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X-ray Diffraction from Microcrystalline Random Layer Structures

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A theoretical study is given of the X-ray scattering from a powder composed of circular planes of atoms. When the planes are grouped into parallel layers, the effects resulting from the tangent plane approximation (*TPA*) are determined for the basal (00*l*) reflections and the role of rotational and displacement disorder are determined for both 00*l* and *hk*0 reflections. When applied to the 002 peaks from partially graphitized carbons, it is found that use of the *TPA* predicts a value of the interlayer spacing which is at worst 2% too small. Analytical expressions for the small angle scattering follow as a special case of the 00*l* reflections. As expected, the 00*l* maxima are appreciably altered when plane displacements become comparable with plane radii, while the shape of *hk*0 maxima are essentially determined by the rotational disorder alone.

Introduction

Warren (1941) has obtained a quantitative interpretation of the X-ray diffraction from random layer lattices in which layers of a crystallite are parallel to one another, but random displacements and rotations may occur between adjacent layers. It is the purpose of this paper to extend this work to the case where partial ordering of the relative plane positions is considered. Also, the effects of using the tangent plane approximation in the case of basal reflections is considered. The materials to which these results are most directly applicable are the partially graphitized carbons such as carbon black.

Use is made of the general powder pattern theorem for randomly oriented powders (Warren & Averbach, 1950) which gives P, the total diffracted power in electron units associated with a given hkl diffraction maximum, in terms of the intensity distribution in reciprocal space. Let $\mathbf{s}_0$ and $\mathbf{s}$ be unit vectors in the direction of the incident and diffracted beams respectively. We let $\mathbf{S}=(\mathbf{s}-\mathbf{s}_0)/\lambda=h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3$ where $\mathbf{b}_1\mathbf{b}_2\mathbf{b}_3$ are the reciprocal lattice translation vectors. Then

$$P=\frac{MjD^2\lambda^3}{4}\iiint\frac{I(h_1h_2h_3)}{\sin\theta}\cdot\frac{dh_1dh_2dh_3}{V_a}$$
$$=\int P(2\theta)d(2\theta)$$

where M is the number of crystals in the sample, j is the hkl multiplicity, D is the sample to detector distance, I is the diffracted intensity in electron units per crystal, V_a is the volume of the three-dimensional unit cell, and $P(2\theta)$ is the distribution of power with scattering angle. Finally, if we want the power per unit solid angle subtended by the detector we have

$$J(2\theta)=P(2\theta)/(2\pi D^2\sin 2\theta)\,. \qquad (1)$$

Referring to Fig. 1, we can write the volume element of reciprocal space in polar coordinates using $S=2\sin\theta/\lambda$ as the radius vector.

$$dV_r=dh_1dh_2dh_3/V_a$$
$$=2\pi S^2\sin\alpha\, d\alpha\, dS=2\pi S^2\frac{\cos\theta}{\lambda}\sin\alpha\, d\alpha\, d(2\theta)\,. \qquad (2)$$

Thus we find for $J(2\theta)$ upon combining (1) and (2),

$$J(2\theta)=\frac{M_j\lambda^2}{8\sin^2\theta}S^2\int_0^\pi I(\alpha, S)\sin\alpha\, d\alpha\,. \qquad (3)$$

In (3) it is assumed that all possible rotations of the crystal about the b_3 axis have been averaged over, so I depends only upon α and S.

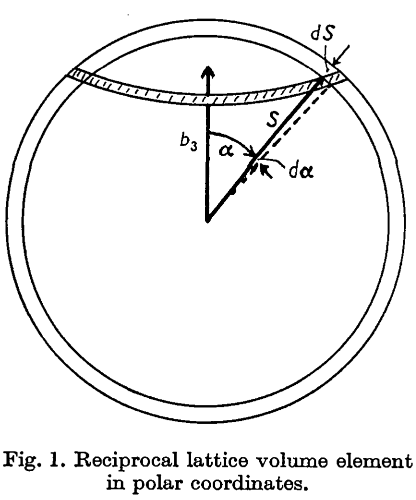

Fig. 1. Reciprocal lattice volume element in polar coordinates.

Diffraction by an array of circular layers

Consider the intensity diffracted by a group of N circular layers each of radius R. The N layers are considered to be parallel to one another, but are allowed to be displaced parallel to themselves and to be rotated about a perpendicular axis through the center of the plane. The layers are numbered from one layer called the reference layer. The center of the jth layer is displaced by a vector $\boldsymbol{\rho}_j$ relative to the center of the reference layer.

Following Warren's notation, $\mathbf{a}_{1j}\mathbf{a}_{2j}$ are the lattice vectors in the plane of the jth layer, $\mathbf{a}_3$ is the interplanar vector perpendicular to $\mathbf{a}_1\mathbf{a}_2$. The intensity from a crystal of N layers is given in electron units by

$$I = \left| \sum_{j=1}^{N} F_j \sum_{m_1 m_2} \exp \{i2\pi\mathbf{S}.(m_1\mathbf{a}_{1j}+m_2\mathbf{a}_{2j}+j\mathbf{a}_3+\boldsymbol{\rho}_j)\}\right|^2 \quad (4)$$

where F_j is the two-dimensional structure factor in the jth layer.

The sum over m_1m_2 can be approximated by an integration over the area of the plane (James, 1954). Thus

$$\sum_{m_1m_2} \exp \{i2\pi\mathbf{S}.(m_1\mathbf{a}_{1j}+m_2\mathbf{a}_{2j})\} = \int_{r=0}^{R}\int_{\varphi=0}^{2\pi} \exp \{i2\pi(\mathbf{S}-\mathbf{H}_j).\mathbf{r}\}\frac{rdrd\varphi}{A_c} \quad (5)$$

where $\mathbf{H}_j=h\mathbf{b}_{1j}+k\mathbf{b}_{2j}+l\mathbf{b}_3$, A_c is area of the two-dimensional cell, $\mathbf{b}_{1j}\mathbf{b}_{2j}\mathbf{b}_3$ denote the vectors reciprocal to $\mathbf{a}_{1j}\mathbf{a}_{2j}\mathbf{a}_3$. The vector $\mathbf{H}_j$ locates the lattice point hkl in the reciprocal lattice of the jth layer. The rotation of the jth layer about its center is given by the angle η_j defined in Fig. 2. The evaluation of (5) depends upon whether $hk0$ or $00l$ reflections are considered.

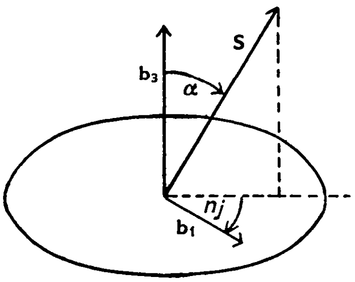

Fig. 2. Orientation coordinates of the jth layer for $hk0$ reflections.

(i) 00*l* *reflections*

In this case all $\mathbf{H}_j=l\mathbf{b}_3$ and $\mathbf{H}.\mathbf{r}=0$ in equation (5). Evaluating the integral in (5) and substituting in (6) gives us

$$I_{00l} = \frac{4\pi R^2}{A_c^2}\cdot\left|\frac{J_1(2\pi RS \sin\alpha)}{2\pi RS\sin\alpha}\right|^2 \times \left|\sum_{j=1}^{N} F_j \exp\{i2\pi\mathbf{S}.(j\mathbf{a}_3+\boldsymbol{\rho}_j)\}\right|^2 . \quad (6)$$

This Bessel function coefficient has a maximum at $\alpha=0$ which is very sharp compared with the variation of F_j with α near $\alpha=0$. Therefore we may take the F_j's out of the summation and evaluate them at $\alpha=0$.

If we label the reference plane as number 1, then we note $\boldsymbol{\rho}_1=0$ by definition. To get the average intensity from crystals with a given orientation relative to $\mathbf{S}$, we must average over the distributions of $\boldsymbol{\rho}_j$. Thus we find

$$\langle I_{00l}\rangle = \int\ldots\int I_{00l}P(\boldsymbol{\rho}_2)\varrho_2 d\varrho_2 d\gamma_2 \times P(\boldsymbol{\rho}_3)\varrho_3 d\varrho_3 d\gamma_3 \ldots P(\boldsymbol{\rho}_N)\varrho_N d\varrho_N d\gamma_N \quad (7)$$

where $P(\boldsymbol{\rho}_j)$, the displacement distribution function, is the probability per unit area of the center of layer j being displaced a distance ϱ_j in the direction η_j. If we assume each layer's displacement is independent of the other displacements,

$$\langle I_{00l}\rangle = \frac{4\pi R^2}{A_c^2}\left|\frac{J_1(2\pi RS\sin\alpha)}{2\pi RS\sin\alpha}\right|^2 |F(\alpha=0)|^2 \times \left[N+2g\left(\frac{\sin(N-1)S\pi a_3\cos\alpha}{\sin\pi Sa_3\cos\alpha}\cdot\cos N\pi Sa_3\cos\alpha\right) + g^2\left(\frac{\sin^2(N-1)\pi Sa_3\cos\alpha}{\sin^2\pi Sa_3\cos\alpha}-(N-1)\right)\right] \quad (8)$$

where

$$g=\int_{\gamma=0}^{2\pi}\int_{\varrho=0}^{\infty}\exp\{i2\pi\mathbf{S}.\boldsymbol{\rho}\}P(\boldsymbol{\rho})\boldsymbol{\rho}d\varrho d\gamma .$$

If $\boldsymbol{\rho}=0$ for all layers, $g=1$ and the square bracketed term in 8 approaches the usual expression,

$$\sin^2 N\pi Sa_3\cos\alpha/\sin^2\pi Sa_3\cos\alpha .$$

We may go from $\langle I_{00l}\rangle$ to $I(\alpha, S)$ in equation (3) by inclusion of absorption and polarization factors giving us

$$J(2\theta) = K\int\langle I_{00l}\rangle\sin\alpha d\alpha \quad (9)$$

where $K=\frac{1}{2}M_jA.(1+\cos^2 2\theta)$ for unpolarized radiation and absorption factor A. It is clear that we can go no further unless the displacement distribution function, $P(\boldsymbol{\rho})$, and thus g is specified.

(*a*) No displacement disorder, $g=1$

We use approximate expressions to avoid the need for numerical integrations, *viz.*

$$(J_1(x)/x)^2 \simeq \tfrac{1}{4}\exp(-x^2/4)$$
$$\sin^2 Nx/\sin^2 x \simeq N^2\exp(-N^2y^2/\pi) \quad (10)$$

where $y=x-x_0$, x_0 being the nearest value of x where $\sin x=0$. With these approximations the integration of (9) is straightforward giving us

$$J_{00l}(2\theta) = \frac{K\pi^2R^4}{A_c^2}N^2|F(\alpha=0)|^2\mathscr{L}(B,C,S) \quad (11)$$

where $B=\pi N^2a_3^2$, $C=\pi^2R^2$, and the form of $\mathscr{L}$ depends upon the parameter $q=B/C$.

$\underline{q<1}$

$$\mathscr{L} = \frac{1}{2((1-q)Cs^2)^{\frac{1}{2}}}[\exp\{-B(S-H)^2\}G(d) - \exp\{-B(S+H)^2\}G(h)] \quad (12)$$

where

$$G(x) = \exp(-x^2)\int_0^x \exp(v^2)dv, \; d = (c/1-q)^{\frac{1}{2}} \times [qH+(1-q)S], \; h = (c/1-q)^{\frac{1}{2}}[qH-(1-q)S].$$

Tables of $G(x)$ are given by Mitchell & Zemansky (1934).

$\underline{q=1}$

$$\mathscr{L} = \frac{1}{4CSH}[\exp\{-B(S-H)^2\} - \exp\{-B(S+H)^2\}] \quad (13)$$

$\underline{q>1}$

$$\mathscr{L} = \frac{1}{2((q-1)CS^2)^{\frac{1}{2}}}[\exp\{-B(S-H)^2\}H(x) + \exp\{-B(S+H)^2\}H(y)] \quad (14)$$

where

$$H(z) = \exp(z^2)\int_0^z \exp(-u^2)du = \exp(z^2).\pi^{\frac{1}{2}} \times (\text{error function of } z)$$

$$x = [c/(q-1)]^{\frac{1}{2}}[(q-1)S-qH]$$

$$y = [c/(q-1)]^{\frac{1}{2}}[(q-1)S+qH].$$

In the limit of very large R, the square bracketed factor in equation (8) varies slowly with α so it can be evaluated at $\alpha=0$ and removed from the α integration. Then instead of integration over the spherical shell of Fig. 1, the integration can be taken over the space between two planes tangent to the spheres at $\alpha=0$. This constitutes the tangent plane approximation (*TPA*) given first by M. von Laue (1926). Considering $g=1$ we obtain

$$\mathscr{L}_{TPA} = \exp\{-B(S-H)^2\}/(4CS^2). \quad (15)$$

We now apply these results to the 002 diffraction maximum in partially graphitized carbons. A nominal value of 3·4 Å is taken for a_3. One finds the following approximations are valid to within 2% for the 002 maximum:

$$G(d) = \frac{1}{2d}, \; \exp\{-B(S+H)^2\}G(h) = 0$$

$$H(y) = \left(\frac{(\pi)^{\frac{1}{2}}}{2}\cdot\exp(y^2)\right) - \frac{1}{2y}.$$

These approximations give us for equations (12), (13), (14).

$$\mathscr{L} = \mathscr{L}_{TPA}\cdot\frac{1}{1+(H-S)/S} \quad (12a)$$

$$\mathscr{L} = \mathscr{L}_{TPA}\cdot S/H \quad (13a)$$

$$\mathscr{L} = \mathscr{L}_{TPA}\left(\frac{\pi c}{\varrho-1}\right)^{\frac{1}{2}}\cdot Se^{x^2}\cdot[1+\text{erf}(x)]. \quad (14a)$$

Equations (12a) to (14a) show the *TPA* results to be multiplied by functions which shift the peak toward higher 2θ angles. This shift remains even after multiplying $J(2\theta)$ by S^2/f^2 as suggested by Franklin (1950). The amount by which the peak maximum is displaced can be found by setting $\frac{\partial}{\partial S}(S^2\mathscr{L})=0$. This gives us

$$q\le 1 \qquad \frac{S_M-H}{H} = \frac{a_3^2}{2\pi^2R^2}$$

$$q>1 \qquad \frac{S_M-H}{H} = \frac{a_3^2}{2\pi^2R^2} + \frac{1}{2N}\left(\frac{(q-1)}{q}\right)^{\frac{1}{2}} \times \left[2|x| + \frac{\partial}{\partial x}\ln(1+\text{erf } x)\right]_{S=H} \quad (16)$$

where S_M is the actual peak maximum and H is the *TPA* peak maximum. For carbons, if $R\ge 5$ Å,* S_M-H/H is $\le 2\%$ for $q\le 1$. For $q>1$ and $R=5$ Å, approximately the same peak shift (2%) is produced for values of N up to 7. If Δa_3 is the error made in measuring a_3 by use of the *TPA*,

$$|\Delta a_3/a_3| = |(S_M-H)/H|.$$

In conclusion regarding the 002 Bragg maximum for carbon, the use of the *TPA* will result in a peak displacement of 2% of H or less toward lower angles. Thus values of a_3 deduced from the position of the maximum will be too small by 2% or less. Graphs of equations (12a) through (14a) showed changes in the peak shapes which are negligible from an experimental viewpoint. These conclusions are in agreement with those of Patterson (1939) who found the *TPA* was in very good agreement with the accurate integration for spherical particles except at very small values of S.

(b) The effect of displacement disorder, $g<1$

We now consider the effect of displacement disorder on the 00l peak. If we assume that $P(\rho)$ is constant up to a maximum displacement radius Y, we find from (8) that $g=2.J_1(2\pi SY\sin\alpha)/(2\pi SY\sin\alpha)$. Replacing $J_1(x)/x$ by $\frac{1}{2}\exp(-\frac{1}{2}x^2)$ as in equation (10), the α integration of equation (9) results in

$$\mathscr{L} = \frac{1}{4CS^2} \times \left[N + \left(\frac{2}{1+Y^2/2R^2}\cdot\frac{\sin(N-1)\pi Sa_3}{\sin\pi Sa_3}\cdot\cos\pi NSa_3\right) + \frac{1}{1+Y^2/R^2}\left(\frac{\sin^2(N-1)\pi Sa_3}{\sin^2\pi Sa_3} - (N-1)\right)\right]. \quad (17)$$

If Y, the maximum displacement radius, is comparable with R, then we see that the 00l coherent interplanar

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* For carbonized coals, values of R as small as 2·9 Å have been reported by Diamond (1958). For carbon blacks, values of R in excess of 5 Å are more usual. (L. Alexander, private communication.)

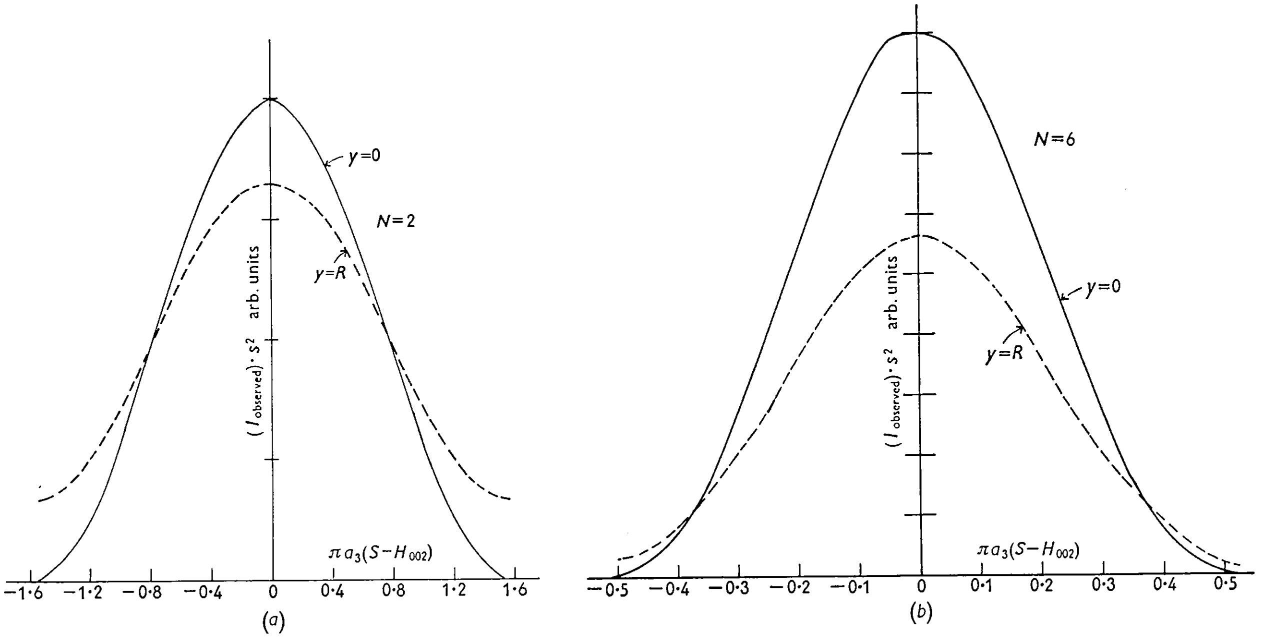

Fig. 3. The effect of displacement disorder on the 002 graphite reflection intensities. (*a*) $N=2$; $Y=0$ (no displacement disorder) and $Y=R$. (*b*) $N=6$; $Y=0$ and $Y=R$.

scattering represented by the last two terms in the bracketed expression of (17) is appreciably decreased, and becomes zero for large Y. This is the result of the coherent scattering dropping off more rapidly with α when Y is not zero.

Fig. 3 gives plots of equation (17) for $N=2$ and for $N=6$ when $Y=0$ and when $Y=R$. It is seen from the figure that the peak shape is altered most for $N=2$. There is a substantial increase in the background scattering and a decrease in the peak height above background. If the apparent increase in background is subtracted, the peak breadth at half-maximum remains unchanged. The peak shape becomes less affected as N increases and the third term of (17) begins to dominate. As N increases, the major affect of displacement disorder on the experimental results is a decrease in the $00l$ peak intensity which is multiplied by a factor $(1+Y^2/R^2)^{-1}$ and an increase in the scattering from independent planes. From these results it is seen that experimentally one has great difficulty in distinguishing between (*a*) a small number of crystals having very little displacement disorder and (*b*) a large number of crystals having a substantial displacement disorder. While other displacement distributions would lead to modifications of equation (17), it is improbable that the main features would be modified.

(ii) *hk*0 *reflections*

The methods used for the $00l$ reflection are also applicable to the $hk0$ reflections. Here the rotational disorder represented by γ_j is found to dominate. Assuming no rotational order so all values of γ_j are equally probable, the displacement disorder is found to have a negligible effect on the peak shapes if R exceeds 5 Å. The results of Warren (1941) which correspond to independent scattering by the individual layers are essentially obtained whether $g=1$ or $g=0$.

(iii) *Small angle scattering*

The derivation of equations (11) to (14) derived for the case of no displacement disorder made no assumptions regarding the magnitude of H. Therefore, in contrast to the tangent plane approximation, these expressions may be directly applied where $H=0$ and $N>1$. In the absence of intercrystalline interference, we find for J, the 000 power per unit area

$$q<1,\ J=J_0r\exp(-BS^2).G(x)/(x),\ \ x=\pi RS(1-q)^{\frac{1}{2}} \quad (18)$$

$$q=1,\ J=J_0r\exp(-BS^2) \quad (19)$$

$$q>1,\ J=J_0r\exp(-BS^2).H(y)/y,\ \ y=\pi RS(q-1)^{\frac{1}{2}} \quad (20)$$

where J_0 is the power per unit area at $S=0$

$$r=|F^2(\alpha=0)|/|F^2(S=0)|$$

and q, $G(x)$, and $H(y)$ are defined in equations (12) to (14). At very small values of S the above expressions for $N>1$ all reduce to

$$J/J_0=r\exp\{-4\pi^2S^2/3\}(R^2/2+(Na_3)^2/4\pi)\,.$$

In equation (10) the integrated area of $\sin^2 Nx/\sin^2 x$ was matched by using $N^2\exp(-N^2x^2/\pi)$. If instead one matches the curvature at $x=0$ we find the exponent is replaced by $(N^2-1)x^2/3$ and

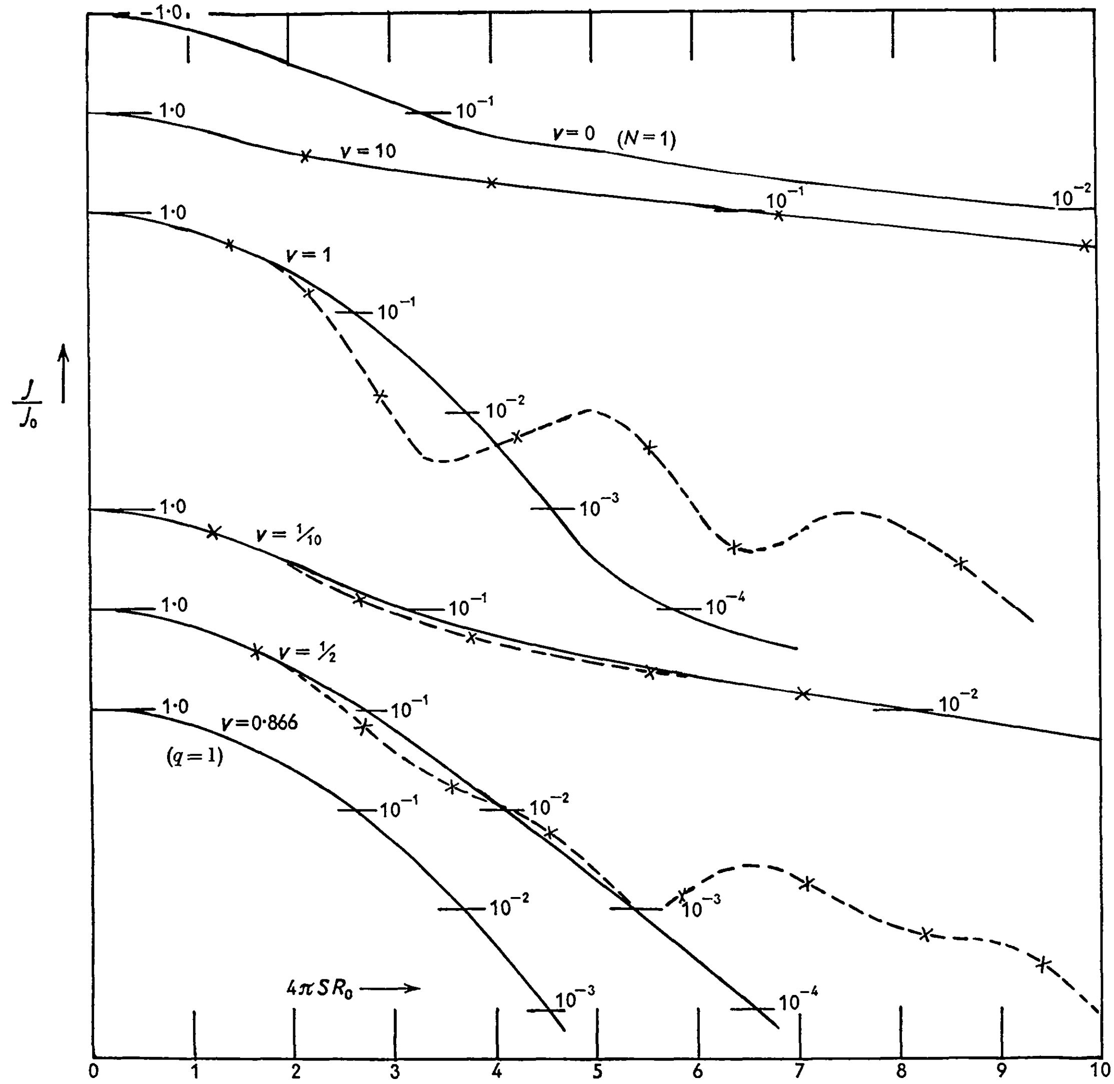

Fig. 4. Small angle scattering from cylinders in the absence of inter-particle interference. — × — × Malmon (1957) results; — present results, equations (18)–(21). v is Malmon's shape parameter, $q = \frac{4}{3}v^2$.

$$J/J_0 = r \exp (4\pi^2 S^2 a_3^2/12 \,.\, \exp (-4\pi^2 S^2/3 \,.\, R_0^2) \,, \quad (21)$$

where $R_0 = (R^2/2 + T^2/12)^{\frac{1}{2}}$ is the radius of gyration for a circular cylinder of radius R and thickness $T = Na_3$. Equation (21) is to be compared with the result of Guinier (1955) which gives

$$J/J_0 = \exp (-4\pi^2 S^2/3 \,.\, R_0^2) \,.$$

At the very small angles where these results are comparable, the factor $r \exp (+4^2 S^2 a_3^2/12)$ is equal to 1 and Guinier's result follows.

In Fig. 4 the equations (18) to (20) are compared with the results of numerical integration by Malmon (1957). The factor r has been left at 1 in these graphs since the structure factor changes slowly compared with the exponential factor. Aside from duplication of the oscillatory behavior, it is clear the present results yield useful analytical approximations to the numerical curves. Where v departs appreciably from 1, the agreement is especially satisfactory.

For the case where $N = 1$ one finds equation (18) is appropriate providing B and q are set equal to zero. Thus for independently scattering layers of radius R we have

$$J/J_0 = r \frac{G(\pi RS)}{(\pi RS)} \,. \quad (22)$$

This equation is also plotted in Fig. 4.

Conclusion

Expressions are obtained (equations (8), (9)) for the diffraction from a powder of crystals made up of parallel circular layers subject to rotational and displacement disordering.

1. Using the Gaussian approximation for the interference functions obtained (equation (10)) the 002 reflections for microcrystalline carbon were investigated.

(*a*) In the absence of displacement disorder, use of the tangent plane approximation for interpreting the 002 diffraction maximum results in a small systematic error in evaluating the interplanar spacing, a_3. For a layer radius in excess of 5 Å, the value of a_3 using the *TPA* will be too small by less than 2%.

(*b*) While rotational disorder plays a negligible rôle in the 002 diffraction, displacement disorder can seriously affect the peak profile. As the displacement disorder increases, the 002 intensity diminishes toward zero. The effect of one type of displacement disorder is evaluated. It is found that experimentally one would find a negligible difference between a given number of crystals showing no displacement disorder and a larger number of crystals showing appreciable displacement disorder. Thus experimental estimates of the fraction of layers stacked in parallel clusters will be a sensitive function of the displacement disorder present in those clusters.

(*c*) Expressions for small angle scattering (000 Bragg maximum) can be deduced directly from expressions for the 002 profile because the *TPA* was not used. The low angle equations give useful approximations to results obtained by numerical integration of the actual interference functions.

2. Results of a similar analysis on the *hk*0 maxima showed that random rotational disorder by itself effectively suppresses interlayer interference effects in carbon for $R > 5$ Å.

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On the crystal structure of aureomycin hydrochloride

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A structure analysis of aureomycin hydrochloride, $C_{22}H_{23}N_2O_8Cl.HCl$, was undertaken in order to clarify certain stereochemical features of this member of the tetracyclin family. The salt crystallizes in the orthorhombic system with four chemical units in the cell, the dimensions of which are

$$a = 11{\cdot}20,\quad b = 12{\cdot}89,\quad c = 15{\cdot}47\ \text{Å}\,,$$

with space group $P2_12_12_1$ (Dunitz & Leonard, 1950; Pepinsky & Watanabé, 1952). Crystalline terramycin hydrochloride is strikingly isomorphous (Pepinsky & Watanabé, 1952).

X-ray data were collected as multi-film Weissenberg exposures, using Cu $K\alpha$ radiation, with intensities visually estimated. The structure analysis was initiated by establishment of the chlorine positions through a systematic study of a three-dimensional sharpened Patterson function. Starting from these positions, numerous iterated structure-factor and electron-density calculations on the IBM 704 and X-RAC were made, with contributions of lighter atoms included as they became discernible in the electron-density maps. Interpretations of these were aided by bounded projections along the *a* and *b* axes. All the atomic coordinates thus obtained were subjected first to least-squares and then differential-synthesis refinement, using the automatic refinement program of Vand & Pepinsky (1958) on the IBM 704. A three-dimensional error index of 0·154 was obtained for the final set of coordinates.

The aureomycin ion is found to possess the structure as proposed on chemical grounds (Hochstein *et al.*, 1953), with the exception of one significant stereochemical