

An Interpretation of Temperature Diffuse Scattering*

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An alternative formulation of temperature diffuse scattering theory is described. The result is in terms of the mean atomic displacements rather than the usual normal mode representation. The theory leads to a direct relation between first and second order diffuse intensity which, by iteration, allows for a correction for the second order contribution without approximation. It seems likely that this theory should be useful for highly anharmonic thermal motion.

Introduction

The usual formulation of the diffraction theory for thermal motion in crystals is in terms of the normal modes of the lattice, the Debye–Waller factor and the diffuse intensity being related to the average states of excitation of these modes of motion (James, 1965). We here offer an alternative formulation of that theory, entirely in terms of the mean atomic displacements. The theory leads to direct relations among first and higher order diffuse scattering components, so that with the harmonic model, higher order diffuse intensity components may be corrected for exactly. Other attempts to account for this component of the diffuse scattering have all invoked a variety of approximations (Olmer, 1948; Joynson, 1954; Jacobsen, 1955; Walker, 1953; Paskin, 1958, 1959; Borie, 1961). It seems possible that this formulation of diffuse scattering theory may be useful for crystals with large anharmonic effects.

Diffraction theory

For simplicity consider a crystal for which all atoms are identical, with one atom per primitive unit cell. Then according to kinematic diffraction theory, the intensity in electron units is given by

$$I = f^2 \sum_p \sum_q \exp [i\mathbf{k} \cdot \mathbf{R}_{pq}] \langle \exp [i\mathbf{k} \cdot (\delta_p - \delta_q)] \rangle.$$

The vectors \mathbf{R}_{pq} are between atomic sites p and q in the average lattice, and the small dynamic displacements δ_p are those resulting from thermal motion. The average indicated is over time. The vector k is 2π times the diffraction vector.

In the harmonic approximation this expression may be written

$$\begin{aligned} I &= f^2 \sum_p \sum_q \exp [i\mathbf{k} \cdot \mathbf{R}_{pq}] \exp [-\frac{1}{2} \langle \{\mathbf{k} \cdot (\delta_p - \delta_q)\}^2 \rangle] \\ &= Nf^2 + f^2 \exp [-\langle \mathbf{k} \cdot \delta \rangle^2] \\ &\times \sum_{p \neq q} \sum_q \exp [i\mathbf{k} \cdot \mathbf{R}_{pq}] \exp \langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle. \end{aligned}$$

In the above N is the total number of atoms in the crystal, and $\langle (\mathbf{k} \cdot \delta)^2 \rangle$ is the Debye–Waller factor $2M$. With the last exponential expanded, this expression may be written

$$I = f^2 \exp [-2M] \sum_p \sum_q \exp [i\mathbf{k} \cdot \mathbf{R}_{pq}] + f^2 \exp [-2M] \sum_p \sum_q \sum_{l=1}^{\infty} \frac{\exp [i\mathbf{k} \cdot \mathbf{R}_{pq}] \langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle^l}{l!}. \quad (1)$$

The first double sum gives the usual sharp but weakened Bragg maxima and is of no further interest. The second summation, I_{TD} , is the diffuse intensity. We may write

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

where

$$I_{TDl} = f^2 \exp [-2M] \sum_p \sum_q \frac{\langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle^l}{l!} \exp [i\mathbf{k} \cdot \mathbf{R}_{pq}].$$

The value of l identifies the order of the diffuse intensity component.

Consider the first order temperature diffuse scattering:

$$I_{TD1} = f^2 \exp [-2M] \sum_p \sum_q \langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle \exp [i\mathbf{k} \cdot \mathbf{R}_{pq}]. \quad (2)$$

Let the vector \mathbf{k} be written in terms of the vectors \mathbf{b}_n reciprocal to the unit cell vectors \mathbf{a}_n :

$$\mathbf{k} = 2\pi(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3).$$

We may write for δ_p

$$\delta_p = x_p\mathbf{a}_1 + y_p\mathbf{a}_2 + z_p\mathbf{a}_3,$$

where x_p , y_p , and z_p are small pure numbers and functions of time.

Then

$$\mathbf{k} \cdot \delta_p = 2\pi(h_1x_p + h_2y_p + h_3z_p)$$

and

$$\begin{aligned} \langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle &= 4\pi^2 \{ h_1^2 \langle x_p x_q \rangle + h_2^2 \langle y_p y_q \rangle + h_3^2 \langle z_p z_q \rangle \\ &+ h_1 h_2 \langle x_p y_q + y_p x_q \rangle + h_2 h_3 \langle y_p z_q \\ &+ z_p y_q \rangle + h_3 h_1 \langle z_p x_q + x_p z_q \rangle \}. \end{aligned} \quad (3)$$

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For diffuse scattering the double sum of equation (2) may be written as N times a single sum. With the expression for $\langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle$ given by equation (3) substituted into (2), there results

$$\begin{aligned} I_{TD1}/(Nf^2 \exp[-2M]) &= h_1^2 \sum_p 4\pi^2 \langle x_p x_q \rangle \\ &\times \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}] + h_2^2 \sum_p 4\pi^2 \langle y_p y_q \rangle \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}] \\ &+ h_3^2 \sum_p 4\pi^2 \langle z_p z_q \rangle \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}] \\ &+ h_1 h_2 \sum_p 4\pi^2 \langle x_p y_q + y_p x_q \rangle \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}] \\ &+ h_2 h_3 \sum_p 4\pi^2 \langle y_p z_q + z_p y_q \rangle \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}] \\ &- h_3 h_1 \sum_p 4\pi^2 \langle z_p x_q + x_p z_q \rangle \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}]. \end{aligned} \quad (4)$$

Clearly equation (4) gives I_{TD1} in terms of the sum of a group of Fourier series, each one multiplied by a factor quadratic in h_i . Let the periodic function $B(h_1, h_2, h_3)$ be defined by

$$B(h_1, h_2, h_3) = \sum_p 4\pi^2 \langle x_p x_q \rangle \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}]$$

and

$$G(h_1, h_2, h_3) = \sum_p 4\pi^2 \langle x_p y_q + y_p x_q \rangle \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}].$$

Then, if the crystal is cubic, equation (4) may be written in terms of the functions B and G :

$$\begin{aligned} I_{TD1}/(Nf^2 \exp[-2M]) &= h_1^2 B(h_1, h_2, h_3) \\ &+ h_2^2 B(h_2, h_3, h_1) + h_3^2 B(h_3, h_1, h_2) + h_1 h_2 G(h_1, h_2, h_3) \\ &+ h_2 h_3 G(h_2, h_3, h_1) + h_3 h_1 G(h_3, h_1, h_2). \end{aligned} \quad (5)$$

All of the information to be recovered from the diffuse intensity distribution is contained in the Fourier coefficients of B and G . They may be recovered by first obtaining the functions B and G from the experimental data:

Let $I' = I_{TD1}/(Nf^2 \exp[-2M])$ and define an operator Δ_1 to be $\Delta_1 I'(h_1, h_2, h_3) = I'(h_1, h_2, h_3) - I'(h_1 - 1, h_2, h_3)$. Then from equation (4), because of the periodic character of B and G :

$$\Delta_1 I' = (2h_1 - 1)B(h_1, h_2, h_3) + h_2 G(h_1, h_2, h_3), \quad (6)$$

and

$$\Delta_1^2 I' = 2B(h_1, h_2, h_3).$$

To recover G , let $\Delta_2 I'(h_1, h_2, h_3) = I'(h_1, h_2, h_3) - I'(h_1, h_2 - 1, h_3)$. Then from equation (5)

$$\Delta_2 \Delta_1 I' = G(h_1, h_2, h_3).$$

The operators Δ_n to be applied to the measurements are ideally suited to be performed on a computer.

Now consider second order temperature diffuse scattering:

$$I_{TD2} = f^2 \exp[-2M] \sum_p \sum_q \frac{\langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle^2}{2} \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}]. \quad (7)$$

The quantity $\langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle^2$ may be readily obtained from equation (3). The square of that expression will contain terms like

$$16\pi^4 h_1^3 h_2 \langle x_p x_q \rangle \langle x_p y_q + y_p x_q \rangle.$$

The corresponding contribution to $I_{TD2}/(Nf^2 \exp[-2M])$ is

$$h_1^3 h_2 \sum_p \langle x_p x_q \rangle \langle x_p y_q + y_p x_q \rangle \exp[i\mathbf{k} \cdot \mathbf{R}_{pq}] = h_1^3 h_2 P(h_1, h_2, h_3). \quad (8)$$

Since a periodic function P whose Fourier coefficients are the product of those of two other functions, B and G , is simply the convolute of the two functions. With the notation

$$\begin{aligned} B(h_1, h_2, h_3) * G(h_1, h_2, h_3) \\ = \int_{h_1=0}^1 \int_{h_2=0}^1 \int_{h_3=0}^1 B(h'_1, h'_2, h'_3) G(h'_1 - h_1, h'_2 - h_2, h'_3 - h_3) \\ \times dh'_1 dh'_2 dh'_3 \end{aligned}$$

we may write from equation (8)

$$P(h_1, h_2, h_3) = B(h_1, h_2, h_3) * G(h_1, h_2, h_3).$$

Introduce the notation that $B_n = B(h_n, h_{n+1}, h_{n+2})$ and $G_n = G(h_n, h_{n+1}, h_{n+2})$, the subscripts being modulo three. Then it is clear that if we square equation (3), and substitute the result into equation (7) to obtain I_{TD2} we obtain

$$\begin{aligned} 2I_{TD2}/(Nf^2 \exp[-2M]) &= \sum_{m=1}^3 \sum_{n=1}^3 h_m^2 h_n^2 B_m * B_n \\ &+ \sum_{m=1}^3 \sum_{n=1}^3 h_m h_{m+1} h_n h_{n+1} G_m * G_n \\ &+ 2 \sum_{m=1}^3 \sum_{n=1}^3 h_m^2 h_n h_{n+1} B_m * G_n. \end{aligned} \quad (9)$$

Discussion

Both first and second order temperature diffuse scattering are expressed in terms of two basic periodic functions as given by equations (5) and (9). The Fourier coefficients of these functions are related to the mean atomic displacements and contain the basic information which one may recover from a set of diffuse scattering data. The separation technique described here is closely related to one (Borie & Sparks, 1965) which has been successfully used to separate diffuse intensity into its components for disordered solid solutions. The functions may be recovered directly from the first order temperature diffuse scattering, and they may then be used to compute the second order contribution. If this

procedure is followed with the initial assumption that all of the scattering is first order, the resultant functions B and G may be used to compute from equation (9) I_{TD2} . This may then be subtracted from the measurements to obtain better values of the first order diffuse intensity. Iteration of this procedure may be followed to self-consistency, yielding values of first and second order temperature diffuse scattering to any precision desired. Expressions similar to, but more involved than, equation (9) may clearly be developed to obtain expressions for higher order diffuse components of the diffraction pattern if that is necessary. Though the day is not long past when the computation involved in equation (9) would have appeared formidable, the above described iteration procedure may be carried out very easily with a modern computer.

If the usual harmonic representation of the atomic displacements in terms of superposed waves is incorporated into equations (2) and (7), they become James's (1965) equation (5.45) for I_{TD1} and Walker's (1953) equation (4) for I_{TD2} . However, though the harmonic model is used, the usual normal mode representation of the diffuse intensity is not. Since the result for I_{TD1}

is not dependent on the harmonic approximation, this representation of first order intensity in terms of the mean atomic displacements is valid even if there are large anharmonic contributions so that the usual theory does not apply. Without the harmonic approximation the simple representation of I_{TD2} in terms of the functions B and G given by equation (9) no longer holds. Even in that case the above described method for correction for I_{TD2} may still be an acceptable approximation.

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Monoclinic–Tetragonal Phase Transition in Zirconia: Mechanism, Pretransformation and Coexistence

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The high temperature X-ray diffraction study of the monoclinic–tetragonal phase transition in ZrO_2 showed that it is spread over a temperature range 930–1220°C. Anomalous intensity changes are observed in the pretransformation region 930–1100°C. Coexistence of phases through hybrid crystal formation in the region 1100–1220°C and the mechanism of transition are discussed. The orientation relationship between the monoclinic (m) and the tetragonal (t) crystal structures consists in the parallelism of the $(100)_m$ plane to $(110)_t$ and of the b_m axis to the c_t axis. A drastic change in a small temperature range during the tetragonal–monoclinic transition is interpreted as a cooperative change in both short and long range interactions. The large thermal hysteresis is attributed to the difference in the mechanism of transition during heating and cooling.

Introduction

The monoclinic–tetragonal transition in ZrO_2 has been extensively investigated (Baun, 1963; Cypres, Wollast & Raueq, 1963; Grain & Garvie, 1965; Hinz & Dietzel, 1962; Sukharevskii, Alapin & Gavrish, 1964; Whitney, 1962; Wolten, 1963, 1964) using differential thermal analysis, dilatometry, high pressure studies and X-ray diffractometry. Considerable disagreement among different investigators prevails regarding the transformation temperature and thermal hysteresis. The disagreement may be due to: (i) the dynamic study of the transition and (ii) the type of impurities present.

Wolten (1963, 1964) described the monoclinic–tetragonal transformation in ZrO_2 to be diffusionless and likened it to the martensitic type of transformation observed in metallic and alloy systems. Athermal kinetics, thermal hysteresis and the shearing mechanism due to the atomic displacements during the transformation are characteristics of the martensitic type of transformation. The electron microscopic studies of Bailey (1964) and metallographic observations by Fehrenbacher & Jacobson (1965) support Wolten's work and attribute a shearing mechanism to the atomic movements during the phase change. Sukharevskii *et al.* (1964) associate an isothermal component in the