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Generalized Temperature-Factor Formulation with Application to Cadmium Selenide and Other Wurtzites

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The generalized temperature factor is formulated within the framework of the one-particle potential in terms of functions derived from the harmonic functions of Stewart. This formulation is then applied to the wurtzite structure and projection analysis is used to eliminate one component of the potential. Inclusion of the generalized temperature factor in the structure-factor expression for wurtzite leads to the appearance of harmonically forbidden reflections and the loss of equivalence of non-symmetry-related reflections which occur at the same Bragg angle. The results of a room-temperature X-ray experiment with cadmium selenide are interpreted within the above model to yield cubic anharmonic parameters $|\beta_{332}| = |\beta_{337}| = |\beta_{313}|$ $(0.13 \pm 0.01) \times 10^{-12}$ erg $Å^{-3}$. These are used to estimate the anharmonic effect on the position parameter u. Some general conclusions are drawn regarding the possibility of observing similar effects in other wurtzite structures.

Introduction

The effects of anharmonic thermal vibrations on the intensities of Bragg reflections have been investigated in a number of cubic structures with both neutrons and X-rays (for a summary see Willis & Pryor, 1975). The interpretation of these effects has been successfully based on the effective one-particle potential (OPP) within the framework of Dawson's (1967) generalized structure-factor formulation. Recently, Mair & Barnea (1975) have extended this treatment to materials having the wurtzite structure. However, while the importance

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of the first-order component in the anharmonic temperature factor was recognized, it was neglected in the potential expansion. Anharmonic contributions to the atomic vibrations in hexagonal zinc have also been considered by several authors and their presence has been established by both neutron and Mössbauer techniques (Nizzoli, 1976; Merisalo & Larsen, 1977; Albanese, Deriu & Ghezzi, 1976).

The present paper details a general formulation of anharmonicity within the OPP approximation in terms of functions derived from the harmonic functions listed by Stewart (1972, 1973). This formulation is then applied to the case of wurtzite. In § 2 the resulting temperature-factor expressions for wurtzite are shown to predict X-ray intensity differences between some

harmonically equivalent reflections, as well as the appearance of a group of harmonically forbidden reflections. This is followed by a discussion of a room-temperature experiment on a large crystal of cadmium selenide. While it was not possible to observe any of the forbidden reflections, significant differences in the intensities of certain harmonically equivalent reflections were observed [for a preliminary report of this work, see also Whiteley, Moss & Barnea (1977)].

The magnitude of the effect of anharmonicity upon the conventionally refined u parameter in cadmium selenide is calculated. An estimate of the relative magnitude of anharmonic effects in other wurtzite structures is presented in the final section.

1. Theory

If the crystal is treated as an Einstein solid, with the coupling between atomic vibrations being neglected, the crystal potential can be replaced by the one-particle potential. This method reproduces essentially the same results as the rigorous lattice-dynamical treatment and can be applied without difficulty to any crystal structure (Willis & Pryor, 1975).

Following Dawson, Hurley & Maslen (1967) the OPP may be expanded in terms of functions obeying the local site symmetry. These functions can be derived directly by a group-theoretical approach or by expanding the potential as a power series in the atomic displacements, retaining only those terms which are invariant under the operations of the point group. A simpler approach utilizes the harmonic basis functions developed by Stewart (1972, 1973) for multipole expansions of the atomic charge density. These functions have been given to fourth order for all point groups in terms of the direction cosines q_x, q_y, q_z of the Bragg vector $\mathbf{Q}$. In general, the OPP may therefore be expressed as:

$$V = \sum_n V_n \tag{1a}$$

where

$$V_n = r^n \sum_{m=0}^{\lfloor \frac{n}{2} \rfloor} \sum_l \beta_{npl} K_{pl}(q_x, q_y, q_z). \tag{1b}$$

$p = n - 2m$, [ ] denotes the integer part, $K_{pl}(q_x, q_y, q_z)$ is the lth harmonic of order p normalized such that $\{K_{pl}\}_{\max} = 1$ (Merisalo & Larsen, 1977), and β_{npl} are coefficients of the potential components V_{npl}.

The anharmonic temperature factor $T(\mathbf{Q})$ may then be evaluated by taking the ensemble average of the potential in the classical limit (Willis, 1969)

$$T(\mathbf{Q}) = \langle \exp(i\mathbf{Q} \cdot \mathbf{u}) \rangle = \frac{\int \exp(-V/k_B T) \exp(i\mathbf{Q} \cdot \mathbf{u}) \, d^3 u}{\int \exp(-V/k_B T) \, d^3 u} \tag{2}$$

where $\mathbf{Q}$ is the scattering vector, $\mathbf{u}$ is the displacement

of the atom from its equilibrium position, k_B is the Boltzmann constant and T is the absolute temperature.

Equation (2) may be evaluated by use of the standard integral I (Gradshteyn & Ryzhik, 1965)

$$I = \int_{-\infty}^{\infty} x^n \exp(-ax^2 - bx + i\gamma x) \, dx$$

$$= \frac{i^n \sqrt{\pi}}{2^n a^{(n+1)/2}} \exp\left[\frac{(b - i\gamma)^2}{4a} \right] H_n \left[\frac{\gamma + ib}{2\sqrt{a}} \right] \tag{3}$$

where H_n is the nth order Hermite polynomial of complex argument.

For all but the five point groups of lowest symmetry $(1, \bar{1}, 2, m, 2/m)$, b is zero (when the OPP is expressed in Cartesian coordinates) and H_n is then a purely real function. This formulation is general and simple, except for the five point groups of lowest symmetry in which a given component of the potential V_{npl} yields both real and imaginary parts in $T(\mathbf{Q})$.

It should be noted that the symmetry restrictions listed by Stewart are referred to a maximum symmetry direction along the z axis with the x axis perpendicular to a principal mirror plane. In general this will necessitate a transformation to give the correct orientation relative to the local atomic environment. By the properties of the Fourier transform this rotation may be applied to either real or reciprocal space.

The local site symmetry in wurtzite $(3m)$ restricts the harmonics K_{pl} appearing in $(1b)$. Retaining only terms to third order reduces $(1a)$ to the form:

$$V = V_0 + V_1 + V_2 + V_3 \tag{4a}$$

where

$$V_0 = \beta_{001} \tag{4b}$$

$$V_1 = \beta_{113} z \tag{4c}$$

$$V_2 = \beta_{225} \tfrac{1}{2}(3z^2 - r^2) + \beta_{201} r^2 \tag{4d}$$

$$V_3 = \beta_{332}(3x^2 - y^2)y + \beta_{337} \tfrac{1}{2}(5z^2 - 3r^2)z + \beta_{313} zr^2. \tag{4e}$$

Here (x, y, z) form a Cartesian coordinate system. The subscripts npl have the following meaning: the first subscript denotes the order of the term, the second denotes the order of the harmonic K_{pl} and the third is the lth harmonic of order p listed by Stewart (1973). The second-order term in the OPP expansion gives the usual hexagonal component in the harmonic approximation.

The assumption that all components of the OPP except V_2 are small, leads to the result:

$$T(\mathbf{Q}) = T_c + iT_c[T_{113} + T_{332} + T_{337} + T_{313}] \tag{5a}$$

$$T_c = \exp[-(u^2 + v^2 + w^2)] \tag{5b}$$

$$T_{113} = -\frac{\beta_{113}}{2k_B Ta_3^{1/2}} H_1(w) \tag{5c}$$

$$T_{332} = - \frac{\beta_{332}}{8k_B Ta_1^{3/2}} [H_3(v) - 3H_2(u) H_1(v)] \qquad (5d)$$

$$T_{337} = \frac{\beta_{337}}{8k_B Ta_3^{1/2}} \left[\frac{H_3(w)}{a_3} - \frac{3H_1(w)}{2} \frac{H_2(u) + H_2(v)}{a_1} \right]$$

$$(5e)$$

$$T_{313} = \frac{\beta_{313}}{8k_B Ta_3^{1/2}} \left[\frac{H_3(w)}{a_3} + H_1(w) \frac{H_2(u) + H_2(v)}{a_1} \right]$$

$$(5f)$$

where

$$u^2 = \frac{\pi^2 p^2}{a_1}, \quad v^2 = \frac{\pi^2 q^2}{a_1}, \quad w^2 = \frac{\pi^2 r^2}{a_3};$$

$$a_1 = \frac{4\pi^2}{B_{11}}, \quad a_3 = \frac{4\pi^2}{B_{33}},$$

B_{11} and B_{33} are the hexagonal Debye–Waller factors in the harmonic approximation, and the indices (pqr) are referred to an orthogonal reciprocal-lattice coordinate system. The required transforms relating (pqr) to the hexagonal Miller indices (hkl), are given in Table 1 and ensure that the potential minima are directed along the antibonding directions. These equations are consistent with the corresponding expressions given by Mair & Barnea (1975), and also illustrate the advantage of using the harmonics formulation in the Cartesian coordinate system [cf. equations (5) and (6)].

Expression (5) for the temperature factor requires four anharmonic parameters. By considering the projection of T_{113} on T_{313} it is, however, possible to show that the first-order potential component is not required and the OPP may then be effectively described by the three third-order functions (see Appendix).

2. The effects of anharmonicity on Bragg intensities

For the purpose of this discussion it is necessary to transform the Cartesian expressions of (5) into the

Table 1. *Transforms between Cartesian* (pqr) *and hexagonal* (hkl) *indices*

$$p \to \frac{h+k}{a_0}; \quad q \to \frac{k-h}{\sqrt{3}a_0}; \quad r \to \frac{l}{c_0}$$

Table 2. *Sign conventions for the third-order anharmonic parameters for each atom of the unit cell with* Cd(1) *at the origin*

	Cd(1)	Cd(2)	Se(1)	Se(2)
β_{332}	+	−	+	−
β_{337}	+	+	−	−
β_{313}	−	−	+	+

direct hexagonal coordinate system. As stated previously, it is possible to neglect V_1; hence the temperature factor takes the form:

$$T = T_c \left(1 - i \frac{\beta_{332} B_{11}^3}{8\sqrt{3}a_0^3 \pi^3 k_B T} \left(\frac{h^3 - k^3}{3} + \frac{h^2 k - hk^2}{2} \right) \right.$$

$$- i \frac{\beta_{337} B_{33} l}{32\pi^3 c_0 k_B T} \left\{ B_{33} \left(3 - \frac{B_{33} l^2}{2c_0^2} \right) \right.$$

$$\left. - B_{11} \left[3 - \frac{B_{11}(h^2 + hk + k^2)}{a_0^2} \right] \right\}$$

$$- i \frac{\beta_{313} B_{33} l}{32\pi^3 c_0 k_B T} \left\{ B_{33} \left(3 - \frac{B_{33} l^2}{2c_0^2} \right) \right.$$

$$\left. \left. + \tfrac{2}{3} B_{11} \left[3 - \frac{B_{11}(h^2 + hk + k^2)}{a_0^2} \right] \right\} \right)$$

$$(6)$$

where

$$T_c = \exp \left\{ - \left[\frac{B_{11}}{3} \frac{(h^2 + hk + k^2)}{a_0^2} + \frac{B_{33} l^2}{4c_0^2} \right] \right\}.$$

It is important to consider the relative orientations of the potential components about each atom of the unit cell. By considering projections along and perpendicular to the c_0 axis, it is possible to establish sign relations between the various anharmonic components. These relations are listed in Table 2 which merely implies the relative signs of the terms, the l-dependent functions for a given atom being given opposite signs to allow anharmonic vibrations along both directions above and below the atom. The absolute signs of the terms must, of course, be obtained in the refinement of the experimental data. With these sign conventions, and further assuming the magnitudes of the individual anharmonic parameters to be the same for both atomic species, the following expression for the generalized structure factor is obtained

$$F(\mathbf{Q}) = (f_A + if_A'')[T_{cA} + iT_{aA}^{(2)}]$$

$$\times \left\{ 1 + (-1)^l \exp \left[\frac{2\pi i(h + 2k)}{3} \right] \right\}$$

$$+ i(f_A + if_A'') T_{aA}^{(1)}$$

$$\times \left\{ 1 - (-1)^l \exp \left[\frac{2\pi i(h + 2k)}{3} \right] \right\}$$

$$+ \exp(2\pi iul) \left[(f_B + if_B'')[T_{cB} + iT_{aB}^{(2)}] \right.$$

$$\times \left\{ 1 + (-1)^l \exp \left[\frac{2\pi i(h + 2k)}{3} \right] \right\}$$

$$+ i(f_B + if_B'')T_{aB}^{(1)}$$

$$\left. \times \left\{ 1 - (-1)^l \exp \left[\frac{2\pi i(h + 2k)}{3} \right] \right\} \right]$$

$$(7)$$

where $T_{aj}^{(2)}$ contains all the l-dependent terms for atom j, $T_{aj}^{(1)}$ involves only h and k, the double prime denotes the imaginary anomalous dispersion component, u is the structural parameter and the subscripts c and a refer to the centrosymmetric and antisymmetric components.

From the above expression several features may be readily seen. Reflections not related by symmetry and occurring at the same $\sin \theta/\lambda$ value will now exhibit different intensities. For example, reflections such as $70l$ and $53l$ will, when anharmonic effects are included, differ in intensity. These differences are due to the third-order term $T_{aj}^{(1)}$. In particular, the 700 and 530 intensity difference, having no l-dependence, will provide a direct measure of the β_{332} parameter which characterizes the third-order potential function in the basal plane. Symmetry-related reflections will, of course, remain equivalent when anharmonicity is included.

By a suitable choice of indices, it is also possible to separate the effect of the l-dependent terms from that due to the pure h,k-dependent function. Thus, reflections for which $h + 2k = 3m$, $l = 2n$ or reflections with $h = k$ will have no contribution from $T_{aj}^{(1)}$. It must be remembered, however, that while two parameters occur in the l-dependence of the anharmonic vibrations, their unique determination may not be possible (Cooper, Rouse & Fuess, 1973).

The component $T_{aj}^{(1)}$ will also give rise to the normally forbidden group of reflections for which $h + 2k = 3m$, $h \neq -k/2$, k or $-2k$, $l = 2n + 1$, where m and n are integers. [A similar effect has also been predicted in zinc by Nizzoli (1976)]. In principle, non-spherical distortions of the atomic charge density should also result in the appearance of these forbidden reflections, since these distortions are subject to the same symmetry restrictions imposed on the OPP expansion. However, the above constraints on the hkl values imply that the lowest available forbidden reflection is already too far out in reciprocal space to show any discernible bonding effect.

It is interesting to note that, apart from reflections for which $h = k$, the appearance of these effects is independent of the presence of anomalous dispersion. Hence, it should be possible to observe these anharmonic effects with both X-ray and neutron methods.

3. Experimental

The X-ray measurements were carried out with the specimen used in the structure determination of cadmium selenide (specimen No. 2 in Freeman, Mair & Barnea, 1977) in the form of a platelet with a $1 \cdot 3 \times 0 \cdot 9$ cm 110 face.

The intensities were measured by the extended-face crystal technique described in previous papers (Mair, Prager & Barnea, 1971; Freeman, Mair & Barnea, 1977) on a XRD-4 General Electric manual diffract-

ometer (powered by a stabilized Philips PW 1320 generator) with Mo $K\alpha$ radiation. Balanced zirconium–yttrium oxide filters were placed in the diffracted beam before the scintillation counter. The crystal face was aligned perpendicular to the φ axis by a laser technique (Moss & Barnea, 1976). Preliminary experiments showed that the divergence of the incident beam was such that for large values of $|\chi|$ the diffracted beam was not completely intercepted by the diffracted-beam aperture. The incident-beam collimator was therefore redesigned to decrease the beam divergence. Each reflection was maximized and centred. Integrated intensities were obtained in a θ–2θ scan ranging over $3 \cdot 5°$ 2θ starting $1 \cdot 5°$ 2θ below the peak maximum. The measurements were carried out at $22 \pm 2 °C$.

The intensities were obtained in the two symmetrical aspects $(2\theta, \chi, \varphi, \omega)$ and $(2\theta, \chi - 90°, \varphi + 180°, -\omega)$ where $\chi = 0$ when the normal to the crystal face is in the plane of incidence. All measured reflections were within the $-45° < \chi < 45°$ octant.

The internal consistency of the intensities was demonstrated by the agreement of the same reflection measured in the two aspects and the agreement between the symmetrically equivalent hkl and khl reflections (the average deviation from the mean was $1 \cdot 25\%$. Fig. 1 illustrates a set of peaks of harmonically equivalent reflections.

4. Discussion

It is convenient to define, in analogy with the Bijvoet ratio, the anharmonic intensity ratio (AIR)

$$\text{AIR} = \frac{I(hkl) - I(h'k'l)}{\frac{1}{2}[I(hkl) + I(h'k'l)]} \qquad (8)$$
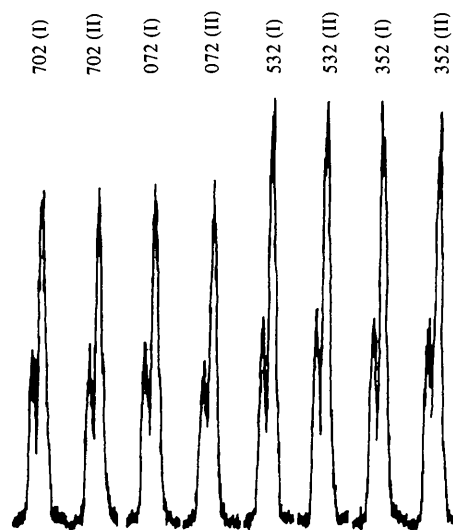

Fig. 1. Harmonically equivalent reflections in the two symmetrical aspects (I and II).

where h,k,h',k' are Miller indices such that

$$h^2 + hk + k^2 = h'^2 + h'k' + k'^2.$$

Table 3 lists a set of observed and calculated AIR and the Bijvoet ratios of $224/22\bar{4}$, $336/33\bar{6}$ and $332/33\bar{2}$. The errors cited in Table 3 are statistically determined standard deviations. The determination of the anharmonic parameters was carried out by a least-squares minimization of the weighted sum of squared residuals of calculated and observed AIR. The weights used were $1/\sigma_i^2$ where the σ_i were the experimental variances. The AIR were calculated with the structural and harmonic thermal parameters of Freeman, Mair & Barnea (1977), the spherical atomic scattering factors of Doyle & Turner (1968) and the dispersion corrections of Cromer & Liberman (1970). The intensities were assumed to be kinematic; this was justified because of the exclusive use of relatively low

Table 3. Calculated and experimental anharmonic intensity and Bijvoet ratios (%)

hkl	Harmonic	Anharmonic	Experimental
700 530	0·0	−13·5	−12·4 ± 3·1
702 532	0·0	−13·7	−15·8 ± 3·9
703 533	0·0	4·4	6·3 ± 1·5
70$\bar{1}$ 53$\bar{1}$	0·0	5·0	8·1 ± 3·4
70$\bar{2}$ 53$\bar{2}$	0·0	−14·0	−14·7 ± 3·9
70$\bar{3}$ 53$\bar{3}$	0·0	4·4	1·5 ± 1·6
70$\bar{5}$ 53$\bar{5}$	0·0	4·4	1·7 ± 2·0
332 33$\bar{2}$	20·7	20·8	20·1 ± 0·5
336 33$\bar{6}$	−27·6	−27·1	−26·6 ± 1·1
224 22$\bar{4}$	33·5	16·1	16·2 ± 2·3

$$|\beta_{332}| = |\beta_{337}| = |\beta_{313}| = 0\cdot13 \times 10^{-12} \text{ erg Å}^{-3}$$

Table 4. Comparison of the anharmonic thermal parameter of CdSe with the average anharmonic parameters of several cubic materials defined by

$$\beta = |\beta_A| = |\beta_B| = \frac{\beta_{\text{eff}}}{[1 + (B_A/B_B)^3]} \frac{1}{3\sqrt{3}}$$

Note that the cubic anharmonic parameters have been divided by $3\sqrt{3}$ to satisfy the normalization condition in (1)

	β
CdSe	0·13 ± 0·01 × 10^{-12} erg A^{-3}
ZnS[1]	0·29 ± 0·08 × 10^{-12}
ZnTe[1]	0·12 ± 0·03 × 10^{-12}
ZnSe[2]	0·13 ± 0·02 × 10^{-12}

References: (1) Cooper, Rouse & Fuess (1973). (2) Barnea, McIntyre & Moss (to be published).

intensities and the relative insensitivity of the AIR to extinction. With the sign conventions of Table 2 and equal magnitudes of all anharmonic parameters assumed, the refinement yielded $|\beta_{332}| = |\beta_{337}| = |\beta_{313}| = (0\cdot13 \pm 0\cdot01) \times 10^{-12}$ erg Å^{-3} with the absolute signs as in Table 2.

The contribution to the mean thermal displacement of an atom from equilibrium in the c_0 direction, $\langle z \rangle$, can be estimated from these values of the anharmonic parameters. The combined effect of the opposite displacement of the atoms due to anharmonic thermal motion results in a decrease of 0·009 Å in the Cd–Se distance along c_0. This is in excellent agreement with the suggestion of Mair & Barnea (1975) that neglect of anharmonicity in the structure refinement of cadmium selenide results in a u parameter greater than that calculated from the c_0/a_0 ratio by 0·0014 ± 0·0002, i.e. a change in the Cd–Se distance along c_0 of 0·010 ± 0·001 Å.

In order to compare the anharmonic thermal parameters of cadmium selenide with those available for the cubic materials ZnTe, ZnS (Cooper, Rouse & Fuess, 1973) and ZnSe (Barnea, McIntyre & Moss, to be published) the latter were converted to average parameters and divided by $3\sqrt{3}$ to satisfy the normalization of (1). These parameters are listed in Table 4.

A unique determination of individual components for the two atomic species or of separate values for β_{337} and β_{313} for each atom was impossible because of the paucity of data.

The same measure of good agreement between the calculated and observe AIR was obtained when V_{113} or V_{313}, singly or in combination, were used in the calculations. An estimate of the β_{113} parameter was obtained by requiring that either potential component should make a similar contribution to $\langle z \rangle$. This results in a relation

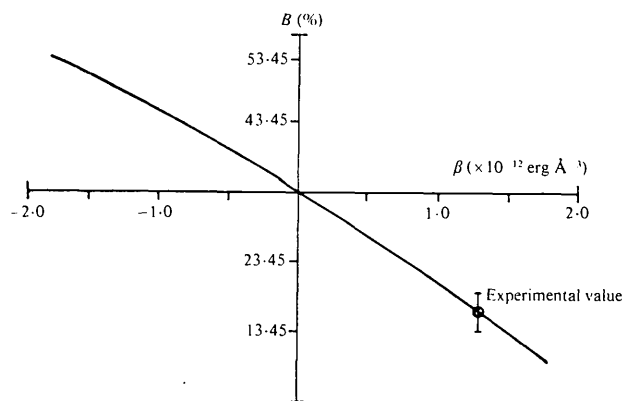$$\beta_{113} = \frac{\beta_{313}}{8\pi^2}[3B_{33} + 2B_{11}]$$

Fig. 2. Calculated variation of the 224 Bijvoet ratio (%) with the third-order l-dependent parameter β, with it assumed that $|\beta_{337}| = |\beta_{313}| \equiv \beta$.

Table 5. *Calculated structure factors for the* 704 *reflection and several forbidden reflections with* $|\beta_{332}| = |\beta_{337}| = |\beta_{313}| = 0.13 \times 10^{-12}$ erg Å^{-3}

hkl	F_{cal}
704	0.884
30$\bar{1}$	0.080
30$\bar{1}$	0.086
60$\bar{1}$	0.196
60$\bar{1}$	0.225
603	0.333
60$\bar{3}$	0.349

or, averaging over the two atomic species,

$$\beta_{113} = 0.086\,\beta_{313}.$$

A stringent test of the use of either of these potential components is provide by the anharmonic effects in the 224 Bijvoet ratio which are purely a function of the *l*-dependent terms. Fig. 2 illustrates the remarkable sensitivity of the 224 Bijvoet ratio to the *l*-dependent anharmonic parameters. This curve could be produced using either V_{113} or V_{313} in the OPP. This is in agreement with the results of the projection analysis presented in the Appendix.

Several unsuccessful attempts were made to observe the forbidden 60$\bar{3}$ reflection. Intensity calculations with the anharmonic parameters determined from the other reflections confirmed that it would be extremely difficult to observe, as its structure factor was less than half as large as that of the weakest observable (704) reflection (Table 5). Although such studies would be very timely, no attempt was made to observe forbidden reflections with neutrons or at elevated temperatures. In any case, the interpretation of such an observation would be complicated by the contribution of thermal diffuse scattering and multiple diffraction.

5. General considerations

Inspection of equations (5) indicates that for wurtzite structures the relative magnitude of the anharmonic term depends crucially on the ratios B_{11}/a_0 and B_{33}/c_0. Possible observation of anharmonic effects at room temperature will thus depend not only on a low Debye temperature but also on these ratios being large. Table 6 lists these ratios and Debye temperatures for a number of wurtzite structures for which data were readily available. An accurate knowledge of the Debye–Waller factors is of course essential for predicting the magnitude of anharmonic effects.

The results of the present work show that it is quite feasible to carry out investigations of anharmonic effects with X-rays, thus providing an alternative and complementary approach to the more commonly used neutron techniques. Indeed, although X-ray structure factors are complicated by bonding and dispersion effects, the intensities often suffer from less extinction

Table 6. *The ratios B_{11}/a_0 and B_{33}/c_0 and Debye temperatures θ_D for some wurtzite structures*

	Atom A		Atom B		
	B_{11}/a_0	B_{33}/c_0	B_{11}/a_0	B_{33}/c_0	θ_D (K)
CdSe[1]	0.34	0.25	0.28	0.14	181[6]
ZnO*[2]	0.10	0.06	0.17	0.11	370[7]
ZnS[3]	0.19	0.09	0.19	0.11	351[6]
AlN*[4]	0.08	0.05	0.25	0.16	1004[5]
BeO*[2]	0.20	0.12	0.10	0.06	1280[6]
CdS[8]	0.30	0.19	0.24	0.15	216[6]

References: (1) Freeman, Mair & Barnea (1977). (2) Sabine & Hogg (1969). (3) Hewat (1972). (4) Jeffrey, Parry & Mozzi (1956). (5) Demidenko, Koshchenko, Sabanova & Gran (1975). (6) Cline, Dunegan & Henderson (1967). (7) Abrahams & Bernstein (1969). (8) J. Castles, private communication.
* Only isotropic temperature factors given.

and are hence more easily interpreted. It should be noted that neglect of anharmonic effects in X-ray work may no longer be automatically justified. In fact, in some instances accurate positional parameters of atoms may only be obtained when anharmonicity is included in the least-squares refinement of the structure (Mair & Barnea, 1975).

APPENDIX

The projection coefficient of a function A upon a function B is defined as

$$P(A/B) = \frac{\int AB\,dr}{(\int A^2 dr)^{1/2}\,(\int B^2\,dr)^{1/2}}$$

and provides a measure of similarity of the functions A and B, somewhat like a correlation coefficient. Identifying A and B with the anharmonic temperature-factor components of (5) leads to the three nonzero projection coefficients $P(T_{113}/T_{337})$, $P(T_{113}/T_{313})$ and $P(T_{337}/T_{313})$. Assuming the integral to be over all space yields the exact expressions

$$P(T_{113}/T_{337}) = \frac{\sqrt{3}(c-1)}{(5c^2 - 6c + 6)^{1/2}}$$

$$P(T_{113}/T_{313}) = \frac{\sqrt{2}(1 \cdot 5c + 1)}{(4 + 6c + 7 \cdot 5c^2)^{1/2}}$$

$$P(T_{337}/T_{313}) = \frac{\sqrt{3}(5c^2 - c - 4)}{(5c^2 - 6c + 6)^{1/2}(15c^2 + 12c + 8)^{1/2}}$$

where $c = B_{33}/B_{11}$. These functions are plotted in Fig. 3.

The diffraction data extends only to a given value of $\sin \theta/\lambda$ and therefore the integration should strictly be carried out to this limit. Since this omits the region in which the differences between the functions are increasing, it has the effect of enhancing the projections

Table 7. *Values of projection coefficients for* CdSe

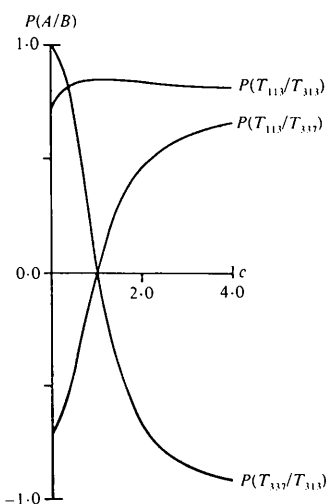|		Integration to infinity	Integration to $\sin \theta/\lambda$ cutoff
$P(T_{113}/T_{337})$	Cd	0·141	0·779
	Se	−0·165	−0·635
$P(T_{113}/T_{313})$	Cd	0·844	0·996
	Se	0·844	0·998
$P(T_{337}/T_{313})$	Cd	−0·213	−0·765
	Se	0·253	0·674

Fig. 3. Non-zero projections between first and third-order anharmonic temperature-factor components in $3m$ site symmetry. Infinite integration limits. $c = B_{33}/B_{11}$.

(see Table 7). It is thus seen that $P(T_{113}/T_{313})$ is very close to unity; hence either of the functions can represent the other.

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