Conclusions

Calculated structure factors based on a model that includes the effects of a tetrahedral and a fourth order cubic distortion of the spherical 'prepared' charge distribution have given a highly significant improvement in the fit to the diamond powder measurements of Göttlicher & Wölfel (1959) and to the silicon single crystal data of Hattori *et al.* (1965), when the HF wave functions of Clementi (1965) are used to describe the spherical 'prepared' distribution.

It is maintained that it is preferable to use full-matrix least-squares, combined with the significance tests of Hamilton (1964, 1965*a*) to analyse the complete set of experimental data for bonding features since in this way more information is obtained about the parameters that define the more complicated structure factor model. This point is becoming well recognized and has been used by Rouse, Willis & Pryor (1968) to analyse their neutron diffraction data on UO_2.

The necessity for placing restrictions on the form of the radial functions associated with the non-spherical distortions, the large e.s.d.'s of the distortion parameters and the dependence of the parameter values on the basis wave functions chosen to describe the spherical 'prepared' charge distribution indicate the need for exercising caution in analysing the experimental measurements for bonding features.

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References

Batterman, B. W. & Chipman, D. R. (1962). *Phys. Rev.* **127**, 690.

Clementi, E. (1965). *I.B.M. J. Res. Devel.* **9**, 2 plus supplement *Tables of Atomic Functions*.

Cooper, M. J., Rouse, K. D. & Willis, B. T. M. (1968). *Acta Cryst.* A**24**, 484.

Cromer, D. T. (1965*a*). *Acta Cryst.* **18**, 17.

Cromer, D. T. (1965*b*). *Acta Cryst.* **19**, 224.

Dawson, B. (1967*a*). *Proc. Roy. Soc.* A**298**, 255.

Dawson, B. (1967*b*). *Proc. Roy. Soc.* A**298**, 264.

Dawson, B. (1967*c*). *Proc. Roy. Soc.* A**298**, 379.

Dawson, B., Hurley, A. C. & Maslen, V. W. (1967). *Proc. Roy. Soc.* A**298**, 289.

Dawson, B. & Sanger, P. L. (1967). *Proc. Roy. Soc.* A**301**, 195.

DeMarco, J. J. & Weiss, R. J. (1965). *Phys. Rev.* A**137**, 1869.

Göttlicher, S. & Wölfel, W. (1959). *Z. Electrochem*, **63**, 891.

Hamilton, W. C. (1964). *Statistics in Physical Science.* New York: Ronald Press Co.

Hamilton, W. C. (1965*a*). *Acta Cryst.* **18**, 502.

Hamilton, W. C. (1965*b*). *Trans. Amer. Cryst. Assoc.* **1**, 17.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040.

Hart, M. & Milne, A. D. (1969). *Acta Cryst.* A**25**, 134.

Hattori, H., Kuriyama, H., Katagawa, T. & Kato, N. (1965). *J. Phys. Soc. Japan*, **20**, 988.

Herman, F. & Skillman, S. (1963). *Atomic Structure Calculations.* London: Prentice Hall.

Kato, N. (1965). Private communication to B. Dawson (see Dawson, 1967*c*).

McDonald, D. L. (1967). *Acta Cryst.* **23**, 185.

Renninger, M. (1955). *Acta Cryst.* **8**, 606.

Rouse, K. D., Willis, B. T. M. & Pryor, A. W. (1968). *Acta Cryst.* B**24**, 117.

Swanson, H. E. & Fuyat, R. K. (1953). *Natl. Bur. Std. Circ. No.* 539, **2**, 5.

Von der Lage, F. C. & Bethe, H. A. (1947). *Phys. Rev.* **71**, 612.

Weiss, R. J. (1964). *Phys. Letters*, **12**, 293.

Weiss, R. J. & Middleton, R. (1965). Private communication to B. Dawson from R.J. Weiss (see Dawson, 1967*b*).

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The Effect of Absorption in the Small Angle Diffraction of X-rays from Stacked Lamellae

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An expression for the scattering from a regular stack of lamellae is developed, maintaining an absorption term in the calculation. The effect of the absorption is to broaden peaks at small Bragg angles. The peaks sharpen with increasing order of diffraction. An expression for the lower angular limit of observable diffraction is evolved.

Introduction

The use of X-ray small angle scattering is widespread in the study of stacked lamellar polymer systems (see Geil, 1963, for a review) and has recently been used to study lamellar spinodal decomposition in an Al–Zn alloy (Rundman & Hilliard, 1967). The scattering by such systems yields peaks at small angles. In polymeric systems several orders are sometimes observed. Taking the stacking to be regular, the small angle peaks are conveniently treated as a diffraction phenomenon. The

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positions of the peaks are given by Bragg's law. Such systems have been treated in mathematical detail by Hosemann & Bagchi (1962), in which treatment variation in lamellar thicknesses, packing irregularities, and finite stacks have been included. A treatment of the simple system of infintely wide plates in perfectly regular stacking is analyzed in an appendix of a paper by Schultz, Robinson & Pound (1967). However, in all treatments the effects of absorption have been neglected. In this brief paper the scattering of the regular system is re-analyzed, including an absorption term. It is shown that the absorption term (1) causes peak broadening to increase with decreasing scattering angle, (2) causes an infinite stack to appear finite, and (3) sets a small angle limit on the observability of the scattering peak.

One is lead intuitively to these results. Consider an alternating periodic sequence of lamellae of types A and B as in Fig. 1. Consistent with the known structure of polymeric materials or spinodally decomposing systems the spacing d is taken to be of the order of 100 Å. In traversing the system of plates at the Bragg angle the intensity of the beam is attenuated as shown in Fig. 1. If d is large, the attenuation can be appreciable. Thus, the stack *appears* to be limited to only a few elements; the beam intensity vanishes with further penetration. Effectively a particle size broadening is set up. The relative penetration increases however, with higher order peaks, as illustrated, since the path traversed between repeat elements is shortened.

Analysis

The scattering system, composed of alternating A and B plates, is illustrated in Fig. 1. It is assumed now that the plates are unlimited in lateral extent. The density function for such a system is given by

$$\varrho(x)=\sum_{n=0}^{N}(\varrho_A P_1+\varrho_B P_2)*\delta(x-nd) \tag{1}$$

in which the asterisk denotes the convolution operation, ϱ_A and ϱ_B are the average densities within the A and B plates respectively, d is the repeat spacing and the fractions P_1 and P_2 are defined by

$$P_1=\begin{cases}1 \text{ if } 0<x\le l\\ 0 \text{ if } l<x\le d\end{cases}$$
$$P_2=\begin{cases}0 \text{ if } 0<x\le l\\ 1 \text{ if } l<x\le d.\end{cases} \tag{2}$$

The amplitude of scattering, $A(S)$, by such a system, when absorption is neglected, is

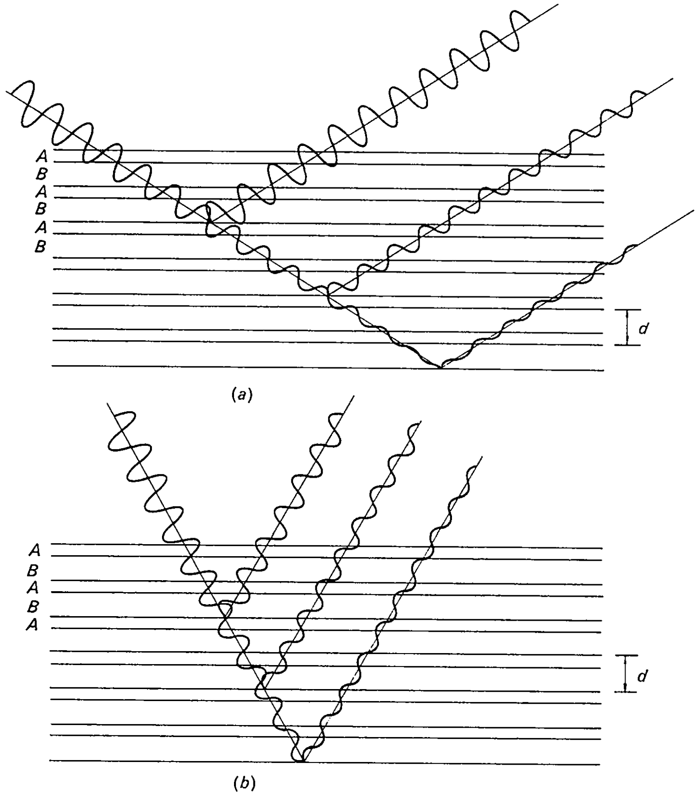

Fig. 1. The absorption problem in scattering from stacked lamellae. (*a*) and (*b*) show 1st and 2nd order diffraction from an alternating, periodic stack of A and B plates of repeat spacing d. As the beam tranverses the stack, it is attenuated less severely in the second order than in the first.

$$A(S)=\int\varrho(x)\exp(2\pi iSx)\mathrm{d}x\,, \tag{3}$$

where

$$S=2\sin\theta/\lambda\,. \tag{4}$$

When absorption is included, (3) becomes

$$A(S)=\int\varrho(x)\exp\left(-\frac{2\mu}{\lambda S}x\right)\exp(2\pi iSx)\mathrm{d}x\,. \tag{5}$$

Inserting (1) into (5), we have

$$A(S)=\sum_{n=0}^{N}\int_0^\infty[(\varrho_AP_1+\varrho_BP_2)*\delta(x-nd)] \times\exp\left(-\frac{2\mu}{\lambda S}x\right)\exp(2\pi iSx)\mathrm{d}x\,. \tag{6}$$

It is pertinent at this juncture to digress in order to develop a theorem which is useful in evaluating (6). Consider now the general integral,

$$F(S)=\int_0^\infty[g(x)*h(x)]L(S,x)\exp(2\pi iSx)\,\mathrm{d}x\,, \tag{7}$$

which is of the form of (6). Expanding the convolution and using the substitution $x=u+v$ we have,

$$\begin{aligned}F(S)&=\int_0^\infty\left[\int_0^\infty g(u)h(x-u)\mathrm{d}u\right]L(S,x)\exp(2\pi iSx)\mathrm{d}x\\&=\int_0^\infty\left[\int_0^\infty h(x-u)L(S,x)\exp(2\pi iSx)\mathrm{d}x\right]g(u)\mathrm{d}u\\&=\int_0^\infty\left\{\int_{-u}^\infty h(v)L(S,u+v)\exp[2\pi iS(u+v)]\mathrm{d}v\right\}\\&\quad\times g(u)\mathrm{d}u\,.\end{aligned} \tag{8}$$

If, now,

$$L(S,u+v)=L(S,u)L(S,v)\,, \tag{9}$$

and if $h(v)$ is zero for all $v<0$, then

$$\begin{aligned}F(S)&=\int_0^\infty\left[\int_0^\infty h(v)L(S,v)\right.\\&\quad\left.\times\exp(2\pi iSv)\mathrm{d}v\right]g(u)L(S,u)\exp(2\pi iSu)\mathrm{d}u\\&=\left[\int_0^\infty g(u)L(S,u)\exp(2\pi iSu)\mathrm{d}u\right]\\&\quad\times\left[\int_0^\infty h(v)L(S,v)\exp(2\pi iSv)\mathrm{d}v\right].\end{aligned} \tag{10}$$

The interrelation expressed by (7) and (10) is formally similar to the convolution theorem. It is, however, different in that (*a*) the limits run from 0 to ∞ rather than $-\infty$ to ∞, (*b*) a factor $L(S,x)$ is incorporated and must possess the special property of equation (9), and (*c*) one of the functions g or h must be non-zero only in the positive half-plane.

Our function $\exp(-2\mu x/\lambda S)$ has the property of (9) and the quantity $(\varrho_AP_1+\varrho_BP_2)$ is zero for all x in the negative half-plane. Thus the modified convolution theorem just derived can be used to expand equation (6). Thus,

$$\begin{aligned}A(S)=\sum_{n=0}^{N-1}\Bigg\{&\left[\int(\varrho_AP_1+\varrho_BP_2)\exp\left(-\frac{2\mu}{\lambda S}x\right)\cdot\exp(2\pi iSx)\mathrm{d}x\right]\\&\left[\int\delta(x-nd)\exp\left(-\frac{2\mu}{\lambda S}x\right)\cdot\exp(2\pi iSx)\mathrm{d}x\right]\Bigg\},\end{aligned} \tag{11}$$

where μ is the linear absorption coefficient. The absorption term derives from the path length $2x/\sin\theta=4x/\lambda S$ traversed by a beam incident at angle θ to the plane of the plates. 2, rather than 4, is used in the exponential since we deal at present with an amplitude, not an intensity. The first factor on the right side of (6) is the structure factor and determines the peak intensities. The second factor defines the positions and breadths of the scattering peaks. We shall confine our attention to the second factor, the lattice factor. Using the substitution

$$\alpha=2\mu/\lambda \tag{12}$$

and expanding in the usual way, the lattice factor $Z(S)$ becomes

$$Z(S)=\frac{1-\exp(-\alpha Nd/S)\exp(2\pi iSNd)}{1-\exp(-\alpha d/S)\exp(2\pi iSd)}\,, \tag{13}$$

where N is the number of plates in the stack. The intensity function $I(S)$ is proportional to $Z^*(S)\,Z(S)$:

$$I(S)=C_1Z^*(S)\,Z(S)=C_1\left\{\frac{1+\exp(-2\alpha Nd/S)-2\exp(-\alpha Nd/S)\exp(2\pi SNd)}{1+\exp(-2\alpha d/S)-2\exp(-\alpha d/S)\exp(2\pi Sd)}\right\} \tag{14}$$

where C_1 contains the structure factor.

If the number of plates N is large, then the absorption terms in the numerator of (14) are very small and can be neglected. In this case, (14) becomes

$$I(s)=C_1[1+\exp(-2\alpha d/S) -2\exp(-\alpha d/S)\cos(2\pi Sd)]^{-1}\,. \tag{15}$$

The peak breadth at half intensity can now be determined. In general, the absorption exponentials are near unity and can be expanded according to $\exp a=\sum_{n=0}^{\infty}\frac{a^n}{n!}$ to the second order. Further, the position of the peak is shifted at most only very slightly from $S=m/d$. Hence, the peak intensity I_p is given approximately by

$$I_p=C_1(m/\alpha d^2)^2\,. \tag{16}$$

The value of S at half intensity is given by

$$\tfrac{1}{2}(\alpha d^2/m)^{-2}=[1+\exp(-2\alpha d/S) -2\exp(-\alpha d/S)\cos(2\pi Sd)]^{-1}. \tag{17}$$

The half height value of S is assumed for now to deviate rather little from m/d. We define

$$\varepsilon = m - Sd\,. \tag{18}$$

Thus,

$$\cos(2\pi Sd) = \cos(2\pi\varepsilon) \simeq 1 - 2\pi^2\varepsilon^2\,. \tag{19}$$

Inserting (19) into (17), we have

$$\tfrac{1}{2}(\alpha d^2/m)^2 = 1 + \exp(-2\alpha d/S) - 2(1 - 2\pi^2\varepsilon^2)\exp(-\alpha d/S)\,. \tag{20}$$

The exponential terms progress only very slowly from unity. Thus the controlling term on the right of (20) is the one in ε. Thus, to a very good approximation, (20) can be written

$$(m/\alpha d^2)^2 = 1/8\pi^2\varepsilon^2\,. \tag{21}$$

Substituting (18) for ε in (21), we have for the position $S_{\frac{1}{2}}$ at half intensity,

$$\sqrt{8}\pi(1 - LS_{\frac{1}{2}}) = (\alpha d^2/m^2) = \alpha L^2 \tag{22}$$

where $L = d/m$ and $LS = 1$ at the Bragg position. Finally, the half breadth at half height is defined by

$$\Delta(LS) = \frac{1}{\sqrt{8}\pi}\,\alpha L^2\,. \tag{23}$$

Examples

The intensity function $I(s)$ is plotted in Fig. 2 for three lamellar materials of widely different absorbing power assuming a repeat spacing $d = 566$ Å.* The materials and their pertinent parameters are listed in Table 1. As expected, the more absorbent materials show the greater peak broadening at low angles, and peak 'sharpening' at higher orders.

Table 1. *Materials and parameters used in absorption effect calculations*

$\lambda = 1{\cdot}54$ Å

Material	μ/ϱ (cm^{-1})	ϱ (g.cm^{-1})	α (cm^{-2})
Linear polyethylene	3·95	0·95	$4{\cdot}88 \times 10^8$
Polytetrafluoroethylene	13·6	2·3	$40{\cdot}7 \times 10^8$
0·78 Al–0·22 Zn	53·4	3·68	256×10^8

The values of the broadening of the first and second order peaks were calculated according to the exact equation (15) and the approximation (23) for the curves of Fig. 2. For all peaks the approximate value agreed to within fifty percent with the exact value.

Apparent stack size and the limiting angle of resolution

We have seen that the effect of absorption is to broaden low angle diffraction peaks. The broadening is due to the inability of the beam to penetrate a large number of repeat units. Thus, an unbounded stack of lamellae appears as a limited stack of N elements. The value of N is determined, by use of the Scherrer equation, to be

$$\Delta(LS) = 1/2mN\,. \tag{24}$$

Substituting (23) into (24), we have for the effective number of repeat elements N,

$$N = \sqrt{2}\pi m/\alpha d^2\,. \tag{25}$$

For the first order peaks of Fig. 2, the values of N are 605 for PE, 68 for PTFE, and 12 for the Al–Zn alloy.

Clearly, there must be limiting cases of high d or μ beyond which a peak can no longer be resolved. We obtain an approximate expression for this condition by reference to the intensity relation, equation (15). We ask for the value of d at which the peak and trough intensities cannot be easily distinguished. To do this, the values of intensity at $S = 1/d$ and $S = 3/2d$ are compared. What intensity ratio is to be used at these two positions (peak and trough) is somewhat arbitrary. Using the condition

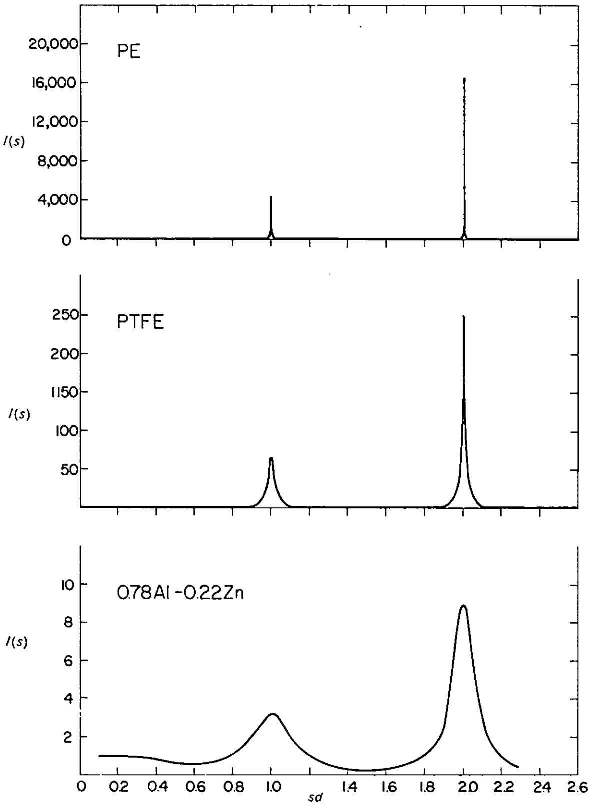

Fig. 2. Calculated scattering curves from an unbounded lamellar system with $d = 566$ Å for polyethylene (PE), polytetrafluoroethylene (PTFE) and an Al–Zn alloy.

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* The relative integrated *intensities* are not the observable intensities, since the absorption of the material outside the lamellar stack has not been accounted for. The integrated intensities, but not the peak shapes, will be affected by the added attenuation.

$$\frac{I(S=1/d)-I(S=3/2d)}{I(S=1/d)}=0\cdot1 \tag{26}$$

to describe the critical ratio, we find for the limiting value of d

$$d_c=\frac{\sqrt{4\cdot8}}{\sqrt{\alpha}}\ . \tag{27}$$

For the materials treated in this paper, the limiting repeat spacings are 9490 Å for PE, 3430 Å for PTFE, and 1370 Å for the Al–Zn alloy.

Discussion

In order for a material to show this effect, the plates need not be broad. For the case of a stack or colony of lamellae embedded in a matrix of the same average electron density, the results still hold, with the proviso that the amplitude function be corrected for the finite platelet width. (The effect of less broad lamellae is itself to broaden the diffraction peaks.)

If the real number of elements in the stack is limited, one needs to solve the exact equation (14). In this case, the numerator can no longer be set equal to unity. Calculations for finite stacks are beyond the scope of the present work. It is expected, however, that the results will be similar to those for the larger aggregates.

The limiting values of d calculated here indicate that advances in low angle resolution to d's in excess of 1μ will be of limited help in studying lamellar systems. It is, for example, evident that the band structure in slowly cooled PTFE (see Geil, 1963) and most eutectic or eutectoid colonies in alloys cannot be observable, due to the combination of high μ and d.

Conclusions

The effect of absorption on X-ray scattering from lamellar stacks has been shown to produce the following characteristics:

(1) Small angle diffraction peaks are broadened, proportionally to the linear absorption coefficient μ and the square of the repeat distance d.

(2) Proceeding to mth order peaks, these should be *sharpened* relative to the first order according to $1/m$.

(3) The effective number of scattering elements decreases sharply with denser material.

(4) Effective upper limits of d which can be resolved can be calculated. For most polymers, these values will be greater than 1000 Å, while for metals the value will be of the order of hundreds of Ångströms.

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References

GEIL, P. H. (1963). *Polymer Single Crystals*. New York: Interscience.

HOSEMANN, R. & BAGCHI, S. N. (1962). *Direct Analysis of Diffraction by Matter*, p. 428. Amsterdam: North Holland.

RUNDMAN, K. B. & HILLIARD, J. E. (1967). *Acta Met.* **15**, 1025.

SCHULTZ, J. M., ROBINSON, W. H. & POUND, G. M. (1967). *J. Polymer Sci.* **5A–2**, 511.

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On Refinement of the Crystal Orientation Matrix and Lattice Constants with Diffractometer Data

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An alternative to the procedure suggested by Busing & Levy [*Acta Cryst.* (1967) **22**, 457] for refining the crystal orientation matrix and (if desired) the crystal lattice parameters is proposed, in which linear observational equations are written with Miller indices as coefficients. Constraining equations appropriate to the crystal symmetry (exact to first order in the corrections) are presented for monoclinic, hexagonal, orthorhombic, tetragonal, and cubic systems.

In a recent paper and an associated report, Busing & Levy (1967*a*,*b*) have presented equations in matrix notation for single-crystal diffractometer angles in terms of the lattice constants and the crystal orientation matrix. In connection with these equations these authors have suggested procedures for refining the orien-