Irrelevance of Atomic Masses for Debye–Waller B Values in the Limit of High Temperatures

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An expression that approximates Debye–Waller B values by a sum of three terms is derived from the theory of lattice dynamics in the harmonic approximation. For cubic crystals (M_κ is the mass of the κth atom in the unit cell):

$$B_\kappa = \alpha_\kappa T + 2\pi^2 \hbar^2 / 3kTM_\kappa + \gamma_\kappa / M^2 T^3 ,$$

where $T \gtrsim \Theta_D/2$ and α_κ and γ_κ are constants, depending on interatomic forces only. It is shown that for temperatures above the Debye temperature Θ_D of the lattice, the second and third terms in the above expression can be neglected. From this, it follows that above the Debye temperature Debye–Waller B values become independent of the atomic masses. Consequently, the heavier atoms in a lattice do not necessarily have the smaller B values.

Introduction

In a crystal lattice, heavier atoms do not necessarily have the smaller Debye–Waller B values. Examples are PbTe (Keffer, Hayes & Bienenstock, 1968), MgO (Raccah & Arnott, 1967; Sanger, 1969), and AgCl (Korhonen & Linkoaho, 1966). In these cases, room-temperature Debye–Waller B values of the heavier atoms (Pb, Mg, and Ag) are larger than those of the lighter atoms (Te, O, and Cl). The phenomenon has been appreciated as rather surprising.

With the aid of the theory of lattice dynamics in the harmonic approximation, a theorem will be derived which states that Debye–Waller B values of individual atoms in a crystal lattice do not depend on the atomic masses when the temperature of the crystal is above its Debye temperature.

For temperatures above half the Debye temperature, an expression is given that allows calculation of B values at any temperature above $\Theta_D/2$ if Debye–Waller values at least one temperature in the region are known (*e.g.* from experiment).

It is hoped that the theorem will contribute to a qualitative understanding of Debye–Waller B values.

Derivation of theorem

The vibrations of an atom in a crystal lattice, moving in a harmonic potential field, can be characterized by a symmetric tensor $\mathbf{U}$, with six independent components. The mean-square amplitude of vibration in the direction of a unit vector $\mathbf{l}$, with components l_α, is given by (Cruickshank, 1956):

$$\langle u^2 \rangle = \sum_{\alpha, \beta} \langle u_\alpha u_\beta \rangle l_\alpha l_\beta . \tag{1}$$

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To evaluate the quantities $\langle u_\alpha u_\beta \rangle$, we adopt formulae and notation of lattice dynamics as presented by Maradudin, Montroll & Weiss (1963).

Eigenvectors and eigenfrequencies, of the phonons present in a lattice, obey the following set of equations:

$$\sum_{\kappa', \beta} D_{\alpha\beta}(\begin{smallmatrix} \mathbf{k} \\ \kappa\kappa' \end{smallmatrix}) e_\beta(\kappa'|\begin{smallmatrix} \mathbf{k} \\ j \end{smallmatrix}) = e_\alpha(\kappa|\begin{smallmatrix} \mathbf{k} \\ j \end{smallmatrix}) \omega_j^2(\mathbf{k}) , \tag{2}$$

where α and β are again the Cartesian coordinates (x,y,z), κ and κ' are indices to number the atoms in the unit cell, $\mathbf{k}$ is the wave vector, $\omega_j(\mathbf{k})$ is the eigenfrequency of the jth branch, and $e(\kappa|\begin{smallmatrix} \mathbf{k} \\ j \end{smallmatrix})$ is the eigenvector of the κth atom, belonging to the jth branch. The r atoms in the unit cell give $3r$ phonon branches. The quantities $D_{\alpha\beta}(\begin{smallmatrix} \mathbf{k} \\ \kappa\kappa' \end{smallmatrix})$ are the elements of the dynamical matrix:

$$D_{\alpha\beta}(\begin{smallmatrix} \mathbf{k} \\ \kappa\kappa' \end{smallmatrix}) = (M_\kappa M_{\kappa'})^{-1/2} \sum_{l'} \varphi_{\alpha\beta}(\begin{smallmatrix} ll' \\ \kappa\kappa' \end{smallmatrix}) \exp[-2\pi i \mathbf{k} . \mathbf{x}(ll')] , \tag{3}$$

where M_κ is the mass of the κth atom, l and l' are indices to number unit cells, $\mathbf{x}(ll') = \mathbf{x}(l) - \mathbf{x}(l')$, and $\mathbf{x}(l)$ is the position of the lth unit cell, while $\varphi_{\alpha\beta}(\begin{smallmatrix} ll' \\ \kappa\kappa' \end{smallmatrix})$ is the negative of the force exerted in the α direction on atom $(\begin{smallmatrix} l \\ \kappa \end{smallmatrix})$, when atom $(\begin{smallmatrix} l' \\ \kappa' \end{smallmatrix})$ is displaced a unit distance in the β direction. The eigenvalue equation (2) can be written more compactly in matrix form:

$$\mathbf{D}(\mathbf{k})\mathbf{E}(\mathbf{k}) = \mathbf{E}(\mathbf{k})\mathbf{\Lambda}(\mathbf{k}) . \tag{4}$$

From this, it follows that

$$\mathbf{D}^{-1}(\mathbf{k}) = \mathbf{E}(\mathbf{k})\mathbf{\Lambda}^{-1}(\mathbf{k})\mathbf{E}\dagger(\mathbf{k}) . \tag{5}$$

The matrix $\mathbf{D}(\mathbf{k})$ is Hermitian; hence, $\mathbf{E}(\mathbf{k})$ is unitary and we obtain from equation (5):

$$(\mathbf{D}^{-1})_{\alpha\beta}(\begin{smallmatrix} \mathbf{k} \\ \kappa\kappa' \end{smallmatrix}) = \sum_j e_\alpha(\kappa|\begin{smallmatrix} \mathbf{k} \\ j \end{smallmatrix}) e_\beta^*(\kappa'|\begin{smallmatrix} \mathbf{k} \\ j \end{smallmatrix}) \omega_j^{-2}(\mathbf{k}) . \tag{6}$$

At this point, we consider the mean products of vibrational amplitudes of the $\binom{l}{\kappa}$th atom (Maradudin et al., 1963, p. 237):

$$\langle u_\alpha(^l_\kappa)u_\beta(^l_\kappa)\rangle = \frac{\hbar}{2NM_\kappa}\sum_{\kappa,j} e_\alpha(\kappa|^k_j)e^*_\beta(\kappa|^k_j)$$

$$\times \frac{\coth{[\hbar\omega_j(\mathbf{k})/2kT]}}{\omega_j(\mathbf{k})}, \quad (7)$$

where N is the number of unit cells in the crystal. The summation is carried out over N values of the wave vector $\mathbf{k}$, distributed through the first Brillouin zone, and, for each value of the wave vector $\mathbf{k}$, over the $3r$ phonon branches. Following Waller (1925), we expand the hyperbolic cotangent:

$$\coth\frac{\hbar\omega}{2kT} = \frac{2kT}{\hbar\omega} + \frac{\hbar\omega}{6kT} - \frac{\hbar^3\omega^3}{360k^3T^3}\cdots, \frac{\hbar\omega}{2kT} < 1 \quad (8)$$

and obtain from equation (7):

$$\langle u_\alpha(^l_\kappa)u_\beta(^l_\kappa)\rangle = \frac{\hbar}{2NM_\kappa}\sum_{\mathbf{k},j} e_\alpha(\kappa|^k_j)\,e^*_\beta(\kappa|^k_j)$$

$$\times [2kT/\hbar\omega_j(\mathbf{k}) + \hbar\omega_j(\mathbf{k})/6kT$$

$$- \hbar^3\omega^3_j(\mathbf{k})/360k^3T^3]\omega^{-1}_j(\mathbf{k}). \quad (9)$$

The condition $\hbar\omega_j(\mathbf{k})/2kT < 1$ is roughly equivalent to $T > \Theta_D/2$, Θ_D being the Debye temperature of the lattice. Θ_D is connected with the maximum phonon frequency, ω_m, as $\hbar\omega_m/k \simeq \Theta_D$. The second and third terms of the expression between square brackets of equation (9) contribute well below 8% when $T \gtrsim \Theta_D$. Neglecting these terms, equation (9) can be written as:

$$\langle u_\alpha(^l_\kappa)u_\beta(^l_\kappa)\rangle = \frac{kT}{NM_\kappa}\sum_{\mathbf{k},j} e_\alpha(\kappa|^k_j)\,e^*_\beta(\kappa|^k_j)\omega^{-2}_j(\mathbf{k}) \quad (10)$$

and with equation (6):

$$\langle u_\alpha(^l_\kappa)u_\beta(^l_\kappa)\rangle = \frac{kT}{NM_\kappa}\sum_{\mathbf{k}} (\mathbf{D}^{-1})_{\alpha\beta} (^k_{\kappa\kappa}). \quad (11)$$

In order to proceed we recognize that:

$$\mathbf{D}(\mathbf{k}) = \mathbf{M}^{-1/2}\mathbf{\Phi}(\mathbf{k})\mathbf{M}^{-1/2}, \quad (12)$$

$$D_{\alpha\beta}(^k_{\kappa\kappa}) = M^{-1}_\kappa\,\Phi_{\alpha\beta}(^k_{\kappa\kappa}), \quad (12a)$$

$$\mathbf{D}^{-1}(\mathbf{k}) = \mathbf{M}^{1/2}\mathbf{\Phi}^{-1}(\mathbf{k})\mathbf{M}^{1/2}, \quad (13a)$$

$$(\mathbf{D}^{-1})_{\alpha\beta}(^k_{\kappa\kappa}) = M_\kappa(\mathbf{\Phi}^{-1})_{\alpha\beta}(^k_{\kappa\kappa}), \quad (13b)$$

where $\mathbf{M}$ is a diagonal matrix with $M_{11} = M_{22} = M_{33} = M_1$, the mass of atom 1, $M_{44} = M_{55} = M_{66} = M_2$, the mass of atom 2, and so on. The matrix $\mathbf{\Phi}(\mathbf{k})$ is defined by:

$$\Phi_{\alpha\beta}(^k_{\kappa\kappa'}) = \sum_{l'} \varphi_{\alpha\beta}(^{l l'}_{\kappa\kappa'})\exp{[-2\pi i\,\mathbf{k}\cdot\mathbf{x}(ll')]}. \quad (14)$$

crystals for temperatures above half the Debye temperature if, at least, one Debye–Waller B value is known in that temperature region, to be calculated. It is emphasized that the elements of $\mathbf{\Phi}$ do not depend on the atomic masses. Substitution of equation (13b) in equation (11) gives:

$$\langle u_\alpha(^l_\kappa)u_\beta(^l_\kappa)\rangle = \frac{kT}{N}\sum_{\mathbf{k}} (\mathbf{\Phi}^{-1})_{\alpha\beta}(^k_{\kappa\kappa}), \quad T \gtrsim \Theta_D. \quad (15)$$

Before commenting on equation (15), we turn our attention to the second and third terms of the expression between square brackets of equation (9). These terms become important when the temperature of the crystal is below its Debye temperature. To evaluate the contributions due to these terms, we use the following properties of the eigenvectors (Maradudin et al., 1963, p. 12):

$$\sum_j e_\alpha(\kappa|^k_j)\,e^*_\beta(\kappa|^k_j) = \delta_{\alpha\beta}, \quad (16)$$

$$\sum_j \omega^2_j(\mathbf{k})e_\alpha(\kappa|^k_j)\,e^*_\beta(\kappa|^k_j) = D_{\alpha\beta}(^k_{\kappa\kappa}). \quad (17)$$

Recalling that the number of $\mathbf{k}$ vectors equals N, we find from equations (9), (12a), (15), (16) and (17):

Table 1. Calculated Debye–Waller B values of KBr (Å²).

The contribution from the first term, which is independent of atomic masses, is indicated by % in parentheses.

Temperature (°K)	B_K*	B_{Br}*	B_K†	B_{Br}†
295	2·2636	2·4584	2·2249 (98·8)	2·4162 (99·5)
275	2·1000	2·2784	2·0778 (98·6)	2·2540 (99·4)
255	1·9393	2·1012	1·9308 (98·4)	2·0920 (99·3)
235	1·7811	1·9267	1·7842 (98·1)	1·9301 (99·2)
215	1·6258	1·7549	1·6379 (97·8)	1·7682 (99·1)
195	1·4732	1·5859	1·4921 (97·4)	1·6065 (98·9)
175	1·3236	1·4195	1·3467 (96·8)	1·4449 (98·7)
155	1·1771	1·2560	1·2021 (96·1)	1·2833 (98·4)
135	1·0342	1·0954	1·0579 (95·1)	1·1214 (98·1)
115	0·8955	0·9382	0·9142 (93·7)	0·9586 (97·7)
95	0·7621	0·7849	0·7695 (92·0)	0·7928 (97·6)
75	0·6362	0·6367	0·6183 (90·4)	0·6172 (99·0)

* Calculated by Reid & Smith (1970).
† Recalculated with equation (19). The two sums have been evaluated indirectly by least-squares fit of equation (19) to the Reid & Smith data for the 12 temperatures indicated in the first column.

$$\langle u_\alpha(^l_\kappa)u_\beta(^l_\kappa)\rangle = \frac{kT}{N}\sum_k (\Phi^{-1})_{\alpha\beta}(^k_{\kappa\kappa}) + \frac{\hbar^2\delta_{\alpha\beta}}{12kTM_\kappa}$$

$$-\frac{\hbar^4}{720k^3T_N{}^3M_\kappa{}^2}\sum_k \Phi_{\alpha\beta}(^k_{\kappa\kappa}),\ T>\Theta_D/2\ . \quad (18)$$

Equation (18) describes the vibration of an atom in a crystal lattice for temperatures above half the Debye temperature of the lattice. From the quantities $\langle u_\alpha(^l_\kappa)u_\beta(^l_\kappa)\rangle$, the anisotropic Debye–Waller B values can be obtained by well known methods (Cruickshank, 1956). At high temperatures, $T>\Theta_D$, only the first term in the right-hand part of equation (18) is of importance, and Debye–Waller B values become independent of the atomic masses.

Two restrictions should be made. Equation (18) has been derived within the harmonic approximation which will certainly be violated at very high temperatures. The second restriction is in dealing with the temperature dependence of the two sums in equation (18). The matrix elements $(\Phi^{-1})_{\alpha\beta}$ $(^k_{\kappa\kappa})$ and $\Phi_{\alpha\beta}(^k_{\kappa\kappa})$ are temperature dependent, *via* the interatomic forces which depend, for example, on the atomic distances. It is expected, however, that the sums will vary only very little with temperature.

Example

For a cubic lattice, the Debye–Waller B value of the κth atom is obtained from equation (18) as:

$$B_\kappa = 8\pi^2\left[\frac{kT}{N}\sum_k (\Phi^{-1})_{\alpha\alpha}(^k_{\kappa\kappa}) + \frac{\hbar^2}{12kTM_\kappa}\right.$$

$$\left. -\frac{\hbar^4}{720k^3T_N{}^3M_\kappa{}^2}\sum_k \Phi_{\alpha\alpha}(^k_{\kappa\kappa})\right]\ . \quad (19)$$

In the above expression the first term in the right-hand part is independent of the atomic mass. The other two terms are inversely proportional to the atomic mass and to the square of the atomic mass. In general, it is very difficult to evaluate the two sums of equation (19), because, for this, a detailed knowledge of the atomic forces is required. We have determined the two sums by a least-squares fit of equation (19), for 12 temperatures, to KBr B values calculated by Reid & Smith (1970). The Debye temperature of KBr is about 160°K (Reid & Smith, 1970) and the 12 temperatures chosen range from 75°K (about half the Debye temperature) up to 295°K. Results are shown in Table 1.

The results in Table 1 show the various contributions to B_κ at temperatures above the Debye temperature (for KBr 160°K) the main contribution to the Debye–Waller B values comes from the mass-independent term of equation (19). Table 1 also shows that equation (19) describes very well, in a large temperature region, the temperature dependence of both the Debye–Waller B values of KBr.

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The Method of Ascent in Symmetry. I. Theory and Tables

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Supergroup tables are presented whereby a representation of a subgroup can be correlated with those representations of the supergroup which are obtained on ascent in symmetry. The method of derivation is explained and various orientations of the subgroup with respect to the supergroup considered. The tables also include the correlations between the double-valued representations of the corresponding double groups.

Introduction

The well-known process of descent in symmetry allows one to discuss how the representations of a given group decompose into representations of a subgroup. Tables have been constructed to facilitate many such correlations and these are very useful in numerous physical problems, *e.g.* the splitting of atomic energy levels in a crystal field.

The reverse correlation, in which we ascend in