

Temperature Diffuse Scattering for Cubic Powder Patterns

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(Received 20 May 1960 and in revised form 1 August 1960)

General expressions for the various orders of temperature diffuse scattering (TDS) for cubic elements are developed which show that the diffuse peaks at the Bragg maxima are broader for the higher order TDS contributions, and which also show that the average value of l th order TDS (in electron units per atom) is $f^2 \exp[-2M](2M)^l/l!$. The relevance of this result to the Warren theory and the more recent Paskin theory for TDS for cubic powders is discussed, and it is shown that the Warren theory is more accurate.

Introduction

Since the appearance of Warren's theory (1953) for temperature diffuse scattering (TDS) for cubic powder patterns, there has been interest in its experimental application, and there have been efforts to refine it theoretically. It was used to determine independently the atomic scattering factor f and the Debye-Waller factor $2M$ of copper (Borie, 1956), and Herbstein & Averbach (1955) modified the original theory to obtain a form valid for temperatures significantly lower than the Debye temperature Θ . More recently, Paskin (1958, 1959) proposed a refinement of the Warren theory, and Chipman & Paskin (1959) used it to interpret the powder patterns of copper and lead. It is the purpose of this paper to show that there are inaccuracies in the Paskin theory, and that the original Warren formulation remains a useful expression for cubic powder patterns.

In general the TDS in electron units may be written

$$I_{TD} = \sum_{l=1}^{\infty} I_{TDl} \quad (1)$$

with I_{TDl} is the l th order TDS, or that part of the diffuse scattering associated with l -phonon processes. At small values of $\sin \theta/\lambda$ the dominant term is I_{TD1} , but at greater distances from the origin in reciprocal space, the higher order terms of equation (1) make increasingly important contributions. Paskin's result is that for a cubic powder pattern, I_{TDl} may be written

$$I_{TDl} = Nf^2 \exp[-2M] \{(2M_D)^l/l!\} C_l,$$

The Debye model of a lattice is used, and it is assumed that only one- and two-phonon processes make significant contributions to equation (1) so that it may be written

$$I_{TD} = Nf^2 \exp[-2M] (2M_D) (C_1 + M_D C_2).$$

The quantity $2M_D$ is similar but not identical to $2M$

in the Paskin theory, and C_1 and C_2 are functions of $\sin \theta/\lambda$ and the cell size. Chipman & Paskin (1959) assert that C_1 has an average value of approximately one, and C_2 of approximately five.

It will be shown here that with the Debye lattice model $2M_D$ and $2M$ must be identically equal, and that $\langle C_l \rangle = 1$ for all l . If it is then supposed that C_l may be well approximated by C_1 for all l , equation (1) becomes

$$I_{TD} = Nf^2 \exp[-2M] (\exp[2M] - 1) C_1,$$

which is the original Warren expression.

Diffraction theory

We begin with the well-known result that for a crystal with one atom per unit cell, the intensity in electron units may be written

$$I = f^2 \sum_m \sum_n \exp[i\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{r}_n)] \times \exp\left(-\frac{1}{2} \langle \{\mathbf{k} \cdot (\boldsymbol{\delta}_m - \boldsymbol{\delta}_n)\}^2 \rangle\right). \quad (2)$$

The vector $\mathbf{k} = 2(\mathbf{s} - \mathbf{s}_0)/\lambda$ where \mathbf{s}_0 and \mathbf{s} are unit vectors in the directions of the incident and scattered radiation, \mathbf{r}_m is a lattice vector, and $\boldsymbol{\delta}_m$ is the instantaneous displacement of the m th atom from its equilibrium position due to thermal motion. The average indicated in the exponent is a time average. If we let $2M = \langle (\mathbf{k} \cdot \boldsymbol{\delta}_m)^2 \rangle$ equation (2) may be written

$$I = f^2 \exp[-2M] \sum_m \sum_n \exp[i\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{r}_n)] \times \exp\langle \mathbf{k} \cdot \boldsymbol{\delta}_m \mathbf{k} \cdot \boldsymbol{\delta}_n \rangle + Nf^2, \quad (3)$$

where N is the total number of atoms in the crystal. If we subtract the Laue-Bragg scattering,

$$f^2 \exp[-2M] \sum_m \sum_n \exp[i\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{r}_n)],$$

the remaining diffuse scattering is

$$I_{TD} = Nf^2 \exp[-2M] \{ \exp[2M] - 1 \} + Nf^2 \exp[-2M] \times \sum_n \exp[i\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{r}_n)] \{ \exp\langle \mathbf{k} \cdot \boldsymbol{\delta}_m \mathbf{k} \cdot \boldsymbol{\delta}_n \rangle - 1 \}. \quad (4)$$

($n \neq m$)

* Operated for the U.S. Atomic Energy Commission by the Union Carbide Corporation.

To obtain (4) the double sum of (3) has been replaced by N times a single sum over all sites except m , which is valid if the crystal is large.

We expand the exponents in both of the braces of (4) to obtain the series form of I_{TD} given by equation (1). Then

$$I_{TDl} = Nf^2 \exp[-2M]((2M)^l/l!) \times \left\{ 1 + \sum_{n \neq m} A_{ln} \exp[i\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{r}_n)] \right\}, \quad (5)$$

where

$$A_{ln} = \langle \mathbf{k} \cdot \delta_m \mathbf{k} \cdot \delta_n \rangle^l / \langle (\mathbf{k} \cdot \delta_m)^2 \rangle^l = (A_{1n})^l. \quad (6)$$

It is clear that A_{ln} is independent of the magnitude of \mathbf{k} . From equations (5.22) and (5.27) of James (1948) it may be seen that for a cubic crystal the angular dependence of A_{ln} on \mathbf{k} is contained in the quantity

$$\sum_{j=1}^3 \coth \left(\frac{1}{2} \frac{h\omega_{\phi j}}{kT} \right) \frac{\cos^2 \alpha_{\phi j}}{\omega_{\phi j}}.$$

Here it is assumed that the thermal motion is a consequence of the superposition of $3N$ elastic waves in the lattice. $\omega_{\phi j}$ is the circular frequency of the lattice wave of phase vector ϕ , and the sum over j is taken over the three independent orthogonal directions of vibration associated with ϕ . The Boltzmann constant k is not to be confused with the vector \mathbf{k} . The angle between the diffraction vector and one of the three vibrational directions is given by $\alpha_{\phi j}$. If for a given ϕ it is assumed that $\omega_{\phi j}$ is independent of j (which is equivalent to assuming that the velocity of the elastic waves is independent of j), then the above expression becomes independent of $\alpha_{\phi j}$.

Hence, for a cubic crystal with the Debye lattice model A_{ln} does not depend on the diffraction vector and the quantity in braces in equation (5) is simply the Fourier series representation of a periodic function $u_l(\mathbf{k})$ in reciprocal space whose average value is unity. In general, A_{ln} is positive since we expect δ_m and δ_n to tend to have common directions. It is less than one and approaches zero as the distance between sites m and n become large enough for the thermal motion of the occupants of the sites to be uncoupled. Hence, $u_l(\mathbf{k})$ has diffuse maxima at the reciprocal lattice points, and from equation (6) the maxima become broader and less pronounced for larger l .

If $u_l(\mathbf{k})$ is averaged over a sphere in reciprocal space to obtain the result for a cubic powder of cell size a that

$$I_{TDl} = Nf^2 \exp[-2M]((2M)^l/l!) C_l,$$

where C_l is a function of the variable $x = 2a \sin \theta/\lambda$ and perhaps of $2B = 2M (\sin \theta/\lambda)^{-2}$, then it is obvious that the average of C^l over x must be unity.

First order TDS with the Debye lattice model

We comment briefly on the various treatments of first order TDS for close-packed cubic powder patterns, in the light of the above result.

Given that the thermal motion of the atoms in a crystal may be represented by the superposition of $3N$ elastic waves, and the assumptions that all waves have the same velocity and that each Brillouin zone may be replaced by a sphere of equal volume of radius g_m , Warren (1953) derived expressions for u_1 and C_1 valid in the high temperature limit that the average energy E of each elastic wave is kT . Using the more general result that $E = \frac{1}{2} h\nu \coth(h\nu/2kT)$, Herbstein & Averbach (1955) obtained an expression for u_1 valid at any temperature:

$$u_1(\mathbf{g}) = [\varphi(\chi)/\chi + \frac{1}{2}]^{-1} g_m / (6g) \coth(\frac{1}{2}\chi g/g_m),$$

where \mathbf{g} is a position vector in reciprocal space from the center of a Brillouin zone, and $\varphi(\chi)$ is the well-known Debye function of the variable $\chi = \Theta/T$. In the limit as χ approaches zero, u_1 takes on the form given by Warren, and its average over a Brillouin zone is unity, as required by equation (5). The form of C_1 given by Herbstein & Averbach for a face-centered cubic element degenerates into the Warren expression for small χ , and does not deviate significantly from it even for χ as large as four. Hence, except at very low temperatures, for most materials the Warren C_1 is adequate.

Second order TDS with the Debye lattice model

We compute C_2 with the Debye model for the case that $E = kT$. The general expression given by Olmer (1948) and Walker (1956) may then be written

$$I_{TD2} = Nf^2 \exp[-2M] (2M)^2 / 2! \frac{g_m^4}{9} (v_b)^{-1} \sum_{Q=1}^8 \int \frac{dv_g}{g^2(y-g)^2}, \quad (7)$$

where v_b is the volume of the reciprocal unit cell. The intensity is a function of the vector \mathbf{y} extending from the point of measurement in reciprocal space to a reciprocal lattice point. The integral is carried out over the volume common to two Brillouin zones

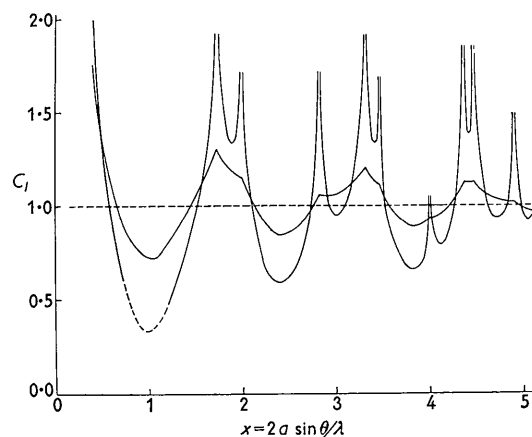


Fig. 1. The functions $C_1(x)$ and $C_2(x)$. Except at the origin C_2 is everywhere finite.

whose centers are separated by a distance y . Since y may be as large as $2g_m$, at any point in reciprocal space one may construct permissible vectors \mathbf{y} to eight nearby reciprocal lattice points for a primitive lattice. The summation over Q accounts for these eight contributions to the second order TDS at any point.

The integral of (7) may be evaluated to give

$$\int \frac{dv_g}{g^2(y-g)^2} = \frac{\pi^3}{y} - \frac{4\pi}{g_m} \left[1 + \frac{1}{4} \frac{y}{g_m} + \dots + \frac{1}{n^2} \left(\frac{y}{g_m} \right)^{n-1} + \dots \right] \quad (8)$$

for $0 \leq y \leq g_m$ and

$$\int \frac{dv_g}{g^2(y-g)^2} = -\frac{\pi^3}{3y} + \frac{4\pi}{y} \left[\frac{(\log g_m/y)^2}{2} + \frac{g_m}{y} \times \left\{ 1 + \frac{1}{4} \frac{g_m}{y} + \dots + \frac{1}{n^2} \left(\frac{g_m}{y} \right)^{n-1} + \dots \right\} \right] \quad (9)$$

for $g_m \leq y \leq 2g_m$. After appropriate averaging of (8) and (9) for a face-centered cubic powder, $C_2(x)$ as shown in Fig. 1 is obtained. The computation of this curve is tedious but not difficult, and the details of the calculation will not be reproduced here. Also shown in Fig. 1 is $C_1(x)$ as given by Warren.

Discussion

Given the above result, certain discrepancies between theory and experiment for copper and lead as reported by Chipman & Paskin (1959) may be understood. In both cases it was found that though there was agreement at high scattering angles, at small 2θ there was apparently more diffuse scattering than could be accounted for by theory, and it was concluded that the extra scattering was due to some real but not understood effect. We now see that, because of the abnormally large value of C_2 used, Chipman & Paskin were forced to choose a small value of $2M_D$ to fit experiment at large 2θ . Hence, in the low angle region where second order TDS contributions are negligible, their computed diffuse scattering is too small by a

factor of approximately $2M_D/2M_W$, where $2M_W$ is the value obtained with the Warren theory. From their data, this is 68% in the case of copper. This correction very nearly accounts for the extra diffuse scattering. For lead, since $2B$ is very large, one may not neglect I_{TDl} for $l > 2$ as is done in the Paskin theory. If we take $2B$ to be five, at the limiting sphere for copper radiation the average value of I_{TD3} is approximately 75% of that of I_{TD1} , and there are significant contributions from I_{TD4} and I_{TD5} .

Though the Warren expression is a good approximation, at large values of $2M$ the assumption that $C_l = C_1$ for all l introduces rather more structure in the diffuse scattering than there should be. From Fig. 1, we see that the actual value of C_2 over the range of x for which it was computed is approximately halfway between $C_2 = C_1$ and $C_2 = 1$ except at the Bragg maxima where the diffuse scattering is not observable. If we take $C_2 = \frac{1}{2}(1 + C_1)$, and $C_l = 1$ for $l > 2$, we obtain

$$I_{TD} = Nf^2 (1 - \exp[-2M]) + Nf^2 \exp[-2M] (C_1 - 1)(2M + M^2). \quad (10)$$

The above result should be accurate for any $2M$, and may be very easily fitted to experimental measurements.

It is a pleasure to acknowledge that discussions with Dr C. J. Sparks helped stimulate this work. Comments by Prof. B. E. Warren were very helpful.

References

- BORIE, B. (1956). *Acta Cryst.* **9**, 617.
- CHIPMAN, D. R. & PASKIN, A. (1959). *J. Appl. Phys.* **30**, 1992.
- HERBSTSTEIN, F. H. & AVERBACH, B. L. (1955). *Acta Cryst.* **8**, 843.
- JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-rays*, p. 200. London: Bell.
- OLMER, P. (1948). *Bull. Soc. Franç. Minér.* **71**, 145.
- PASKIN, A. (1958). *Acta Cryst.* **11**, 165.
- PASKIN, A. (1959). *Acta Cryst.* **12**, 290.
- WALKER, C. B. (1956). *Phys. Rev.* **103**, 547.
- WARREN, B. E. (1953). *Acta Cryst.* **6**, 803.