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The Debye–Waller Factor for Polyatomic Solids. Relationships Between X-ray and Specific-Heat Debye Temperatures. The Debye–Einstein Model

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Abstract

The Debye–Waller factor for a polyatomic crystal is derived in the Debye approximation. If the crystal has a basis of p atoms per lattice point, it is shown that the specific-heat Debye temperature, Θ_D, and the X-ray Debye temperature, Θ_M, are related by $\Theta_D \simeq \Theta_M p^{1/2}$ in the classical limit. The Debye and Einstein theories are then combined to yield an expression for the Debye–Waller factor of a polyatomic solid. The acoustic phonon modes are described with a Debye approximation, and the optic modes with an Einstein model. For temperatures above the Debye temperature, the Debye and Einstein parts of the Debye–Waller factor have the same dependence on temperature and diffraction vector. Thus, the two parts cannot be distinguished.

I. Introduction

In general, the thermal vibration of the atoms in a crystal causes the intensities of Bragg reflections to decrease. The vibration magnitude of an atom in a unit cell primarily depends upon the temperature, its mass, and its surroundings: the way it is bonded to its neighbors (local symmetry). That is, each kind of atom in a unit cell has its own vibration amount which, in general, is anisotropic, and its effect on diffracted intensities is referred to as the temperature factor or as the Debye–Waller factor. In the case of isotropic vibrations, a Debye temperature Θ_M can be extracted from such factors. The physical interpretation of temperature factors is direct when discussions are restricted to diffraction measurements. However, the connection between thermal parameters and Debye temperatures extracted from specific-heat (Θ_D) or thermal-expansion measurements is difficult.

In 1912, Debye published the theory of specific heat in solids. Two years later, he succesfully quantified the decrease of X-ray intensities (Debye, 1914) where Θ_M, the characteristic Debye temperature, is introduced as the key parameter. Subsequently, Zener & Bilinsky (1936) showed that Θ_M is not exactly the same as the Debye temperature, Θ_D, of the specific-heat model. The difference is in the averaging between the velocities of the longitudinal and transverse phonons. Later, Barron, Leadbetter, Morrison & Salter (1966) stated that Θ_M should deviate from Θ_D by only a few percent. Expanding on Blackman's (1956) ideas, Barron *et al.* (1966) further pointed out that this approximation does not hold in all cases since real crystals do not strictly obey the Debye assumptions. Moreover, they demonstrated that more realistic frequency distributions could be described by temperature-dependent Debye temperatures, $\Theta_D(T)$ and $\Theta_M(T)$. Later, Reeber (1974) introduced a correspondence between lattice characteristic temperatures and Debye temperatures applied to the zinc-blende, the caesium chloride, and the alkali halide structures. These authors did not, however, show a relationship between Θ_D and Θ_M, which is one of the goals of this paper.

The Debye model is valid only for simple cubic monatomic solids. However, it has frequently been applied to polyatomic crystals. The same equations and nomenclature are used, although the physical interpretation of the Debye temperature is not as clear. It is the purpose of this paper to put the application to polyatomic crystals on a more rigorous basis. In contrast to the monatomic case, it will be shown that Θ_M and Θ_D differ widely for compounds. For purposes of illustration, the formalism will be applied to diatomic solids (see Table 1), in particular to GaAs and CdTe where the agreement between Θ_D and the corresponding value calculated from Θ_M is outstanding.

In the modified Debye theory, there is no distinction between the acoustic and the optic branches of the phonon dispersion curves. That is, all branches are equivalent. Integrations are done in an 'extended' Brillouin zone, which has a volume containing a number of wave vectors equal to the number of atoms in the crystal. A more realistic approach is outlined below, in which the Debye expression is used for the acoustic modes only and the optic modes are grouped

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Table 1. *Comparisons between experimental X-ray and specific-heat Debye temperatures in the classical limit for diatomic solids*

Numbers between parentheses indicate the temperatures at which the determinations have been made. A "*P*" in front of a θ_M value indicates an X-ray powder measurement. References are given in an abbreviated form. The first three letters of the principal author's name are followed by the year of publication.

Compound	Structure type	θ_D(K)	Reference	θ_M(K)	θ_M(K)$\sqrt{2}$	Reference
GaAs	ZnS	~355	Nov-61	247	349	Arn-63
InSb	ZnS	240	Pie-66	153	216	Bil-76
CdTe	ZnS	~200	Dem-69	141	199	Wal-70
			Bir-75			Zub-75
						Hor-86
HgTe	ZnS	112 (0)	Rus-70	73 (32)	103	Ske-72
LiF	NaCl	645 (300)	Nue-67	623 (300)	881	Mar-78
NaCl	NaCl	275 (300)	Nue-67	265 (300)	375	Mar-78
		290 (∞)	Bar-57	280 (300)	396	Ges-71
KCl	NaCl	235 (∞)	Bar-57	216 (300)	305	Mar-78
				204 (300)	288	Cha-71
				218 (300)	308	Pat-73
				P 213 (300)	301	Pat-69
KBr	NaCl	188 (∞)	Bar-57	148 (300)	209	Mar-78
		174 (0)	Sha-70	160 (300)	226	Pat-73
		123 (300)	Sha-70			
PbS	NaCl	227 (200)	Par-54	*P* 144 (300)	204	Sub-78*a*
RbCl	NaCl			*P* 157 (300)	222	Jar-67
SmS	NaCl	269 (100)	Smi-72	*P* 155 (300)	219	Sub-77
		266 (300)	Bad-73			
SmSe	NaCl	206 (100)	Smi-72	*P* 153 (300)	216	Sub-77
$TiN_{0\cdot99}$	NaCl	485 (70)	Roe-76			
$TiN_{0\cdot9}$	NaCl			332 (300)	470	Chr-78
CsCl	CsCl	162 (300)	Vet-70	151 (300)	214	Bar-66
CsBr	CsCl	179 (∞)	Red-72	*P* 118 (300)	167	Sub-78*b*
		120 (300)	Vet-70			
CsI	CsCl	101 (∞)	Red-72	*P* 101 (300)	143	Sub-78*b*
		105 (300)	Vet-70			
TlCl	CsCl	157 (∞)	Red-72	*P* 101 (300)	143	Sub-78*b*
				P 95	135	Haa-77
TlBr	CsCl	118 (∞)	Red-72	*P* 95 (300)	134	Sub-78*b*

into one band and treated in the Einstein (1907) approximation. In this model, integrations are done in a 'reduced' Brillouin zone. Since the optic branches are often relatively flat, they can be described reasonably well by one frequency. Such a model has sometimes been used to interpret specific-heat data by Brening & Schroder (1952), Bichsel (1979) and Geibel, Rietschel, Junod, Pelizzone & Muller (1985) and others. The necessity of the Debye-Einstein model can be seen, for instance, in the case of a diatomic compound CdTe for which the phonon dispersion curves were measured by Rowe, Nicklow, Price & Zanio (1974) using inelastic neutron scattering. These curves show the optic branches lying around 4·4 THz which is equivalent to $\Theta_E \simeq 210$ K. Therefore, even at quite low temperatures the optic modes are occupied.

The paper is organized as an extended theory section and a discussion. The first two theory parts can be found in most textbooks as, for instance, in Ashcroft & Mermin (1976). The formalism is, however, closer to that of Willis & Pryor (1975).

II. Theory

II.1. *Background*

As shown by James (1982), the intensity of a Bragg reflection is proportional to the magnitude of the structure factor, $F(\mathbf{H})$, or its square, $[F(\mathbf{H})]^2$, depending upon the nature of the crystal: perfect or mosaic, respectively. The structure factor can be computed as

$$F(\mathbf{H}) = \sum_{j=1}^{p} f_j(\mathbf{H}) \exp(-M_j) \exp(-i\mathbf{H}\,.\,\mathbf{r}_j), \quad (1)$$

where $\mathbf{H}$ is the diffraction vector, $|\mathbf{H}| = 4\pi(\sin\theta)/2$, $\mathbf{r}_j$ is the position of the jth atom in the unit cell, p is the number of atoms in the unit cell, $f_j(\mathbf{H})$ is the atomic form factor of the jth atom, $\exp(-i\mathbf{H}\,.\,\mathbf{r}_j)$ is a phase factor indicating the contribution of the jth atom in the unit cell, and $\exp(-M_j)$ is the temperature factor describing the atomic motions about the crystallographic position $\mathbf{r}_j$. Let $\mathbf{u}_j$ be the average deviation of the jth atom from $\mathbf{r}_j$. From Willis & Pryor (1975) one finds that

$$M_j = \tfrac{1}{2}\langle|\mathbf{H}\,.\,\mathbf{u}_j|^2\rangle \quad (2)$$

where the angle brackets denote an average over a time period which is long compared with vibrational periods.

A well known result of lattice dynamics is that a crystal with N unit cells and p atoms per unit cell has $3pN$ normal modes of vibration. These $3pN$ eigenfrequencies form $3p$ branches in the dispersion relations with N allowed wave vectors in each branch.

Each mode is represented by a wave vector $\boldsymbol{\kappa}$, an index s, labelling the branch, a frequency $\omega_s(\boldsymbol{\kappa})$, an amplitude $A_s(\boldsymbol{\kappa})$, and a normalized $3p$-dimensional eigenvector $\boldsymbol{\varepsilon}_s(\boldsymbol{\kappa})$. The eigenvectors can be written as

$$\boldsymbol{\varepsilon}_s(\boldsymbol{\kappa}) = \begin{bmatrix} \boldsymbol{\varepsilon}_s(1,\boldsymbol{\kappa}) \\ \boldsymbol{\varepsilon}_s(2,\boldsymbol{\kappa}) \\ \vdots \\ \boldsymbol{\varepsilon}_s(p,\boldsymbol{\kappa}) \end{bmatrix}. \tag{3}$$

Each $\boldsymbol{\varepsilon}_s(j,\boldsymbol{\kappa})$ is a three-dimensional vector representing the direction of displacement of the jth atom from its crystallographic position. The normalization condition on the eigenvector is

$$\boldsymbol{\varepsilon}_s(\boldsymbol{\kappa}) \cdot \boldsymbol{\varepsilon}_{s'}(\boldsymbol{\kappa}) = \sum_{j=1}^{p} \boldsymbol{\varepsilon}_s(j,\boldsymbol{\kappa}) \cdot \boldsymbol{\varepsilon}_{s'}(j,\boldsymbol{\kappa}) = \delta_{s,s'}. \tag{4}$$

At a particular instant, the position of the jth atom in the unit cell is the sum of the contributions from each normal mode,

$$\mathbf{u}_j(t) = \frac{1}{m_j^{1/2}} \sum_{s=1}^{3p} \sum_{\boldsymbol{\kappa}} \boldsymbol{\varepsilon}_s(j,\boldsymbol{\kappa}) A_s(\boldsymbol{\kappa}) \times \exp\left[-i(\boldsymbol{\kappa} \cdot \mathbf{r}_j - \omega_s(\boldsymbol{\kappa})t)\right]. \tag{5}$$

The mass-normalized amplitudes $A_s(\boldsymbol{\kappa})$ are complex. They contain phase factors that change randomly with time, corresponding to the creation and annihilation of phonons. The desired quantity is the time average of $|\mathbf{H} \cdot \mathbf{u}_j|^2$. Thus,

$$\langle|\mathbf{H}\cdot\mathbf{u}_j|^2\rangle = \Bigg\langle \frac{1}{m_j} \sum_{\substack{s,s' \\ \boldsymbol{\kappa},\boldsymbol{\kappa}'}}^{s} [\mathbf{H}\cdot\boldsymbol{\varepsilon}_s(j,\boldsymbol{\kappa})][\mathbf{H}\cdot\boldsymbol{\varepsilon}_{s'}(j,\boldsymbol{\kappa}')] \times A_s^*(\boldsymbol{\kappa}) A_{s'}(\boldsymbol{\kappa}') \exp\{i[\omega_s(\boldsymbol{\kappa}) - \omega_{s'}(\boldsymbol{\kappa}')]t\} \times \exp[-i(\boldsymbol{\kappa}-\boldsymbol{\kappa}')\cdot\mathbf{r}_j] \Bigg\rangle \tag{6}$$

where, for a given term in the sum of (6), the time average of $\langle A_s^*(\boldsymbol{\kappa}) A_{s'}(\boldsymbol{\kappa}') \exp\{i[\omega_s(\boldsymbol{\kappa}) - \omega_{s'}(\boldsymbol{\kappa}')t]\}\rangle$ is zero if $\omega_s(\boldsymbol{\kappa}) \neq \omega_{s'}(\boldsymbol{\kappa}')$.

However, if $\boldsymbol{\kappa} \neq \boldsymbol{\kappa}'$ and $s \neq s'$, the random time-dependent phases in the amplitudes cause the average to be zero even when $\omega_s(\boldsymbol{\kappa}) = \omega_{s'}(\boldsymbol{\kappa}')$. This leaves

$$\langle|\mathbf{H}\cdot\mathbf{u}_j|^2\rangle = \frac{1}{m_j} \sum_{s,\boldsymbol{\kappa}} [\mathbf{H}\cdot\boldsymbol{\varepsilon}_s(j,\boldsymbol{\kappa})]^2 |A_s(\boldsymbol{\kappa})|^2. \tag{7}$$

Since this is a harmonic model, the total energy E in the crystal containing N unit cells is twice the kinetic energy,

$$E = \sum_{n=1}^{N} \sum_{j=1}^{p} m_j |\dot{u}_j|^2. \tag{8}$$

The relation between the energy per normal mode, $E_s(\boldsymbol{\kappa})$, and the amplitudes is found by differentiating (5), which yields $\dot{u}_j$. Then by averaging over time and using the orthonormality condition (4), one obtains

$$E = \sum_{s,\boldsymbol{\kappa}} E_s(\boldsymbol{\kappa}) = \sum_{s,\boldsymbol{\kappa}} N\omega_s^2(\boldsymbol{\kappa}) |A_s(\boldsymbol{\kappa})|^2. \tag{9}$$

Therefore,

$$M_j = \frac{1}{2Nm_j} \sum_{s,\boldsymbol{\kappa}} [\mathbf{H}\cdot\boldsymbol{\varepsilon}_s(j,\boldsymbol{\kappa})]^2 \left[\frac{E_s(\boldsymbol{\kappa})}{\omega_s(\boldsymbol{\kappa})^2}\right]. \tag{10}$$

The normal modes are solutions of the Schrödinger equation for a particle in a harmonic potential well. Thus, the energy eigenvalues are

$$E_s(\boldsymbol{\kappa}) = \hbar\omega_s(\boldsymbol{\kappa})[\eta_s(\boldsymbol{\kappa}) + \tfrac{1}{2}] \tag{11}$$

where the occupation numbers are

$$\eta_s(\boldsymbol{\kappa}) = \{\exp[\hbar\omega_s(\boldsymbol{\kappa})/k_BT] - 1\}^{-1}. \tag{12}$$

II.2. *The Debye model*

Debye's assumption was that all waves travelled at the same speed v. The dispersion relation is then $\omega_s(\boldsymbol{\kappa}) = \kappa v$ when $\omega_s(\boldsymbol{\kappa})$ is less than some maximum frequency ω_M, and zero for larger frequencies. The allowed wave vectors are so closely spaced that the sum over $\boldsymbol{\kappa}$ in (10) can be replaced by an integral:

$$\frac{1}{N}\sum_{\boldsymbol{\kappa}} \rightarrow \left(\frac{a}{2\pi}\right)^3 \int \mathrm{d}^3\boldsymbol{\kappa}.$$

$\boldsymbol{\varepsilon}_s$ is a function only of the direction of $\boldsymbol{\kappa}$, and ω_s and E_s are functions of the magnitude of $\boldsymbol{\kappa}$. Hence, the angular part of the integral is simple. For the radial part, a characteristic Debye temperature Θ_M is defined by $k_B\Theta_M = \hbar\omega_M = \hbar v/\boldsymbol{\kappa}_M$. $\boldsymbol{\kappa}_M$ is the radius of a sphere in reciprocal space containing pN wave vectors ($3pN$ normal modes), each wave vector occupying a volume $(2\pi/a)^3/N$.

In a monatomic solid, there are only three branches. A polyatomic solid has $3p$ branches which are commonly represented as all in a single Brillouin zone, the 'reduced zone'. An alternative, but equally valid representation, is an 'extended-zone' scheme in which there are p zones, each containing three branches. Both representations have a total of $3p$ branches. In the Debye model, only three branches ($s = 1, 2, 3$) are assumed to exist. Thus the extended-zone scheme must be used, and this extended zone is treated as a single Brillouin zone. In other words, there is only one Brillouin zone, but its volume is large enough to contain a factor of p times more wave vectors than the Brillouin zone of a monatomic solid. The two representations are identical when $p = 1$.

$$M_j = \frac{3ph^2|\mathbf{H}|^2}{2m_jk_B\Theta_M}\left[\frac{\varphi(x)}{x} + \frac{1}{4}\right]\sum_s |\boldsymbol{\varepsilon}_s(j)|^2, \tag{13}$$

where $x = \Theta_M/T$ and the Debye integral function is

$$\varphi(x) = \frac{1}{x}\int_0^x \frac{y\,\mathrm{d}y}{e^y - 1}. \tag{14}$$

Note that the Debye temperature is the same for all atoms. The only dependence on j is in the atomic mass m_j, and in the sum over the eigenvectors. Using the orthonormality condition and replacing $|\mathbf{H}|$ by $4\pi(\sin\theta)/2$, one can write

$$\sum_{j=1}^{p} m_j M_j = \frac{6ph^2}{k_B\Theta_M}\left[\frac{\varphi(x)}{x}+\frac{1}{4}\right]\frac{\sin^2\theta}{\lambda^2}. \qquad (15)$$

The individual M_j cannot be found without further knowledge of the polarization vector $\boldsymbol{\varepsilon}_s(j, \boldsymbol{\kappa})$.

II.3. *The Debye-Einstein model*

The dispersion relations for the Debye-Einstein model are

$$\omega_s(\boldsymbol{\kappa}) = \begin{cases} \kappa v & 0 \le \omega \le \omega_M; \quad s=1,2,3 \\ 0 & \omega > \omega_M; \quad s=1,2,3. \\ \omega_E & s>3 \end{cases} \qquad (16)$$

The Debye temperature is defined as before: $\hbar\omega_M = k_B\Theta_M$. An Einstein temperature is similarly defined by $\hbar\omega_E = k_B\Theta_E$. Consider a diatomic solid. In the Debye model, the integration yielding (13) is done in the first and second Brillouin zones (which were treated as a single zone, as explained above). In the Debye-Einstein model, however, the acoustic and optic modes are each integrated in the first Brillouin zone only (the reduced-zone scheme). Fig. 1 illustrates the comparison between the Debye and the Debye-Einstein models as applied to a diatomic crystal (Ashcroft & Mermin, 1976).

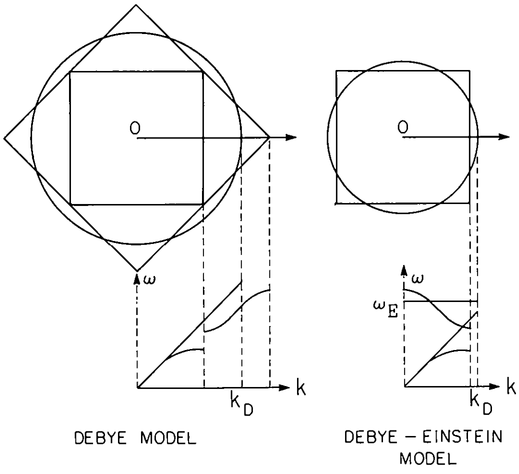

Fig. 1. Comparison of the Debye and Debye-Einstein models for a diatomic solid. The Debye model has a linear dispersion relation and it is integrated in a sphere having a volume equal to the volume of the first two Brillouin zones. The Debye-Einstein model uses a linear dispersion relation for the acoustic modes, a constant for the optic modes, and it is integrated only in the first Brillouin zone (courtesy of Professor N. W. Ashcroft and Professor N. D. Mermin).

The sum in (10) is again converted into an integral. κ_M is the radius of a sphere containing only N wave vectors. The integration of the optic branches is carried out in a sphere containing $(p-1)N$ wave vectors. The final result is

$$\sum_{j=1}^{p} m_j M_j = \frac{6h^2}{k_B\Theta_M}\left[\frac{\varphi(x)}{x}+\frac{1}{4}\right]\frac{\sin^2\theta}{\lambda^2} + \frac{2(p-1)h^2}{k_B\Theta_E} \times\left[\frac{1}{\exp(x_E)-1}+\frac{1}{2}\right]\frac{\sin^2\theta}{\lambda^2} \qquad (17)$$

where $x_E = \Theta_E/T$. By analogy with the Debye case, the left-hand side of (17) is pmM. Thus, the average thermal parameter is

$$M = \frac{6h^2}{pmk_B\Theta_M}\left[\frac{\varphi(x)}{x}+\frac{1}{4}\right]\frac{\sin^2\theta}{\lambda^2} + \frac{2(p-1)h^2}{pmk_B\Theta_E} \times\left[\frac{1}{\exp(x_E)-1}+\frac{1}{2}\right]\frac{\sin^2\theta}{\lambda^2}. \qquad (18)$$

In the classical limit, the Debye and Einstein parts of this expression have the same dependence on temperature and on $(\sin\theta)/\lambda$. That is, if $T > \Theta_M$, then $\varphi(x)/x + \frac{1}{4} \simeq T/\Theta_M$. If $T \ge \Theta_E$ also, then $1/[\exp(x_E)-1]+\frac{1}{2} \simeq T/\Theta_E$. Thus, both terms in (18) are linear in T and in $[(\sin\theta)/\lambda]^2$. That is, a least-squares fit to the data is not able to distinguish between the two terms. However, the optic modes contribute less to the mean square displacement, notably at low temperatures. Hence, a reasonable solution to the problem is to extract a Θ_E from the measured phonon density of states (when available) and fit the data by varying Θ_M only. It should be stated that the Debye temperature in this model is different from Θ_M in the pure Debye model and also from Θ_D. For a diatomic crystal, the Debye temperature in this model should be $\sim\sqrt{2}$ smaller than Θ_M in the Debye model, and a factor of ~ 2 smaller than Θ_D.

III. Discussion

III.1. *The Debye model*

For a monatomic solid $p=1$ and (15) reduces to Debye's result,

$$M = \frac{6h^2}{mk_B\Theta_M}\left[\frac{\varphi(x)}{x}+\frac{1}{4}\right]\frac{\sin^2\theta}{\lambda^2}. \qquad (19)$$

For the more general case containing p atoms per unit cell, the left-hand side of (15) is approximately equal to pmM if m is the average atomic mass and M is the average thermal parameter. Equation (15) then reduces to the monatomic expression, (19), regardless of p.

In polyatomic crystals, each kind of atom has a different M_j. Often, the thermal parameter M_j for each atom is assumed to be given by (19), where m

is the mass of the particular atom, and each atom has its own 'Debye temperature'. While these 'Debye temperatures' no longer have the same physical meaning as the real Debye temperature, they are still good measures of the mean square atomic displacements.

Thermodynamic quantities are calculated from a single Debye temperature representing the compound investigation and not from individual Debye temperatures describing the motions of the atoms in the compound. In polyatomic solids, this single Θ_M is a mean of the individual Debye temperatures. Certain reflections must be used to extract this average Θ_M from X-ray diffraction data. For example, in a diatomic alloy, AB, the magnitude of the structure factor can be proportional to the form factors f_A+f_B, f_A-f_B, or $(|f_A|^2+|f_B|^2)^{1/2}$ in the case of a zinc-blende compound. Structure factors of the first type should be used to find the average Debye temperature, although the last form is also suitable if the A and B atoms have similar masses (Walford & Schoeffel, 1970). When F is proportional to f_A-f_B, Bilderback & Colella (1976), Colella (1977), and Horning & Staudenmann (1986) have observed that the structure factor F can increase with increasing temperature. Thus, reflections of this type are not to be used. They are necessary, however, when trying to extract Debye temperatures for individual atoms.

Since the Debye theory is most commonly used in the measurement of the specific heat, it is important to point out the relationship between the results of the two methods. Zener & Bilinsky (1936) showed that the Debye temperatures for the longitudinal, Θ_L, and transverse, Θ_T, modes are averaged differently to obtain the overall Debye temperature. The average in the X-ray case is

$$3/\Theta_M^2 = 1/\Theta_L^2 + 2/\Theta_T^2 \tag{20a}$$

while

$$3/\Theta_D^3 = 1/\Theta_L^3 + 2/\Theta_T^3 \tag{20b}$$

for specific-heat data. Barron *et al.* (1966) pointed out that Θ_D and Θ_M should be different by no more than about a few percent, provided that the crystals are still purely Debye-like in their frequency distributions. For polyatomic crystals, however, the difference between Θ_D and Θ_M becomes more important. When m and M are taken as the average atomic mass and thermal parameter, respectively, the left-hand side of (15) becomes pmM. This latter p cancels the p on the right-hand side of (15) resulting in an expression identical to the monatomic equation; that is, valid for any p. On the other hand, the specific heat is the temperature derivative of the total energy [see (8)]:

$$C_V = \frac{\partial}{\partial T}\left(\sum_{n=1}^{N}\sum_{j=1}^{p} m_j|\dot{u}_j|^2\right) = \frac{12}{5}\pi^4 Npk_B\left(\frac{T}{\Theta_D}\right)^3. \tag{21}$$

In contrast to the X-ray case, the p on the right-hand side of (21) is not cancelled by a p on the left-hand side.

From inspection of (19) and (21), one can see that Θ_D and Θ_M are significantly different. The thermal parameter, M_j, accounts for the motion of only one atom, while the specific heat reflects the collective motion of all atoms. Finding a relationship between Θ_D and Θ_M requires that a thermal parameter reflecting the motions of all atoms must be postulated. In the classical limit ($T > \Theta_M$), $\varphi(x)/x + \frac{1}{4}$ reduces to T/Θ_M. Therefore

$$M = \frac{6h^2T}{mk_B\Theta_M^2}\frac{\sin^2\theta}{\lambda^2}, \tag{22}$$

where m is the average mass and M is the average thermal parameter. Note that (22) is valid for any p. Let M' be a quantity that describes the collective motion of all atoms. This is accomplished by inserting a factor of p in the numerator of (22), analogous to the p in (21), and by replacing Θ_M by Θ'_M:

$$M' = \frac{6ph^2T}{mk_B{\Theta'_M}^2}\frac{\sin^2\theta}{\lambda^2}. \tag{23}$$

Θ'_M is then a quantity which has the same physical interpretation as Θ_D. Here, m is still the average mass of the atoms. If these two expressions were fit to the same data, then $M = M'$, yielding the relation

$$\Theta_D \simeq \Theta'_M = p^{1/2}\Theta_M. \tag{24}$$

Thus, rather than comparing Θ_D to Θ_M for polyatomic solids, Θ_D should be compared to $p^{1/2}\Theta_M$. Θ_D and $p^{1/2}\Theta_M$ should still differ by a small amount because of the different averaging over longitudinal and transverse modes (Barron *et al.*, 1966), and also because of the deviations of the real crystal behavior from the Debye assumptions. This comparison should be made at a temperature where the crystal thermal parameters are in the 'classical' regime; that is, in a temperature range where $\Theta_D(T)$ and $\Theta_M(T)$ are roughly constant.

It is clear that the approximation made above will work best for solids composed of atoms with similar masses. Two examples are the semiconductors GaAs and CdTe, both having the cubic zinc-blende structure. Ga and As have nearly equal masses, as do Cd and Te, and both X-ray and specific-heat Debye temperatures are available and well characterized. These are diatomic solids, so $p=2$. Table 1 lists Θ_D, Θ_M and $\Theta_M\sqrt{2}$ for these crystals as well as other examples having the CsCl and the NaCl crystal structures. In particular, the agreement between Θ_D and $\Theta_M\sqrt{2}$ is excellent for GaAs and CdTe. In general, it is difficult to find references pertaining to the subject of the present article: they concern either Θ_D or Θ_M with very little overlap between these two physical quantities. Some articles, such as that of Martin &

O'Connor (1978), have extensive quotations from scattering works, and others, such as Smirnov (1972), are relevant only to specific heat and/or thermal-expansion measurements. Table 1 is not intended to be exhaustive but sufficient to show that the agreement between Θ_D and $\Theta_M\sqrt{2}$ is outstanding for a few cases and reasonable otherwise. In those latter cases, the agreement could probably be better if measurements were conducted as for CdTe and GaAs. The fluctuations between the above-mentioned quantities are too randomly distributed to extract information about the deviation trends.

III.2. *The Debye-Einstein model*

If one applies the Debye-Einstein model to the CdTe X-ray diffraction data (Horning & Staudenmann, 1986), the resultant Debye temperature is $\Theta_M = 103$ K when using an Einstein temperature of $\Theta_E = 210$ K. As expected, this is smaller than Θ_M in the pure Debye model (141 K) by a factor of $\sim\sqrt{2}$, and smaller than the specific-heat Debye temperature ($\sim$200 K) by a factor of two.

The major advantage of the Debye-Einstein model is that it is a better physical description of a polyatomic solid than the Debye approximation alone. From a practical standpoint, however, there is no real improvement. The Debye and Einstein models are crude. If one wants a detailed understanding of the lattice dynamics, better models are available. Therefore, the Debye and Debye-Einstein theories are useful because they provide two things: (i) a single quantity, Θ_M, to characterize and compare different solids, and (ii) a useful number for calculating other quantities such as X-ray intensities, the energy band gap temperature dependence *etc.*, regardless of its physical meaning. With respect to the first point, the Debye model can accomplish as much as the Debye-Einstein model with only one parameter. Moreover, this model should be compared to a specific-heat Debye-Einstein model. This procedure is not widely used with specific-heat measurements, so little comparison could be done. In contrast, the Debye model is often used with both types of experimental measurements and thus they can be easily compared. Finally, if experimentally measured dispersion curves are not available for the crystal in question, then the Debye-Einstein model is even less useful.

IV. Concluding remarks

In summary, we have extended the monatomic Debye model to the case of polyatomic solids. Debye's theory has been used in the past for these types of crystals, but with little justification. The purpose of this paper was to fill that gap, and to put earlier results on a more rigorous basis. Our results show why X-ray and specific-heat Debye temperatures are quite different for polyatomic solids ($p > 1$). Experimental data for several diatomic compounds substantiate these claims. In addition, an expression for the Debye-Waller factor has been derived, which arises from putting together the Debye and Einstein models. This combined model was treated in a reduced-zone representation while the purely Debye model was treated in an extended-zone representation. The derivation and interpretation are again straightforward, but the practical application of the Debye-Einstein model is more limited than that of the Debye model.

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Simple Statistics for Intensity Data from Twinned Specimens

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Abstract

The statistics of intensity data from hemihedrally twinned specimens are analyzed in terms of a new parameter and are shown to take a simple form in both the centrosymmetric and non-centrosymmetric cases. This analysis provides a sensitive method for determining the twinning fraction. The effects of intensity measurement errors on the observed statistics are discussed.

Introduction

When a crystal lattice posesses a rotational symmetry axis which is not a symmetry element of the space group of the crystal, crystal specimens may grow as merohedral twins. In this case, the reciprocal lattices of the different crystal twin domains of the specimen exactly overlap. The resulting diffraction intensities are given by linear combinations of the true untwinned intensities of reflections which are related by the twinning operation. In order to extract the true intensities from the observed intensities, one must be able to determine the twinning fraction (fractional volume of the specimen) for each of the separate twins. Several methods have been described for approximating the twinning fraction (Fisher & Sweet, 1980; Murray-Rust, 1973; Britton, 1972; Rees, 1980). A statistical treatment for hemihedral twinning (two twin domains) has been developed by Rees (1980). In that treatment, the statistical distribution for centrosymmetric reflections cannot be determined analytically. In addition , the intensities must be normalized prior to analysis. In the present treatment, these problems are avoided by deriving the statistics of a parameter H, which is a function of the two twin-related intensity measurements in hemihedral twinning. In the discussions which follow, we assume that the untwinned intensities obey Wilson's (1949) statistics and that intensities for untwinned reflections are independent.

Statistics for centrosymmetric reflections

Let

$$H=(q-p)/(q+p) \tag{1}$$

where p and q are intensity measurements of reflections related by the twinning operation. (Criteria by which weak pairs of reflections may be rejected without bias are discussed in the *Errors* section.) With a twinning fraction of α $(0<\alpha<\frac{1}{2})$,

$$p=(1-\alpha)|F_1|^2+\alpha|F_2|^2 \tag{2a}$$

and

$$q=\alpha|F_1|^2+(1-\alpha)|F_2|^2 \tag{2b}$$

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