

and the average number of atoms in any of the three ω regions is

$$M_{\omega} = \frac{1}{\alpha^2} (T-1)^2 / (T-S)^2. \quad (32)$$

If we begin with an atom in one of the $\frac{1}{4}(T-3S)$ defective configurations, of the $T-1$ possible boundaries there are $\frac{1}{4}(T-3S)-1$ fictitious boundaries, $3(T-3S)/4$ defect/defect boundaries, and $3S$ defect/ ω boundaries. Hence the probability that a boundary is real is

$$[3(T-3S)/4 + 3S]/(T-1) = \frac{3}{4}(T+S)/(T-1)$$

and the average number of atoms in any of the four defective regions is

$$M_D = \frac{16}{9\alpha^2} (T-1)^2 / (T+S)^2. \quad (33)$$

Equations (32) and (33) relate M_{ω} and M_D to α , T , and S , quantities which are essentially fictitious and not observable. We prefer to express them in terms of the experimentally measurable η and γ . With the aid of equations (3) and (25) we find that

$$M_{\omega} = \frac{1}{4}(2\gamma+3)^2 / [(\gamma+1)^2(1-\eta)^2], \quad (34)$$

and

$$M_D = \frac{4}{9}(2\gamma+3)^2 / [(\gamma+2)^2(1-\eta)^2]. \quad (35)$$

A complete statistical description of the structure of the hexagonal plane should include not only the average sizes of the various regions, but as well the relative numbers of regions to be found in the plane. Consider a plane containing M atoms. Let there be V regions which are ω_1 . If we choose an atom at random, the probability that it is in an ω_1 region is

$$\frac{VM_{\omega}}{M} = \frac{S}{T} = 1/(2\gamma+3)$$

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On the Dependence of X-ray Debye-Waller Parameters on Atomic Form Factors

BY ROBERT F. STEWART*

Department of Physics, University of Western Australia, Nedlands, W. A. 6009, Australia

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An analysis of powdered-diamond diffraction data with Hartree-Fock and standard molecular C atomic form factors yields the Debye-Waller parameters 0.20 ± 0.01 and $0.172 \pm 0.009 \text{ \AA}^2$ respectively. The lattice-dynamic value, which is calculated here from published phonon dispersion curves measured by inelastic neutron scattering, is $0.149\text{--}0.150 \text{ \AA}^2$ at 298°K . It is shown that a small amount of an orbital product, $\chi_{1s}^{\text{SCF}} \chi_{2s}^{\text{STO}}$, in the core atomic scattering factor can dramatically alter the Debye-Waller parameter. For diamond, this latter scattering factor gives a value of $0.134 \pm 0.009 \text{ \AA}^2$.

The determination of an accurate Debye-Waller factor for simple monatomic crystals by absolute X-ray diffraction intensities is generally limited by the model for

* Alfred P. Sloan Fellow. Present address: Department of Chemistry, Carnegie-Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, U.S.A.

by equation (3). So with equation (34), the number of ω_1 regions per atom in the plane is

$$\frac{V}{M} = \frac{4(\gamma+1)^2(1-\eta)^2}{(2\gamma+3)^3}. \quad (36)$$

Let there be W regions associated with one of the four possible defective configurations of Fig. 3 in the plane of M atoms. Then

$$M = 3VM_{\omega} + 4WM_D$$

and from equations (34), (35), and (36) the number of defective regions of a particular type per atom in the plane is

$$\frac{W}{M} = \frac{9}{8} \frac{\gamma(\gamma+2)^2(1-\eta)^2}{(2\gamma+3)^3}. \quad (37)$$

This means that though the average size of a defect region in the plane is a relatively insensitive function of γ [equation (35)], their number density in the plane decreases rapidly as γ becomes small.

With the values of $\gamma=0.24$ and $\eta=0.055$ found from the measurements, from equations (34) and (36), for any one of the three kinds of ω regions, there are on the average 2.20 atoms per region and 0.130 regions per atom in the plane. From equations (35) and (37), for one of the four kinds of defect regions, there are 1.20 atoms per region and 0.029 regions per atom in the plane. The hexagonal planes are very imperfect.

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crystal diffraction. In particular, thermal diffuse scattering and extinction phenomena make it difficult to infer true Bragg structure factors from a set of accurately measured intensities of X-ray scattering. Even if these difficulties can be successfully overcome, the analysis for the Debye-Waller factor at a single tem-

perature must rely on a theoretical atomic form factor, which is a non-constant function of the X-ray scattering vector. (For neutron diffraction the same complication in coherent scattering length does not occur.) In practice one usually uses the one-electron density function from a spin-restricted Hartree-Fock atomic wave function for the atomic scattering factor. Such a representation may well be inappropriate for the atom in a crystal. In any event the inference of the Debye-Waller factor rests on the assumption that the one-electron density follows a small nuclear displacement so that the time-averaged one-electron density function is a simple convolution of the stationary charge density onto the nuclear distribution function. In the limit of small displacements the assumption is reasonable. In the present note we will adopt this position, but will pursue the question on the reliability of a Hartree-Fock atomic form factor.

The author has pointed out that 'standard molecular' scattering factors for the first-row atoms are more appropriate for a valence charge-density analysis of organic molecular crystals than are form factors comprised of products of Hartree-Fock 2s and 2p atomic orbitals (Stewart, 1970). Coppens (1971) has reported that atomic thermal parameters, based on the use of standard molecular scattering factors in structure refinements of X-ray data, are in closer agreement with neutron diffraction results than a similar refinement based on Hartree-Fock atomic scattering factors. The standard molecular scattering factors have smaller amplitude than a Hartree-Fock form factor at larger values of $\sin \theta/\lambda$. This is due to the neglect of a density contribution on and near ($\leq 0.1 \text{ \AA}$) the nucleus that arises from the square of the 2s Hartree-Fock atomic orbital. In a qualitative way, the standard molecular scattering factor will account for a drift of charge density off the nucleus in the formation of a chemical bond for a first-row atom. An illustration of the different Debye-Waller parameters from these atomic scattering factors is given below.

An accurate set of X-ray diffraction structure factors has been published by Göttlicher & Wölfel (1959). These workers report a Debye-Waller factor, $B = 0.2007 \text{ \AA}^2$ which was derived by fitting the higher-angle data ($\sin \theta/\lambda < 0.7 \text{ \AA}^{-1}$) to a Hartree-Fock atomic scattering factor. The data are absolutely scaled. For the study reported here, all seventeen data points are included in the error function

$$\varepsilon = \sum_{g_w} (1/\sigma^2/g_w) [f_{g_w} - f \exp(-Bx^2)]^2 \quad (1)$$

where $x = \sin \theta/\lambda$ and f_{g_w} and σ_{g_w} are the data points and estimated standard deviations, respectively (Göttlicher & Wölfel, 1959). The function, f , is the atomic scattering factor of interest with which the one-dimensional error function (1) is minimized with respect to B , the Debye-Waller parameter. The results for two Hartree-Fock scattering factors and a standard molecular scattering factor are given in Table 1. The second

Hartree-Fock entry for C is the so-called prepared valence state which is derived from the 5S state of C. The two Hartree-Fock results are in substantial agreement whereas the standard molecular scattering factor affords a possibly significantly lower Debye-Waller parameter.

Table 1. *Diamond powder X-ray Debye-Waller factors for different atomic scattering factors*

$R_w = \{\varepsilon/\sum(f_{g_w}/\sigma_{g_w})^2\}^{1/2}$. The last entry is the lattice dynamic value for diamond.

	f	$B(\text{\AA}^2)$	R_w
H-F	$(1s)^2(2s)^2(2p)^2$	0.204 ± 0.014	0.0379
H-F	$(1s)^2(2s)^2(2p)^3$	0.195 ± 0.016	0.0408
Standard molecular	$(1s)^2(L)^4$	0.172 ± 0.009	0.0240
Cusp-constrained core	$(ccK)^2(L)^4$	0.134 ± 0.009	0.0247
Lattice dynamic calculation		$0.149 - 0.150$	

The true Debye-Waller factor for diamond can be calculated from a frequency spectrum of the solid. The appropriate expression, as given by Blackman (1937), is

$$B = 2h^2/(mkT) \int_0^\infty g(v) \{1/u(e^u - 1) + \frac{1}{2}u\} dv \quad (2)$$

where $u = hv/kT$ and $g(v)$ is the normalized total density of normal vibrations in the crystal. The dispersion curves for phonons in diamond have been measured, (Dolling & Cowley, 1966; Warren, Yarnell, Dolling & Cowley 1967), so that $g(v)$ is known experimentally and (2) may be easily computed. The simple average, $\langle v^{-1} \rangle$, is given by Dolling & Cowley (1966) and amounts to a zero-point contribution of 0.128_8 \AA^2 to the Debye-Waller factor. The temperature-dependent term is small and can be safely estimated with a Debye spectrum since the equivalent Debye cut-off frequencies are relatively insensitive to the moments, $\langle v^n \rangle$, of the distribution function $g(v)$ for diamond (Dolling & Cowley, 1966). For the $\langle v^{-2} \rangle$ moment the equivalent Debye frequency is $3.96 \times 10^{13} \text{ sec}^{-1}$ and for $\langle v^{-1} \rangle$ it is $3.87 \times 10^{13} \text{ sec}^{-1}$. These Debye frequencies are the extremes for the moments $\langle v^{-2} \rangle$ through $\langle v^6 \rangle$. Thus at $T = 298^\circ \text{K}$, the thermal average adds an amount between 0.0202 to 0.0216 \AA^2 to the Debye-Waller factor. The lattice-dynamic value for B , from (2), is $0.149 - 0.150 \text{ \AA}^2$. This result is considerably below the X-ray values listed in Table 1.

The data of Göttlicher & Wölfel are not corrected for thermal diffuse scattering, but such additional intensities to the Bragg peak should be small since the elastic constants are rather large. The neglect of diffuse scattering in the analysis of X-ray diffraction data always results in a *low* determination of the Debye-Waller parameter. From the relations given by Lucas

(1969) and the elastic constants of diamond listed in Kittel (1967), we conclude that inclusion of thermal diffuse scattering in the analysis will increase B by no more than 0.01 \AA^2 . This correction would introduce further discrepancy between the Debye-Waller parameter based on the Hartree-Fock or the standard molecular atomic scattering factors and the lattice dynamic value from (2). If extinction were appreciable in the Göttlicher & Wölfel data, a high estimate of the Debye-Waller parameter would result. The extinction would have to reduce the intensity by at least 10% to account for the discrepancy. This is probably too large for the powder data.

If it is assumed that the lattice-dynamic value for B is correct and that the Göttlicher-Wölfel data is correctly reduced to structure factors (an error no larger than 2-3%), then it can be inferred that the atomic scattering factor has too large an amplitude at the larger $\sin \theta/\lambda$ values ($\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$). This means that the atomic density function has too much charge on and near the carbon nucleus for the description of the static charge density of carbon in the diamond lattice. One could attempt to solve the equations of motion for the electrons in the potential of stationary carbon nuclei at the diamond lattice sites. A recent self-consistent field calculation (Euwema, Wilhite & Suratt, 1973) may well provide a satisfactory solution. Such a task, however, is not the intent of the present communication. Instead, an *ad hoc* construction of a density function is outlined below.

If one were to span the crystal wave function for diamond by the atomic-orbital basis functions, χ_{1s}^{SCF} , χ_{2s}^{STO} and higher orbitals, but without further inclusion of $1s$ and $2s$ type basis functions, then the one-electron density function would necessarily contain components of the form $(\chi_{1s}^{\text{SCF}})^2$ and $\chi_{1s}^{\text{SCF}} \chi_{2s}^{\text{STO}}$. In the present discussion, χ_{1s}^{SCF} is the Hartree-Fock atomic orbital (Clementi, 1965) with the lowest eigenvalue for the isolated atom, and χ_{2s}^{STO} is a standard molecular Slater-type orbital (Hehre, Stewart, & Pople, 1969). Neither the atomic Hartree-Fock nor the standard molecular density functions contain a density contribution from $\chi_{1s}^{\text{SCF}} \chi_{2s}^{\text{STO}}$. Rather than attempt a quantum-chemical solution, one can estimate the amount of $\chi_{1s}^{\text{SCF}} \chi_{2s}^{\text{STO}}$ in the density function from the nuclear cusp condition.

For a many-electron wavefunction, which solves the non-relativistic Schrödinger equation, Kato (1957) has shown that certain cusp constraints must be invoked because of the Coulombic singularities which result when the electrons touch the atomic nucleus or each other. This rigorous condition places a constraint on the one-electron density function for both atoms (Steiner, 1963) and molecules (Pack & Brown, 1966). The appropriate relation is

$$[(\partial \bar{\rho} / \partial r) / \bar{\rho}] r_{j=0} = 2Z \quad (3)$$

where $\bar{\rho}$ is the spherically averaged one-electron density function about the j th nucleus with an atomic number of Z . Hartree-Fock wave functions for the first row

atoms, as tabulated by Clementi (1965), do not satisfy (3). [In the same compilation, second-row atoms do satisfy the cusp condition.] For example the Hartree-Fock wave function for $\text{C}(^3P)$, tabulated by Clementi, has a value of -12.02920 for (1). We correct this small defect by including a small amount of the orbital product $\chi_{1s}^{\text{SCF}} \chi_{2s}^{\text{STO}}$ in the core density function.

For a carbon atom, a cusp-constrained core density function is

$$\rho_{cc} = 0.957605(\chi_{1s}^{\text{SCF}})^2 + 0.042395N\chi_{1s}^{\text{SCF}}\chi_{2s}^{\text{STO}} \quad (4)$$

where $N = 1/\int \chi_{1s}^{\text{SCF}} \chi_{2s}^{\text{STO}} dr$. The function (4) can be populated with two electrons and used to calculate a cusp-constrained core scattering factor. Note that (4) has less charge on the nucleus than a 'standard molecular' density function (about 4% less) and the gradient of the density, (4), at $r=0$ is also less than a 'standard molecular' result by $\sim 4\%$.

The construction above depends crucially on a slightly inexact representation for χ_{1s}^{SCF} . A numerical Hartree-Fock wave function for an atom does satisfy the nuclear cusp condition; for this case no contribution of $\chi_{1s}^{\text{SCF}} \chi_{2s}^{\text{STO}}$ is needed to satisfy (3). Thus the estimate of $\chi_{1s}^{\text{SCF}} \chi_{2s}^{\text{STO}}$ in the density function for carbon that is displayed in (4) is a consequence of the analytical expansion (Clementi, 1965) for χ_{1s} . Nevertheless it is instructional to explore the influence of the density function (4) on the determination of the Debye-Waller parameter for diamond powder diffraction data.

The scattering factor from (4) has a smaller amplitude of scattering at $\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$ than a pure-core scattering factor by about 10%. Estimates in the change in B can be made for the case where the crystal contains one atom per unit cell and the sampling of diffraction data is sufficiently dense to replace the least-squares sum with an integral over $\sin \theta/\lambda$. For this case the absolute change in B for a change in the scattering factor is

$$\Delta B = \int (\Delta f/x^2 f) f^2 x^6 \exp(-2Bx^2) dx / \int f^2 x^6 \times \exp(-2Bx^2) dx \quad (5)$$

where x is $\sin \theta/\lambda$ in \AA^{-1} and the integration is restricted to the Ewald sphere. The relative differences in B are most pronounced for small values of B . For a C atom the relative change, $\Delta B/B$ is -0.22 for $B=0.2 \text{ \AA}^2$ but only -0.02 for $B=2 \text{ \AA}^2$ when compared to a result from a Hartree-Fock scattering factor. Thus the cusp constraint, as we have introduced it *via* (4), can dramatically alter the X-ray value of a Debye-Waller parameter for a monatomic crystal that has an inherently small mean-square amplitude of vibration. The value of B , which minimizes the error function (1) for a scattering factor based on (4), is given as the fourth entry in Table 1. It is much less than the other X-ray values and is even below the lattice dynamical result. When (4) was assigned a variable electron-population parameter in the least-squares error function,

the same Debye–Waller parameter was found and the population parameter was 2.01 ± 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

BY SABRI ERGUN

*Spectro-Physics, Pittsburgh Energy Research Center, U. S. Bureau of Mines,
Pittsburgh, Pennsylvania 15213, U.S.A.*

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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 $h=4\pi \sin \theta/\lambda$, θ being the Bragg angle and λ , the wavelength. If, owing to strain, an interatomic distance l is altered by δ , we need to evaluate.