\,, \\ v &= \tan(\varphi+\nu) + \frac{\cos \Delta}{\sin \theta} \frac{\cos \varphi}{\cos(\varphi+\nu)} \\ &\qquad \times (1+\tan^2 \varphi + \tan^2 \psi)^{\frac{1}{2}}\,. \end{aligned}\right\} \tag{37}$$

The corresponding equations for $\mu = \frac{1}{2}\pi$ are obtained by writing φ for ψ, and $-\psi$ for φ in (37).

We now investigate the conditions which must hold if a polar arc is to be resolvable by tilting the specimen in this way. The condition that two arcs touch at the meridian is given by (30), which after substitution of v from (37) becomes (for the rectangular distribution):

$$\cos^2 \Delta (1+\cos^2 \varphi_0 \tan^2 \psi_0) = \cos^2(\theta+\varphi_0+\nu)\,. \tag{38}$$

The arcs will overlap if the left-hand side of (38) is greater than the right. Resolution will be possible if a value of ν exists such that

$$\cos^2 \Delta (1+\cos^2 \varphi \tan^2 \psi) < \cos^2(\theta+\varphi+\nu) \tag{39}$$

for all values of φ between $\pm\varphi_0$, and of ψ between $\pm\psi_0$. Consideration of this equation shows that it is most easily satisfied at $\nu = -\theta$, i.e. if the polymer film is tilted at the Bragg angle, in which case (39) reduces to

$$\tan^2 \Delta > \tan^2 \varphi_0 + \tan^2 \psi_0\,. \tag{40}$$

A polar arc which is not resolved at this value of ν cannot be resolved at all.

The corresponding condition for the elliptical case may be derived from (38) and (40) by putting $\psi_0 = 0$ in these equations, provided $\varphi_0 > \psi_0$, i.e. a polar arc can be resolved if $\Delta > \varphi_0$.

The preceding equations may be used to calculate the largest arc which is not resolvable. An equation similar to (40), but having an equality sign, applies to this arc. Two distinct cases arise as in § 5, characterised by the same conditions, and we assume as before that ψ_0 is small. In the first, substitution of Δ from the above equality into equation (25) with $\mu = 0$ (which is the same as (37) with $\nu = 0$) gives values of u and v, from which, by equation (7), we obtain for the lower extremity

$$\sin(\chi+\psi_0) = \cos\psi_0 \tan\varphi_0 \tan\theta + \cos\psi_0/\cos\theta\,. \quad (41)$$

The corresponding equation for the second case is

$$\cos(\chi+\psi_0) = \frac{1}{\cos\theta}\left\{\frac{\tan^2\psi_0+\tan^2\psi_0}{1+\tan^2\varphi_0+\tan^2\varphi_0}\right\}^{\frac{1}{2}}. \quad (42)$$

An arc which is longer than would be expected from (41) or (42) therefore cannot be a single reflexion.

Finally, it is perhaps worth pointing out that the equations relevant to specimens with fibre orientation may be deduced from the equations given in this paper for the elliptical distribution, with $\varphi_0 = \psi_0$.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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On the crystal structure of guanidinium bromate.

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In an early X-ray investigation of guanidinium iodide by Theilacker (1935) an improbably small value, 1·18 Å, was reported for the C–N distance in the guanidinium ion. Raman spectra indicate a distance of 1·33 Å (Kellner, 1941).

In order to obtain other X-ray evidence on the structure of the guanidinium ion we attempted to find a guanidinium salt which would allow a simple X-ray determination of its structure by heavy-atom techniques and Fourier syntheses of projections. From among several salts the bromate was selected for further investigation bocauso of its flat unit cell.

Guanidinium bromate, $C(NH_2)_3BrO_3$, *seems* to be monoclinic with

$$a = 3{\cdot}77,\ b = 33{\cdot}46,\ c = 9{\cdot}11\ \text{Å};\ \beta = 99^\circ\,.$$

The density is 2·16 g.cm.$^{-3}$, requiring 8 molecules per unit cell. It forms twins with common a and b axes, but different c axes. Since reflexions hkl were observed only for $h+k = 2n$, it was assumed that the C face (001) is centred. A Patterson synthesis of the [100] projection excluded the presence of m or 2, leaving Cc as the only possible monoclinic space group. The presence of the weak reflexions 001 and 005, however, is in contradiction with this space group. This means that the crystals are not actually monoclinic but triclinic. This again is in contradiction with the equality $F^2_{hkl} = F^2_{h\bar{k}l}$, which was observed without any exception on the zero-, first- and second-layer-line Weissenberg photographs about the a axis. The discrepancy can be explained either by assuming that the deviation from monoclinic symmetry is too small to cause an appreciable difference between F^2_{hkl} and $F^2_{h\bar{k}l}$ or by a second twinning, such that each reflexion hkl of one of the twins coincides with $h\bar{k}l$ of the other.

Tentatively rejecting the second possibility, the position of the bromine atoms could be easily found from the [100] Patterson projection and a generalized Patterson projection (Cochran & Dyer, 1952) based on the $1kl$ reflexions. The configuration of these atoms was in agreement with the space group Cc; in addition to this it showed centres of symmetry in the [100] projection. By application of the vector convergence method (Beevers & Robertson, 1950), a triangular guanidinium ion and the three oxygen atoms of the BrO_3-ion appeared in the [100] projection. As a first approximation it was then assumed that the whole structure belongs to the space group Cc and that its [100] projection is centrosymmetrical. A Fourier refinement of the atomic coordinates led to a reliability factor $\Sigma||F_o|-|F_c||\div\Sigma|F_o|$ of 0·16 for the $0kl$ structure factors. Assuming a flat trigonal guanidinium ion, a C–N distance of 1·34 Å could be deduced with reasonable certainty from the final Fourier synthesis (estimated probable error 0·04 Å).

Attempts to account for the observed reflexions 001 and 005, such that for no hkl the deviation from the equality $F^2_{hkl} = F^2_{h\bar{k}l}$ would exceed the experimental errors, were not successful. It was concluded that a small deviation from monoclinic symmetry exists, which is masked by an approximately 50–50% twinning. Since we were not successful in obtaining single crystals, a further refinement of the atomic coordinates had to be abandoned.

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