

the same Debye–Waller parameter was found and the population parameter was  $2.01 \pm 0.03$ . Evidently the cusp-constrained density function (4) does not have quite enough charge in the neighborhood of the nucleus.

As pointed out above, the construction of (4) is along tenuous lines, but at least serves to illustrate the importance of electronic details in a calculated atomic scattering factor. A difficult, but accurate, quantum-chemical calculation of the electronic wavefunction for diamond is probably needed to correctly describe the X-ray scattering at the large values of  $\sin \theta/\lambda$  ( $> 0.7 \text{ \AA}^{-1}$ ). A Hartree–Fock core scattering factor appears to be insufficient for the case studied here. It should also be noted that a detailed charge-density analysis of the valence structure of diamond (Stewart, 1973) does not significantly alter the results in Table 1.

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## Strain Effects on Diffraction Profiles of Random-Layer Lattices

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In previous treatments of diffraction by random-layer lattices the effect of strain has been neglected. In this study the applicability of Cauchy's, Gauss's and Laplace's distributions to strain in layered lattices is examined and equations for the intensity profiles have been developed which take the strain effect into account. An analysis of the scattering intensities of glassy carbon revealed that the strain distribution has a Cauchy form and the contribution of strain to the widths of the observed intensity profiles ranges from 43 to 85%.

### Introduction

The peculiar shape of the two-dimensional reflections produced by random-layer lattices was explained quantitatively by Warren (1941). Later work mainly concerned some of the simplifications made in the derivation of the Warren equation and alternative approaches in deriving similar equations (Wilson, 1949; Brindley & Mering, 1951; Warren & Bodenstein, 1966; Ruland, 1967). The above treatments involved the concept of small layers. Ergun (1970) noted that in carbons the existence of small layers having sizes indicated by the line widths of their diffraction profiles is not substantiated by electron-microscope observations or small-angle scattering and proposed a defective lattice theory. A recent study of the Fourier transforms of the

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intensities of a glassy carbon (Ergun & Schehl, 1973) revealed that the observed widths of the peaks are largely produced by strain. For example, strain accounts for 57 and 78% of the observed widths of the 11 and 41 reflections, respectively, of the glassy carbon studied. For an authentic interpretation of the observed profiles it appears that it is necessary to develop equations that take the strain into account.

### Theory

For an isotropic sample the contribution to the interference function of an interatomic distance  $l$  is given by  $\sin(hl)/hl$ , with  $h=4\pi \sin \theta/\lambda$ ,  $\theta$  being the Bragg angle and  $\lambda$ , the wavelength. If, owing to strain, an interatomic distance  $l$  is altered by  $\delta$ , we need to evaluate.

$$p(h, l, \delta) = \langle \sin(l + \delta)h / (l + \delta)h \rangle$$

$$= \int_{-\infty}^{\infty} [\sin(l + \delta)h / (l + \delta)h] \varphi'(\delta) d\delta \quad (1)$$

in which  $\varphi'$  is the frequency function.

Particularly attractive for evaluating  $p$  is the Cauchy distribution, the frequency function of which is given by

$$\varphi'(\delta) = \sigma / (\sigma^2 + \delta^2) \pi \quad (2)$$

in which the parameter  $\sigma$  defines the distribution. Replacing  $\sin X/X$  by  $\text{Re} \int_0^1 \exp(iXu) du$ , we obtain

$$p = \text{Re} \int_0^1 \int_{-\infty}^{\infty} [1 / (\sigma^2 + \delta^2)] \exp ih(l + \delta)u d\delta du$$

$$p = \int_0^1 \exp(-h\sigma u) \cos(hlu) du \quad (3)$$

Upon integration we obtain

$$p = [\exp(-h\sigma) / (1 + \delta^2/l^2)] [\sin(hl)/hl]$$

$$+ [\sigma/h(l^2 + \sigma^2)] [(1 - \exp(-h\sigma) \cos(hl))].$$

Since  $l \gg \sigma$ , i.e., the indeterminacy  $\sigma$  of  $l$  is much smaller than  $l$ ,

$$p = \exp(-h\sigma) \sin(hl)/hl \quad (4)$$

The frequency function of the Gaussian and Laplace distributions may be expressed as

$$\varphi'(\delta) = (1/2\sigma\sqrt{\pi}) \exp(-\delta^2/4\sigma^2), \quad (5)$$

$$\varphi'(\delta) = (1/2\sigma) \exp(-|\delta|/\sigma), \quad \sigma > 0 \quad (6)$$

respectively. By similar substitutions we obtain

$$p = \int_0^1 \exp(-h^2\sigma^2u^2) \cos(hlu) du \quad (\text{Gaussian}) \quad (7)$$

$$p = \int_0^1 [1 / (1 + \sigma^2h^2u^2)] \cos(hlu) du \quad (\text{Laplace}). \quad (8)$$

Simple solutions to equations (7) and (8) may be obtained if  $h\sigma \ll 1$ ; we then may replace  $\exp(-h^2\sigma^2u^2)$  and  $1/(1 + h^2\sigma^2u^2)$  by  $1 - h^2\sigma^2u^2$  and arrive at identical solutions using the Laplace and Gaussian distributions. With further simplifications involving the relative magnitudes of  $\sigma$  and  $l$ , we obtain

$$p \simeq (1 - h^2\sigma^2) \sin(hl)/hl \quad (9)$$

$$p \simeq \exp(-h^2\sigma^2) \sin(hl)/hl \quad (9a)$$

$$p \simeq [1 / (1 + h^2\sigma^2)] \sin(hl)/hl \quad (9b)$$

Equations (4), (9a), and (9b) may be derived more simply as follows. Replace, in equation (1),  $\sin(l + \delta)h$  by  $\sin(lh) \cos(\delta h)$ , neglect  $\delta h$  in the denominator and perform the integration by substituting equations (2), (5) and (6) respectively. Evidently such a simplification is more valid for Cauchy's distribution than for the others because a rigorous derivation of equation (4)

does not require the questionable assumption that  $h\sigma$  is always small.

For simplicity we may consider a lattice containing one kind of atom. The interference function may be expressed as

$$j(h) = \sum_q g(l_q) n(l_q) \langle \sin(l_q + \delta_q)h / (l_q + \delta_q)h \rangle$$

where  $n(l)$  is the number of neighboring atoms at a distance  $l$  from any atom in a lattice of infinite extent,  $g(l)$  is a function that modifies  $n(l)$  for the presence of defects or discrete particles. From equations (1), (4) and (9) we observe that the above equation may be expressed as

$$j(h) = \eta(l) g(l) n(l) \sin(hl)/hl \quad (10)$$

with the understanding that  $l$  is a subscripted variable and the right-hand side of equation (10) involves the necessary summation. In equation (10),  $\eta(l)$  is the coefficient of  $\sin(hl)/hl$  in equation (9) or (4). For a rigid lattice  $\eta(l) = 1$ . The function  $\eta$  modifies the interference function for strain.

As to the relation of  $\delta$  to  $l$ , we may consider  $l$  to be made up of  $m$  distances each having a length  $l/m$  and displacement  $\delta_1$ . If the displacements are random and have the same distribution, the average of  $m$  distributions is the same as each distribution. This follows from a common property of the Gaussian, Laplace, and Cauchy distributions, that is, each distribution reproduces itself by composition (cf. Cramer, 1951). For the Gaussian and Laplace distributions  $\sigma^2(l) = m\sigma^2(l/m)$  and for Cauchy's distribution  $\sigma(l) = m\sigma(l/m)$ . Thus we have

$$\eta_C(l) = \exp(-h\sigma l) \quad (11a)$$

$$\eta_G(l) = \exp(-h^2\sigma^2 l) \quad (11b)$$

$$\eta_L(l) = 1 / (1 + h^2\sigma^2 l) \quad (11c)$$

for Cauchy's, Gauss's, and Laplace's distributions respectively. In equations (11), the  $\sigma$ 's represent the indeterminacy of unit distances; they do not necessarily have the same value for every distribution.

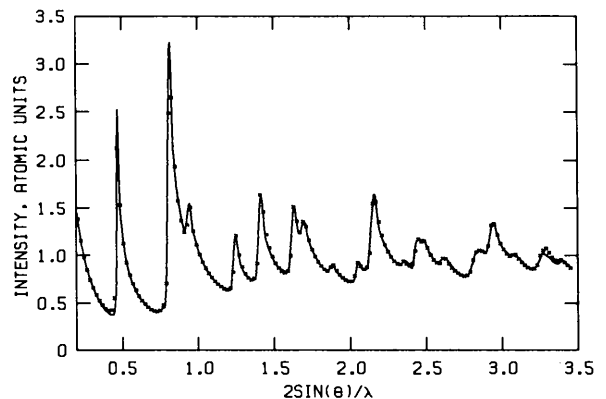


Fig. 1. Experimental (solid line) and theoretical (crosses) scattering intensities of a glassy carbon.

For a defective lattice

$$g(l) = \exp(-\alpha l), \quad \alpha > 0 \quad (12)$$

in which  $\alpha = 2/L$ ,  $L$  being the mean value of defect-free distances (Ergun, 1970). In equations (10)–(12) the variables  $n$  and  $l$  characterize the lattice (*cf.* Ergun, 1970) and their formulation and numerical calculations using a computer, present no special difficulty. However, if  $\alpha$  and  $\sigma$  are small, the calculations may involve several thousand interatomic distances and hence become tedious. Under such conditions it is advantageous to resort to the lattice-sum technique by which equations are developed for the profiles of individual reflections.

If the strain effect is neglected, the profiles of the two-dimensional  $hk$  reflections of isotropic random-layer lattices may be expressed as (Ruland, 1967; Ergun & Berman, 1973)

$$j(h) = (\pi m F^2 / n A h) \int_0^\infty g(r) J_0(h_0 r) \sin(hr) dr \quad (13)$$

in which  $m$  is the multiplicity factor,  $F^2$  is the geometric structure factor,  $A$  is the area of the unit cell,  $n$  is the number of atoms in it,  $h_0 = 2\pi/z$ ,  $z$  being the distance of separation of the  $\{hk\}$  lines,  $J_0$  is the Bessel function of zero order. We may modify the integrand of equa-

tion (13) by  $\eta(r)$  for the strain effect. Integrating we obtain

$$j(h) = (\pi m F^2 / 2n A h \sqrt{Ch}) T(Y) \quad (14)$$

in which  $T(Y)$  is defined by

$$T(Y) = [(Y^2 + 1)^{1/2} + Y / (Y^2 + 1)]^{1/2} \quad (15)$$

$$Y = (h^2 - h_0^2 - C^2) / 2Ch \quad (16)$$

$$C = \alpha + \sigma h \quad (\text{Cauchy's distribution}) \quad (17a)$$

$$C = \alpha + \sigma^2 h^2 \quad (\text{Gauss's or Laplace's distribution}). \quad (17b)$$

The function  $T$  has maximum at  $Y = 1/\sqrt{3}$ , and  $T_{\max} \approx 1.14$ .

Equations (10) and (14) yield identical profiles. The former is applicable to any lattice, the latter is for random-layer lattices only. Although equation (14) gives the profiles of individual peaks, the observed profile cannot be reproduced without considering the influences of the other peaks. Each peak rises very sharply and falls slowly. The observed profile of a peak is influenced by all of the peaks appearing at lower angles and a few neighboring peaks at higher angles.

#### Evaluation of defect and strain effects

The theory of distortion in a lattice is complex and has been the subject of numerous studies (*cf.* Warren, 1959; Keating, 1968; Ergun, 1973). In a strict sense a random distribution of distortion is not valid in that strain in the lattice is a function of distance from defects (or faults), being greatest in the vicinity of defects. However, composition of a large number of non-random components produces an approximately random distribution (Cramer, 1951); for this reason three commonly encountered random distributions have been considered in this study, the primary objective being the derivation of intensity equations that take strain effect in random-layer lattices into account.

Detailed analyses of the atomic radial distribution functions of turbostratic carbons indicated that the strain distribution has a Cauchy form (Ergun & Schehl, 1973; Ergun, 1973). Thus equation (14) with  $C$  defined by equation (17a) should reproduce the observed profiles. The experimentally obtained interference function of a glassy carbon is shown in Fig. 1 as a solid line. The parameters  $m$ ,  $F^2$ ,  $n$ ,  $A$ , and  $h_0$  that appear in equation (14) concern the unit-cell structure and are readily calculated. The two-dimensional unit cell of carbons is a  $60^\circ$  rhombus with  $a = 2.461 \text{ \AA}$  and  $n = 2$ . The two atoms are at  $0, 0; \frac{1}{3}, \frac{2}{3}$ . Thus  $m = 2$  if  $h = k = 0$ , 12 if  $h = k \neq 0$ , 24 if  $0 \neq h \neq k \neq 0$ ;  $F^2 = 4$  if  $(h - k) \bmod 3 = 0$ , 1 otherwise;  $A = 5.246 \text{ \AA}^2$ ; and  $h_0 = (4\pi/a\sqrt{3}) (h^2 + k^2 + hk)^{1/2}$ . To reproduce theoretically the observed interference function we need to know the values of  $\alpha$  and  $\sigma$  in equation (17a). In principle these parameters are obtained by matching the calculated and observed

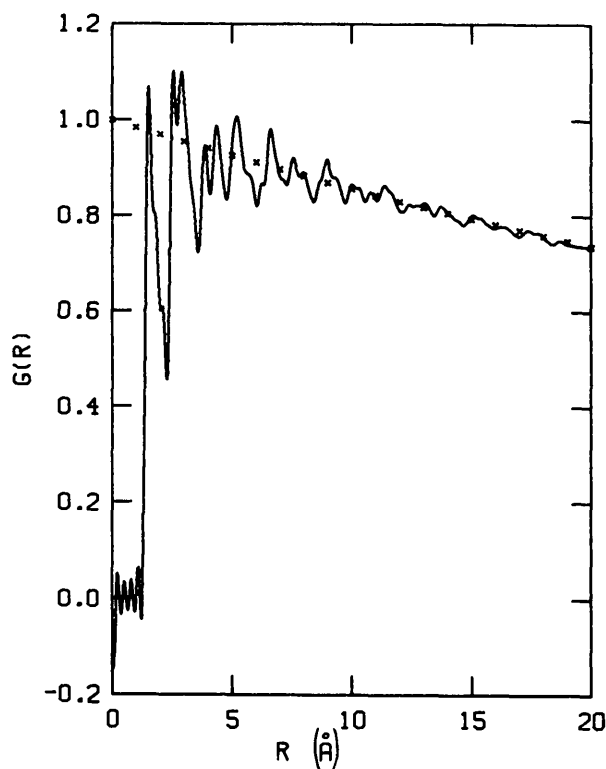


Fig. 2. The function  $G(R)$ . Solid line is obtained numerically from equation (18) using the experimental intensity data; crosses are obtained from equation (19) with  $\alpha = 0.0233$ .

profiles using a procedure that minimizes the differences.

The defect parameter  $\alpha$  can be determined simply and directly by numerical evaluation of the integral (Ergun, 1973)

$$G(R) = (2/\pi^2 R^2 \rho) \int_0^R \int_0^H h r i(h) \sin(hr) dh dr \quad (18)$$

in which  $i(h) = j(h) - 1$ ,  $H$  is the maximum value of  $h$  ( $\approx 22$  for Ag  $K\alpha$ ),  $\rho$  is the atomic density of the layers, and  $R$  is the radial distance. At  $R > 7$  the function  $G(R)$  may be approximated by (Ergun, 1973)

$$G(R) = (2/\alpha^2 R^2) [1 - (1 + \alpha R) \exp(-\alpha R)]. \quad (19)$$

The function  $G(R)$  as determined numerically from equation (18) using experimental  $i(h)$  is shown in Fig. 2 (solid line). At  $R = 20 \text{ \AA}$  the plot yielded a value of 0.736 for  $G(R)$  which, from equation (19), corresponds to 0.0233 for  $\alpha$ . Graphical representation of equation (19) for  $\alpha = 0.0233$  is included in Fig. 2 (crosses). The function  $G(R)$  involves an area integral of the atomic radial distribution function and, hence, is the normalized coherent atomic density; its systematic decrease with  $R$  constitutes a measure of the diminution (due to defects) of coherence with increase in distance. Having evaluated  $\alpha$ , determination of  $\sigma$  by profile matching becomes much simpler.

### Discussion

The calculated theoretical profile with  $\alpha = 0.0233$  and  $\sigma = 0.0060$  is shown in Fig. 1 as crosses. The agreement between the theoretical and experimental intensities is rather remarkable in view of the fact that it has not been possible before to reproduce theoretically the observed intensity profiles of carbon over an angular range covering more than one peak. As will be apparent, the neglect of strain in previous theoretical treatments was largely responsible for the failure.

An examination of equations (14) and (15) reveals that the peak shape is largely determined by  $T(Y)$  and that the peak width is nearly linear with  $C$  (the linearity is not obvious but can be verified). Substituting  $\alpha = 0.0233$  and  $\sigma = 0.0060$  in equation (17a), we may cal-

culate  $C$  and the contribution of strain to  $C$ . The results are shown in Table 1 for the prominent two-dimensional reflections of the carbon studied. From the Table we observe that the widths of the 10, 11, 21, 30 and 41 reflections would correspond to the mean defect-free distances of 49, 37, 29, 26, and 19  $\text{\AA}$  respectively, whereas the actual value of the mean defect-free distance is  $2/\alpha = 86 \text{ \AA}$ . In reality, the influence of the neighboring reflections does not permit determination of the correct peak widths (save the 10 peak) and the observed widths do not increase linearly with  $h_0$  as dictated by equation (17a). It is clear that a study of the structure requires a careful profile analysis over an angular range covering several peaks (a minimum of 2). The equations required for such an analysis have been developed in this study.

Table 1. Widths,  $C = \alpha + \sigma h$ , and the corresponding linear dimensions of some prominent  $hk$  reflections of carbon for  $\alpha = 0.0233$  and  $\sigma = 0.0060$

| Reflections | Width $C$ | Percent due to strain<br>$100 \times (1 - \alpha/C)$ | Corresponding dimension $2/C$ |
|-------------|-----------|--|-------------------------------|
| 10          | 0.041     | 43   | 49                            |
| 11          | 0.054     | 57   | 37                            |
| 21          | 0.069     | 66   | 29                            |
| 30          | 0.077     | 70   | 26                            |
| 41          | 0.105     | 78   | 19                            |

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