

- FINK, M. & KESSLER, J. (1966). *Z. Physik*, **196**, 504.
 GLAUBER, R. & SCHOMAKER, V. (1953). *Phys. Rev.* **89**, 667.
 HILGNER, W. & KESSLER, J. (1965). *Z. Physik*, **187**, 119.
 HOERNI, J. A. (1962). In *International Tables for X-Ray Crystallography*. Vol. III. p.222. Birmingham: Kynoch Press.
 IBERS, J. A. (1958). *Acta Cryst.* **11**, 178.
 IBERS, J. A. & HOERNI, J. A. (1954). *Acta Cryst.* **7**, 405.
 LENZ, F. (1954). *Z. Naturforschung*, **9a**, 185.
 LIPPERT, W. (1956). *Optik*, **13**, 506.
 LIPPERT, W. (1958). *Z. Naturforschung*, **13a**, 273, 1089,
 LIPPERT, W. (1964). Third Europ. Conf. Electron Micr., Prag. Proc. p. 19.
 MOLIÈRE, G. (1947). *Z. Naturforschung*, **2a**, 133.
 MOTT, N. F. & MASSEY, H. S. (1965). *The Theory of Atomic Collisions*, London: Oxford Univ. Press.
 ZEITLER, E. & BAHR, G. F. (1964). Third Europ. Conf. Electron Micr., Prag, Proc. p.17.
 ZEITLER, E. & OLSEN, H. (1964). *Phys. Rev.* **136**, A, 1546.
 ZEITLER, E. & OLSEN, H. (1967). In Vorbereitung.

Acta Cryst. (1968). **A24**, 93

The Effect of Preferred Orientation on the Intensity Distribution of (hk) Interferences*

BY W. RULAND AND H. TOMPA

Union Carbide European Research Associates, S.A., Brussels 18, Belgium

(Received 20 March 1967)

The X-ray scattering produced by a distribution of two-dimensional lattices with preferred orientation, a problem which arises *e.g.* in the study of anisotropic structures of non-graphitic carbons, is given a rigorous theoretical treatment for infinite and perfect lattices and approximations are given for finite and imperfect lattices as well as for structures with partial positional correlations. As an example of the application, the observed intensity distributions of (hk) interferences of a highly oriented carbon fiber are compared with calculated intensity distributions.

1. Introduction

The intensity diffracted by a two-dimensional lattice is represented in reciprocal space by a periodic array of parallel rod-like intensity distributions. A random distribution of such lattices produces the asymmetric interference lines first discussed by von Laue (1932) for infinitely large and perfect lattices, for which one obtains for given s_h

$$I(s) = \frac{1}{2\pi s \sqrt{(s^2 - s_h^2)}} \quad \text{for } s > s_h$$

$$= 0 \quad \text{for } s < s_h$$

or

$$I(s) = \text{Re} \frac{1}{2\pi s \sqrt{(s^2 - s_h^2)}}, \quad (1)$$

where $I(s)$ is the intensity as a function of the absolute value s of the reciprocal space vector \mathbf{s} ($s = 2 \sin \theta / \lambda$) and s_h is the distance of the rod of index $h (= hk)$ from the origin of reciprocal space; Re means the real part. The intensity along the rod is considered to be unity. Warren (1941), Wilson (1949), Brindley & Méring (1951), Warren & Bodenstein (1966) and Ruland (1967a) have treated the problem of random distributions of two-dimensional lattices of finite size.

The present paper deals with non-random distributions of two-dimensional lattices, a problem which

arises *e.g.* in non-graphitic carbon structures with preferred orientation. The problem has been treated by Guentert & Cvikevich (1964) for a special case of the orientation function ($|\cos^n \varphi|$) and a unique direction in reciprocal space (perpendicular to the axis of cylindrical symmetry of the preferred orientation). The purpose of this paper is to give a general treatment of the problem.

2. Theoretical

2.1 It is required to find the Fourier transform of an assembly of two-dimensional regular arrays (planes). It is assumed that there is no preferred orientation within the plane, that the angular distribution of the perpendiculars to the plane (the orientation distribution) against a fixed direction ('primary axis') is given by $g(\beta)$ but that there is no preferred orientation of the perpendiculars to the plane around the primary axis (cylindrical symmetry). The primary axis may be the fiber axis in the case of fibers or the perpendicular to the plane of deposition in the case of pyrolytic carbons, for example.

The Fourier transform of a two-dimensional regular array of points is a set of parallel rods, each of which can be represented by

$$I(\mathbf{s}) = \delta(\mathbf{s}_{12} - \mathbf{s}_h) \quad (2)$$

where \mathbf{s}_{12} is the projection of \mathbf{s} perpendicular to the rod. If there is no preferential orientation within the plane each rod goes over into a cylinder and the intensity distribution is

* Research sponsored in part by a United States Air Force Subcontract under Union Carbide Corporation's Prime Contract AF 33(615)-2760.

$$I(\mathbf{s}) = \frac{1}{2\pi s_h} \delta(s_{12} - s_h) = \frac{1}{2\pi s_h} \delta(s \sin \tau - s_h),$$

where τ is the angle between the vector \mathbf{s} and the axis of the cylinder. We take the primary axis as the polar axis of the set of spherical coordinates s, φ, ψ , and use a set of Euler angles α, β, γ as defined by Margenau & Murphy (1956) to characterize the orientation of the cylinder. The angle α is counted from the plane containing the primary axis and \mathbf{s} ; the angle γ does not appear in the expressions owing to the absence of preferred orientation within the planes. Then (Fig. 1)

$$\cos \tau = \cos \beta \cos \varphi + \sin \beta \sin \varphi \cos \alpha.$$

The distribution of the planes around the primary axis is taken into account by integrating over α , the orientation distribution of the cylinder axes by multiplying by $g(\beta) \sin \beta$ and integrating over β , so that the intensity is given by

$$I(s) = \frac{1}{2\pi s_h} \int_0^\pi \int_{-\pi/2}^{\pi/2} \delta(s \sin \tau - s_h) g(\beta) \sin \beta d\beta d\alpha.$$

The colatitude β goes from 0 to π , the azimuth α only over half the circle so as not to count the same direction twice. For further development it is convenient to replace α and β by τ and η as integration variables, where η is the angle between the plane containing \mathbf{s} and the primary axis and the plane containing \mathbf{s} and the cylinder axis, as shown in Fig. 1. The Jacobean $\partial(\alpha, \beta)/\partial(\tau, \eta)$ can be written

$$\frac{\partial(\alpha, \beta)}{\partial(\tau, \eta)} = \frac{\partial(\alpha, \beta)}{\partial(\tau, \beta)} = \begin{pmatrix} \partial\alpha \\ \partial\tau \end{pmatrix}_\beta = \begin{pmatrix} \partial\alpha \\ \partial\tau \end{pmatrix}_\beta \cdot \begin{pmatrix} \partial\tau \\ \partial\eta \end{pmatrix}_\tau = \begin{pmatrix} \partial\alpha \\ \partial\tau \end{pmatrix}_\beta \cdot \begin{pmatrix} \partial\eta \\ \partial\beta \end{pmatrix}_\tau.$$

From the above expression for $\cos \tau$

$$\left(\frac{\partial\alpha}{\partial\tau}\right)_\beta = \frac{\sin \tau}{\sin \beta \sin \varphi \sin \alpha}$$

and from the analogous equation

$$\cos \beta = \cos \varphi \cos \tau + \sin \varphi \sin \tau \cos \eta$$

$$\left(\frac{\partial\eta}{\partial\beta}\right)_\tau = \frac{\sin \beta}{\sin \varphi \sin \tau \sin \eta}$$

so that the Jacobean is $\sin \tau / \sin \beta$ and

$$I(s) = \frac{1}{2\pi s_h} \int_0^{2\pi} d\eta \int_0^\pi \delta(s \sin \tau - s_h) g(\beta) \sin \tau d\tau.$$

We introduce $\sin \sigma = s_h/s$ and note that

$$\int \delta(y-a) f(x) dx = \frac{f(a)}{\left(\frac{dy}{dx}\right)_{y=a}};$$

then

$$I(s) = \frac{1}{2\pi s_h} \frac{\sin \sigma}{\cos \sigma} \int_0^\pi g(\beta) d\eta = \frac{1}{\pi s \sqrt{(s^2 - s_h^2)}} \int_0^\pi g(\beta) d\eta.$$

The orientation distribution $g(\beta)$ is so normalized that

$$\int_0^\pi \int_{-\pi/2}^{\pi/2} g(\beta) \sin \beta d\beta d\alpha = 1$$

or

$$\int_0^\pi g(\beta) \sin \beta d\beta = \frac{1}{\pi}, \quad (3)$$

so that if the distribution is constant over the surface of the sphere, $g(\beta) = 1/(2\pi)$, and with this value we obtain the well-known Laue expression (1). It is convenient to express the effect of the orientation distribution on the intensity distribution by writing

$$I(s) = \frac{1}{2\pi s \sqrt{(s^2 - s_h^2)}} \cdot F(\sigma, \varphi),$$

where

$$F(\sigma, \varphi) = 2 \int_0^\pi g(\beta) d\eta \quad (4)$$

is a function of σ (or s_h/s) and φ and

$$\cos \beta = \cos \varphi \cos \sigma + \sin \varphi \sin \sigma \cos \eta. \quad (5)$$

For $\varphi = 0$ equation (4) reduces to

$$F(\sigma, 0) = 2\pi g(\sigma).$$

If there is no cylindrical symmetry about the primary axis the orientation distribution is a function not only of β but of α as well and $g(\beta)$ must be replaced by $g(\alpha, \beta)$, suitably normalized; the angle α can be expressed in terms of the other angles by the formulae of spherical trigonometry, Fig. 1.

2.2 We can evaluate $F(\sigma, \varphi)$ if $g(\beta)$ is represented by the Poisson kernel* (Ruland, 1967b)

$$g(\beta) = \frac{1}{2\pi} \frac{\sqrt{q}}{\operatorname{ar} \operatorname{th} \sqrt{q}} \frac{1+q}{(1+q)^2 - 4q \cos^2 \beta}, \quad (6)$$

where it is more convenient to write $\sqrt{q}/\operatorname{ar} \operatorname{th} \sqrt{q}$ here and in what follows in the form $\sqrt{(-q)}/\operatorname{arc} \operatorname{tg} \sqrt{(-q)}$ if q is negative and $g(\beta)$ satisfies the normalization requirement (3). If $q = 1$ or -1 , $g(\beta)$ differs from zero only for $\beta = 0$ or $\pi/2$, respectively; $q = 0$ gives the random distribution.

The evaluation of $F(\sigma, \varphi)$ reduces here to the evaluation of

$$\int_0^\pi \frac{d\eta}{(1+q)^2 - 4q \cos^2 \beta},$$

which can be expressed in terms of integrals of the form

$$\int_0^\pi \frac{d\eta}{1+q \pm \sqrt{q} \cos \beta};$$

after substitution from (5) these are of the form

$$\int_0^\pi \frac{d\eta}{a \pm b \cos \eta},$$

the value of which is $\pi/\sqrt{(a^2 - b^2)}$.

* For the definition of the Poisson kernel see e.g. Carslaw (1930).

The result of the calculation is

$$F(\sigma, \varphi) = \frac{\sqrt{q}}{\operatorname{arth} \sqrt{q}} \left[\frac{(A^2 - B)^{\frac{1}{2}} + A}{2(A^2 - B)} \right]^{\frac{1}{2}}, \quad (7)$$

where

$$A = (1 + q)^2 + 4q(\cos^2 \varphi - \sin^2 \sigma),$$

$$B = 16q(1 + q)^2 \cos^2 \varphi \cos^2 \sigma.$$

For $\varphi = 0$ this reduces to

$$F(\sigma, 0) = \frac{\sqrt{q}}{\operatorname{arth} \sqrt{q}} \frac{1 + q}{(1 + q)^2 - 4q \cos^2 \sigma} = 2\pi g(\sigma),$$

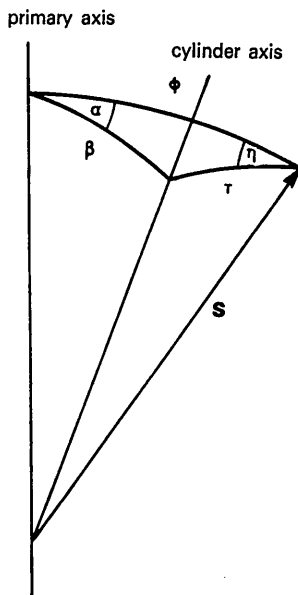


Fig. 1. Geometrical relationships of s , primary axis, and cylinder axis.

for $\varphi = \pi/2$ to

$$F\left(\sigma, \frac{\pi}{2}\right) = \frac{\sqrt{q}}{\operatorname{arth} \sqrt{q}} \frac{1}{[(1 + q)^2 - 4q \sin^2 \sigma]^{\frac{1}{2}}}.$$

A computer program (ERA 508) has been written in Fortran for the IBM 1620 computer to evaluate $F(\sigma, \varphi)$ from (7) for given values of q . Figs. 2 and 3 show the values obtained for $q = 0.8$ and $q = -0.8$, respectively, as functions of φ for a series of values of s/s_h . These two values of q represent fairly narrow distributions around $\varphi = 0$ and $\varphi = \pi/2$, respectively. The displacement of the maximum of $F(\sigma, \varphi)$ and therefore of $I(s)$ (since the Laue factor does not depend on φ) is clearly shown. The exact position of the maximum in s -space can be computed by a program ERA 534 and the points obtained have been plotted in Fig. 4 for a series of values of q . For a given value of s the maximum of the intensity as a function of φ lies at the point of intersection of the circle $s = \text{constant}$ with the curve for the appropriate value of q .

2.3 Guentert & Cvikevich (1964) have given an analytical expression for $F(\sigma, \varphi)$ if $g(\beta) = |\cos^n \beta|$ and $\varphi = \pi/2$. It is not difficult to evaluate $F(\sigma, \varphi)$ for the general case with this value of $g(\beta)$; substitution into (4), changing the integration variable by (5) and evaluation of the integrals gives

$$F(\sigma, \varphi) = 2/\pi \sum_{k=0}^n \binom{n}{k} (\cos \varphi \cos \sigma)^{n-k} \times (\sin \varphi \sin \sigma)^k \frac{\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{k}{2} + 1\right)}.$$

For the case treated by Guentert & Cvikevich the above expression consists of the term $k = n$, $2/\pi \sin^n \sigma$

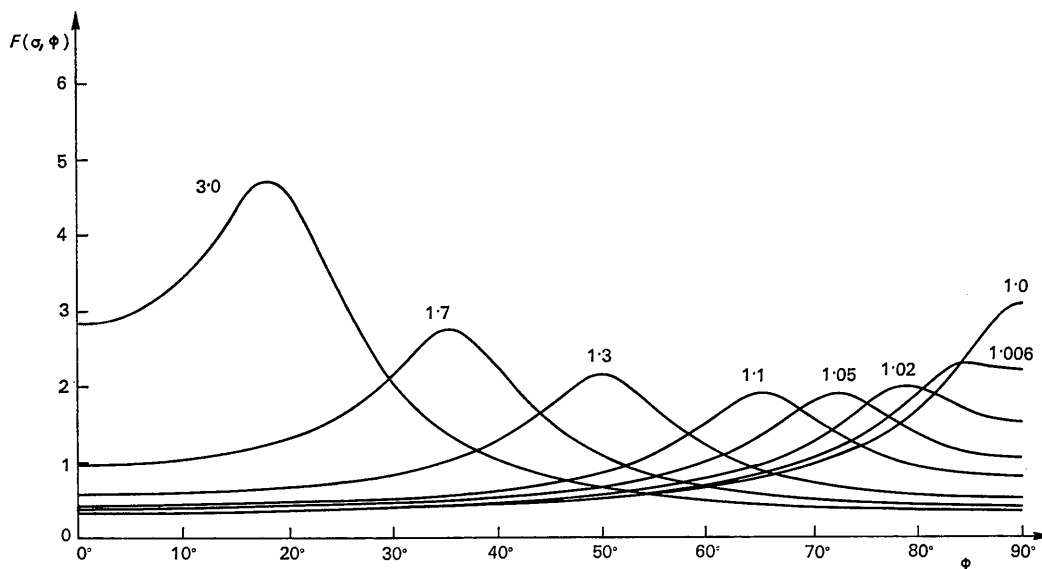


Fig. 2. $F(\sigma, \varphi)$ as function of the angle φ for Poisson kernel with $q = 0.8$ and for values of s/s_h indicated.

$\Gamma[(n+1)/2]/\Gamma(n/2+1)$, as given by the authors, except for the constant factor. For $\varphi=0$ it reduces to $2\pi \cos^n \sigma$.

If $g(\beta)=|\sin^n \beta|$, an analytical expression can be obtained for $F(\sigma, \varphi)$ for even values of n , though it is

rather involved, but for odd values of n (4) reduces to an elliptical integral and methods of numerical integration appear to be more suitable whatever the value of n .

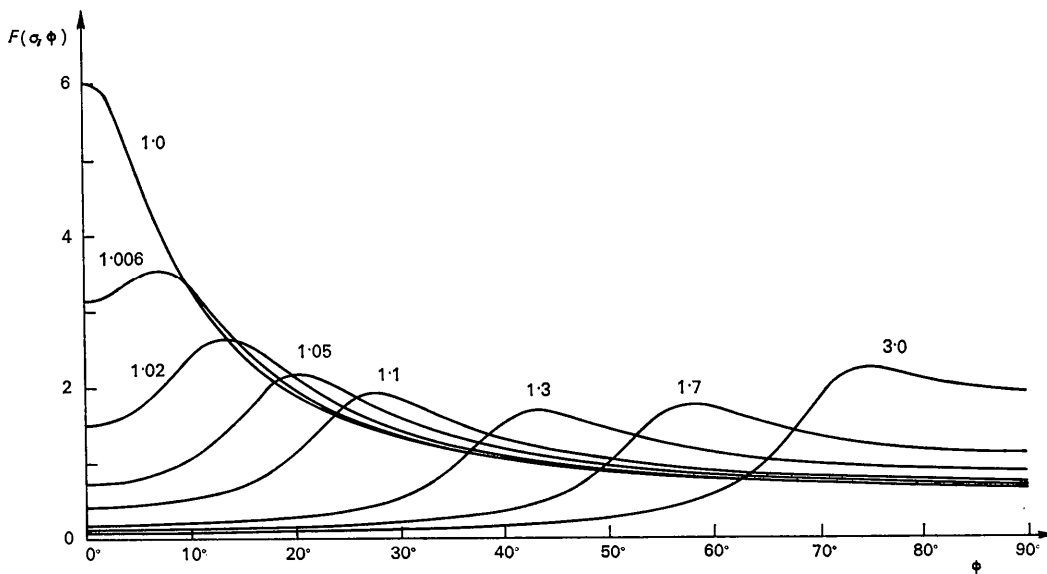


Fig. 3. $F(\sigma, \varphi)$ as function of the angle φ for Poisson kernel with $q = -0.8$ and for values of s/s_h indicated.

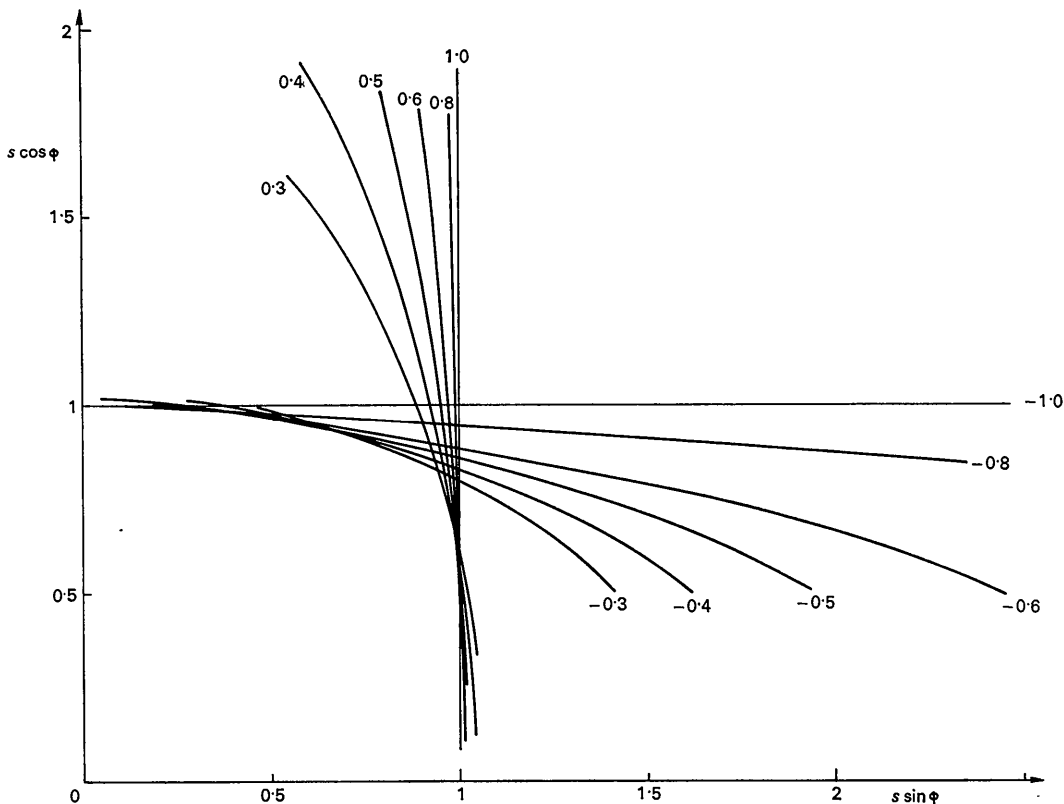


Fig. 4. Maxima of $F(\sigma, \varphi)$ for constant s and $s_h = 1$ for Poisson kernel with values of q indicated.

2.4 In the general case $g(\beta)$ can be represented as a Fourier-cosine series; since it is taken to be symmetrical about $\beta=\pi/2$ only terms of even order appear:

$$g(\beta) = \sum_{n=0}^{\infty} P_n \cos 2n\beta .$$

The treatment of this case is all the more interesting as the Fourier coefficients P_n are sometimes more easily accessible than the complete expression for $g(\beta)$ (Ruland, 1967b). We have then

$$F(\sigma, \varphi) = 2 \sum_{n=0}^{\infty} P_n \int_0^{\pi} \cos 2n\beta d\eta = \sum_{n=0}^{\infty} P_n F_n(\sigma, \varphi) .$$

To obtain $F_n(\sigma, \varphi)$ we write

$$\cos 2n\beta = \sum_{k=0}^n (-1)^k K(n, k) \cos^{2n-2k}\beta ;$$

[the $K(n, k)$ appear as the coefficients of x^{2n-2k} in the Chebyshev polynomial† $T_{2n}(x)$] and each power of $\cos^2\beta$ can be treated as in § 2.3. The result is

$$F_n(\sigma, \varphi) = 2\pi (-1)^n \sum_{l=0}^n (-1)^l K(n, n-l) \sum_{j=0}^l \binom{2l}{2j} \times \binom{2j}{j} (\cos \varphi \cos \sigma)^{2(l-j)} (\sin \varphi \sin \sigma/2)^{2j} . \quad (8)$$

A computer program (ERA 545) has been written in the SPS language to compute $F_n(\sigma, \varphi)$ for given values of σ and φ for $n=0$ to 25; since there is considerable loss of significance due to the alternation of terms thirty significant digits are carried during the computations.

† For the definition of Chebyshev polynomials see e.g. Duschek (1961).

A second program (ERA 556) computes $F(\sigma, \varphi)$ for given values of P_n . The consistency of programs 508 on the one hand and programs 545 and 556 on the other has been confirmed by computing $F(\sigma, \varphi)$ for the Poisson kernel with the latter program with $P_0=1$, $P_n=2q^n$, and an appropriate normalization factor.

2.5 The expressions so far obtained are strictly valid only for infinitely large and perfect layer structures since the cross-section of the (hk) rod has been represented by a Dirac delta distribution.

For finite and/or imperfect layers equation (2) has to be replaced by

$$I(\mathbf{s}) = I_h(\mathbf{s}_{12} - \mathbf{s}_h) \quad (9)$$

where $I_h(\mathbf{s}_{12})$ is the intensity distribution in the cross-section of the rod of index h ($=hk$). A treatment of the problem starting from this equation would, however, be rather involved and it is thus of interest to formulate the problem in a slightly different way. Assuming s_h to be in the direction of s_1 , equation (9) can be written in the form

$$I(\mathbf{s}) = [\delta(s_1 - s_h)\delta(s_2)] * [I_h(\mathbf{s}_{12}) \cdot \delta(s_3)] \quad (10)$$

where $*$ stands for convolution. Averaging over all orientations within the plane will cause most of the details of I_h in the s_2 direction to vanish so that the result will be almost the same if (11) is written instead of (10),

$$I(\mathbf{s}) \simeq [\delta(s_1 - s_h)\delta(s_2)] * [\{I_h\}(s_1)\delta(s_2)\delta(s_3)] , \quad (11)$$

where

$$\{I_h\}(s_1) = \int_{-\infty}^{\infty} I_h(\mathbf{s}_{12}) ds_2 .$$

In that case, one can also show that

$$I(\mathbf{s})\delta(\mathbf{s} \simeq_{12} - \mathbf{s}_h) * I'_h(\mathbf{s}) \quad (12)$$

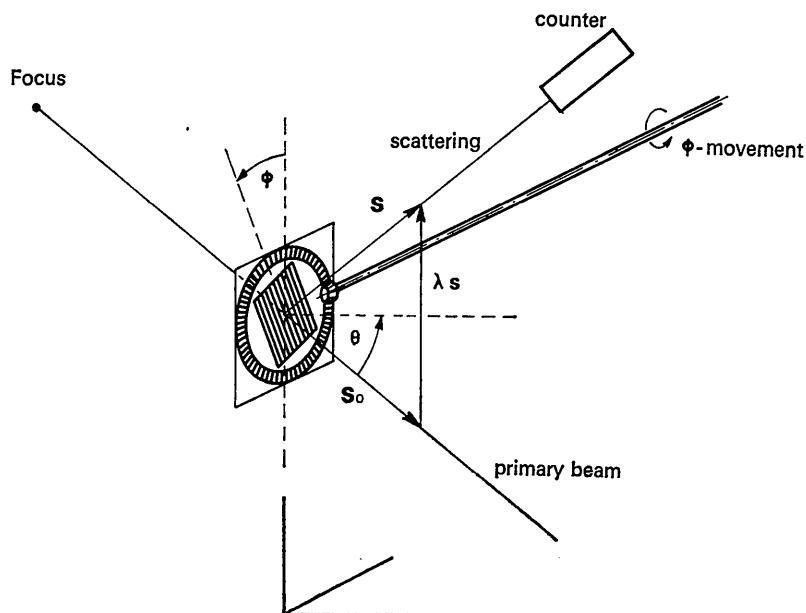


Fig. 5. Fibre equipment for diffractometer.

is an acceptable approximation for (9), where $I'_h(s)$ is a spherically symmetrical distribution related to I_h by the definition

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I'_h(s) ds_2 ds_3 = \int_{-\infty}^{+\infty} I_h(\mathbf{s}_{12}) ds_2.$$

Taking (12) as the starting point, it is obvious that none of the operations of § 2.1 interfere with the function I'_h and the final result is thus

$$I(s, \varphi) \simeq \left[\text{Re} \frac{1}{2\pi s \sqrt{(s^2 - s_h^2)}} \cdot F(\sigma, \varphi) \right] * I'_h(s). \quad (13)$$

At this point it is of interest to recall that the function $F(\sigma, \varphi)$ can be considered as varying slowly compared with the Laue factor, except for extremely narrow orientation distributions [$g(\beta)$ tending towards $\delta(\beta)$ or $\delta(\beta - \pi/2)$]. In all other cases equation (13) can thus be further simplified by the approximation

$$I(s, \varphi) \simeq \left[I'_h(s) * \text{Re} \frac{1}{2\pi s \sqrt{(s^2 - s_h^2)}} \right] \cdot F(\sigma, \varphi),$$

which means that the Laue factor can be replaced by the line profile of the completely random arrangement of layers, $J_h(s)$, giving

$$I(s, \varphi) \simeq J_h(s) \cdot F(\sigma, \varphi). \quad (14)$$

2.6 A further complication can occur in that the intensity along the rod is not constant, an effect which can be due *e.g.* to the partial ordering of adjacent layers. In this case equation (9) has to be replaced by

$$I(\mathbf{s}) = \delta(\mathbf{s}_{12} - \mathbf{s}_h) \cdot G(s_3), \quad (15)$$

where $G(s_3)$ determines the intensity variations along the rod. Since $I(s)$ is non-zero only for $s_{12} = s_h$, $G(s_3)$ can be written in the form

$$G'(s) = G[\sqrt{(s^2 - s_h^2)}]$$

and the result of the operations described in § 2.1 is thus

$$I(s, \varphi) = \text{Re} \frac{G[\sqrt{(s^2 - s_h^2)}]}{2\pi s \sqrt{(s^2 - s_h^2)}} \cdot F(\sigma, \varphi).$$

If the intensity variation along the rod occurs together with a non-negligible width of the cross-section of the rod, equation (9) has to be replaced by

$$I(\mathbf{s}) = I_h(\mathbf{s}_{12} - \mathbf{s}_h) G(s_3)$$

which, following the arguments given in § 2.5, can be approximated by

$$I(\mathbf{s}) \simeq [\delta(\mathbf{s}_{12} - \mathbf{s}_h) * I'_h(s)] \cdot G(s_3).$$

This expression can in its turn be approximated by

$$I(\mathbf{s}) \simeq [\delta(\mathbf{s}_{12} - \mathbf{s}_h) \cdot G(s_3)] * I'_h(s)$$

provided that G is a slowly varying function as compared with I'_h , an assumption which is justified in many practical cases. The operations described in § 2.1 then give

$$I(s, \varphi) \simeq \left[\text{Re} \frac{G'(s)}{2\pi s \sqrt{(s^2 - s_h^2)}} \cdot F(\sigma, \varphi) \right] * I'_h(s)$$

from which one obtains the approximation

$$I(s, \varphi) \simeq J_h(s) \cdot G[\sqrt{(s^2 - s_h^2)}] F(\sigma, \varphi)$$

if $G'(s)$ and $F(s, \varphi)$ can be considered as slowly varying compared with the Laue form.

3. Experimental

An experimental check of the theoretical predictions has been made in the study of preferred orientation in a highly oriented carbon fiber. The measurements were carried out on a counter diffractometer using the scattering geometry shown in Fig. 5. In order to increase the intensity yield and simplify absorption corrections a great number of fibers are mounted parallel on a frame. The frame is fixed on a sample holder in such a way that the plane formed by the parallel fibers is perpendicular to the plane defined by \mathbf{S}_0 (the unit vector in the direction of the primary beam) and \mathbf{S} (the unit vector in the direction of the observed scattering) and parallel to \mathbf{s} . The latter condition is maintained by the usual $\theta/2\theta$ ratio between the movement of the sample holder and the counter. The frame can be rotated within the plane formed by the fibers, the angle of rotation is equivalent to the angle φ as defined above.

The distribution of layer normals was obtained by an analysis of circular scans on the 002 and 004 reflexions which yields directly the Fourier coefficients P_n as discussed in § 2.4. From these coefficients values of $F(\sigma, \varphi)$ were computed as functions of φ for $s/s_h = 1.1$, thus outside the main interference ring, and the results were compared with measurements at the same s/s_h value in the region of the (10) and (11) interferences. The result is shown in Fig. 6. The agreement between observed and calculated intensities is satisfactory outside the region influenced by the 00 l reflexions. The profile of the streak discussed in § 2.2 appears clearly.

A comparison of observed and calculated intensities at smaller s/s_h values shows systematic deviations which can be explained by a correlation between the

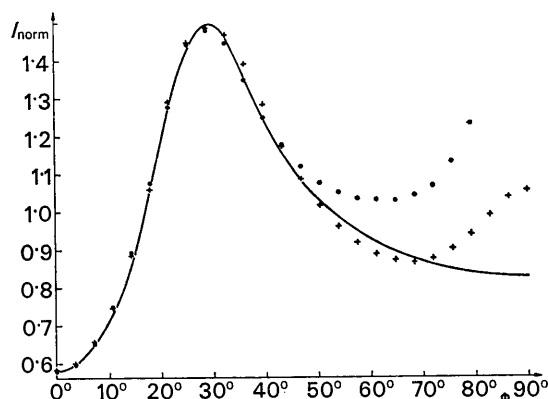


Fig. 6. Scattering diagram of carbon fibre with high preferred orientation as function of φ for $s/s_h = 1.1$. Full line: computed curve; crosses: observed profile for (10) interference; dots: observed profile for (11) interference.

size (and/or the perfection) of the graphitic layers and the orientation of the layer planes in the sense that the larger and more perfect layers tend to be more perfectly aligned parallel to the fiber axis. An investigation of this effect is facilitated by the use of approximations similar to equation (14) considering J_h to be a function of s and φ . A detailed study of this effect is in progress.

We are indebted to Mr J.P. Pauwels for technical assistance, to the staff of our Computer Centre for the numerical results, and to Dr R. Bacon for supplying the sample of carbon fibre.

References

BRINDLEY, G. W. & MÉRING, J. (1951). *Acta Cryst.* **4**, 441.

CARSLAW, H. S. (1930). *Introduction to the Theory of Fourier's Series and Integrals*, 3rd edition, p.250–254. New York: Dover Publications.

DUSCHEK, A. (1961). *Vorlesungen über höhere Mathematik*, p.47. Wien: Springer-Verlag.

GUENTERT, O. J. & CVIKEVICH, S. (1964). *Carbon*, **1**, 309.

LAUE, M. VON (1932). *Z. Kristallogr.* **82**, 127.

MARGENAU, H. & MURPHY, G. M. (1956). *The Mathematics of Physics and Chemistry*, 2nd edition, p.286. New York: Van Nostrand.

RULAND, W. (1967a). *Acta Cryst.* **22**, 615.

RULAND, W. (1967b). *J. Appl. Phys.* In the press.

WARREN, B. E. (1941). *Phys. Rev.* **59**, 693.

WARREN, B. E. & BODENSTEIN, P. (1966). *Acta Cryst.* **20**, 602.

WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 245.

Acta Cryst. (1968). **A24**, 99

Application de la Théorie Dynamique de la Diffraction X à l'Étude de la Diffusion du Bore et du Phosphore dans les Cristaux de Silicium

PAR JACQUES BURGEAT

Département Physique–Chimie–Métallurgie, Centre National d'Études des Télécommunications, 92 Issy-les-Moulineaux, France

ET DANIEL TAUPIN

Centre de Calcul Numérique, Laboratoire de Physique Théorique et Hautes Energies, Faculté des Sciences, 91 Orsay, France

(Reçu le 8 mai 1967)

The dynamical theory of X-ray scattering of distorted crystals is applied to the case of silicon crystals in which boron has been diffused. Double spectrometer reflexion profiles can thus be theoretically computed. Agreement with the experimental profiles is good except that computed junction depths are higher than the values measured by metallographic methods. On the other hand, the present method leads to a reliable determination of the diffusion coefficient of boron in the case of relatively high concentrations.

On sait que la présence de bore diffusé dans les cristaux de silicium crée une contraction du réseau cristallin (Horn, 1955) variable avec la profondeur, modifie le profil des raies de diffraction X et le pouvoir réflecteur des cristaux diffusés (Burgeat, 1963, 1965). Cette modification de la diffraction X se retrouve avec la diffusion du phosphore dans le silicium.

L'étude expérimentale des profils de raies sur les échantillons diffusés est réalisée au diffractomètre double dans la disposition $(n, -n)$ (James, 1948), le premier cristal étant aussi parfait que possible. La diffusion du bore est réalisée dans des cristaux de silicium de type N (dopés au phosphore) et la profondeur de pénétration de l'impureté diffusée est repérée par l'épaisseur de la couche inversée ou profondeur de jonction.

On admettra pour l'étude théorique du profil de raie obtenue (Burgeat, 1965), que l'impureté diffusée (bore ou phosphore) provoque une contraction du réseau cristallin à priori isotrope et proportionnelle à leur con-

centration (loi de Vegard). Dans le cas présent ces impuretés sont concentrées au voisinage de la surface et tendent par conséquent à donner à l'échantillon une forme concave (Queisser, 1961). En pratique l'épaisseur de l'échantillon est très grande (1 à 2 mm) devant celle de la couche diffusée et la raideur de l'ensemble est telle qu'aux températures de diffusion il y a création de dislocations parallèles à la surface (Prussin, 1961).

Du point de vue des rayons X (nous sommes dans le cas de Bragg symétrique – réflexion 400) tout se passe comme si nous avions un cristal dont les plans (400) restent parallèles et plans, mais dont l'intervalle réticulaire d_H est fonction de la distance z à la surface.

La propagation des rayons X (au voisinage de la condition de Bragg) dans un tel cristal a déjà été étudiée (Taupin, 1964); elle est régie par le système différentiel suivant (II.6.3):

$$i \frac{\lambda}{\pi} \gamma_H \frac{dD_H}{dz} = \psi_0 D_H + \psi_H D_0 - \alpha_H D_H \quad (1)$$