Acta Cryst. (1984). B**40**, 521-530

Anharmonic Thermal Vibrations and the Position Parameter in Wurtzite Structures. I. Cadmium Sulphide

By Andrew W. Stevenson,* Miroslav Milanko and Zwi Barnea

School of Physics, University of Melbourne, Parkville, Victoria 3052, *Australia*

(*Received* 30 *June* 1983; *accepted* 12 *March* 1984)

Abstract

Intensity measurements have been carried out with an extended-face single crystal of hexagonal CdS using Mo $K\alpha$ X-radiation at room temperature. The Bragg intensities were analysed by using the one-particle potential (OPP) within the framework of Dawson's [*Proc. R. Soc. London Ser. A* (1967), **298**, 255-263] generalized structure-factor formulation with allowance for cubic anharmonic effects. The position parameter in the wurtzite structure which is not determined by symmetry is evaluated, and its dependence on the temperature-factor model used is demonstrated. The most reliable determination of this position parameter, with allowance for cubic anharmonicity, is 0·37715 (8). The observation of significant differences between the intensities of non-symmetry-related reflections occurring at the same Bragg angle demonstrates the possibility of measuring the anharmonicity of thermal vibrations.

Introduction

The effects of anharmonic thermal vibrations on the intensities of Bragg reflections have been investigated using neutrons, X-rays and γ-rays in a number of structures (see, for example, Willis & Pryor, 1975; Tanaka & Marumo, 1983). The studies of anharmonicity in hexagonal structures include those of zinc (Albanese, Deriu & Ghezzi, 1976; Merisalo & Larsen, 1977, 1979; Merisalo, Järvinen & Kurittu, 1978; Kurki-Suonio, Merisalo & Peltonen, 1979; Vahvaselkä, 1980), cadmium (Merisalo, Peljo & Soininen, 1978; Field, 1982), beryllium (Larsen, Lehmann & Merisalo, 1980) and Li_3N (Zucker & Schulz, 1982). Nizzoli (1976) has discussed anharmonicity in h.c.p. crystals generally, as have Mair & Barnea (1975) for crystals with the wurtzite structure. Whiteley, Moss & Barnea (1977, 1978) have also discussed anharmonicity in wurtzite structures and reported some of the consequences of this effect for CdSe.

In this paper the interpretation of anharmonic effects is based on the use of the one-particle potential (OPP) within the framework of Dawson's (1967) generalized structure-factor formulation. The constraints imposed on the cubic anharmonic parameters, which appear in the temperature-factor expression, are those discussed by Fakineos, Stevenson & Barnea (1982). The choice of these constraints is particularly important if an accurate determination of the wurtzite position parameter is desired.

The consequences of anharmonic thermal vibrations manifest themselves in a variety of ways, the most readily observable being the intensity differences which occur between non-symmetry-related reflections with the same Bragg angle (Whiteley, Moss & Barnea, 1978 - hereafter referred to as WMB), due to one of the third-order antisymmetric temperature-factor terms. Several of these intensity differences, in excess of 10%, are reported in the present work.

1. Theory

Cadmium sulphide is a semiconducting material which exhibits pyroelectricity. It possesses the non-centrosymmetric hexagonal wurtzite structure, for which the atomic positions are

$$\text{Cd}: (\tfrac{1}{3}, \tfrac{2}{3}, 0), (\tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{2})$$

$$\text{S}: (\tfrac{1}{3}, \tfrac{2}{3}, u), (\tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{2}+u),$$

where u (the wurtzite position parameter) is the ratio of the distance between adjacent Cd and S atoms along the c axis and the lattice parameter c. This position parameter is not determined by symmetry and is one of the parameters refined in this analysis.

The generalized structure factor $F(\mathbf{S})$ can be expressed [following Dawson (1967)] as

$$F(\mathbf{S}) = \sum_j f_j(\mathbf{S})\, T_j(\mathbf{S}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}_j), \qquad (1)$$

where $\mathbf{S}$ is the scattering vector and $f_j(\mathbf{S})$ and $T_j(\mathbf{S})$ are the atomic scattering factor and temperature factor of the jth atom in the unit cell, with position vector $\mathbf{r}_j$, respectively. $f_j(\mathbf{S})$ and $T_j(\mathbf{S})$ represent the Fourier transforms of the at-rest atomic charge distribution $\rho_j(\mathbf{r})$ and the probability density function $t_j(\mathbf{r})$, respectively. In general, $\rho_j(\mathbf{r})$ and $t_j(\mathbf{r})$ may be non-centrosymmetric, resulting in the following complex

---

* Present address: CSIRO Division of Chemical Physics, PO Box 160, Clayton, Victoria 3168, Australia.

0108-7681/84/060521-10$01.50

expressions for $f_j(\mathbf{S})$ and $T_j(\mathbf{S})$:

$$f_j(\mathbf{S}) = f_{c,j}(\mathbf{S}) + if_{a,j}(\mathbf{S}), \qquad (2a)$$

$$T_j(\mathbf{S}) = T_{c,j}(\mathbf{S}) + iT_{a,j}(\mathbf{S}), \qquad (2b)$$

where the subscripts c and a refer to the centrosymmetric and antisymmetric components, respectively.

Moss (1977) has determined that in wurtzite structures bonding effects are small. We shall, therefore, neglect the antisymmetric terms $f_{a,j}(\mathbf{S})$ in this analysis and $f_{c,j}(\mathbf{S})$ will represent the free-atom spherical scattering factor. In the case of X-rays we need to include the real and imaginary anomalous-dispersion corrections (f'_j and f''_j, respectively) in the atomic scattering factor, and so (2a) is rewritten as

$$f_j(\mathbf{S}) = f_{c,j}(\mathbf{S}) + f'_j + if''_j. \qquad (3)$$

The substitution of (2b) and (3) in (1) will yield the familiar expression for the generalized structure factor (see Dawson, 1967).

Mair & Barnea (1975) and WMB have derived equivalent expressions for the anharmonic temperature factor for wurtzite, expanding the OPP as a power series (to third order) in the atomic displacements from appropriate positions (Mair & Wilkins, 1981) within the restrictions imposed by the local site symmetry ($3m$). Fakineos, Stevenson & Barnea (1982) have also derived an equivalent expression, using a group-theory approach. The Debye temperature for CdS has been reported as 216 K (Cline, Dunegan & Henderson, 1967) and so the classical form of the OPP temperature factor is valid (Mair & Wilkins, 1976).

In the present paper we use the form of the anharmonic temperature factor given by WMB [see equation (6) of that paper], in which ten parameters can be refined (the conventional hexagonal temperature parameters B_{11} and B_{33}, and the cubic anharmonic parameters β_{313}, β_{332} and β_{337}, for each atomic species). Any attempt to refine all these parameters results in large correlations, unreliable parameter values and large e.s.d.'s. The analysis in this paper, is, therefore, in terms of the three models described by Fakineos, Stevenson & Barnea (1982) [I: $\beta_{313} = \beta_{332} = \beta_{337} = 0$; II: $|\beta_{313}| = |\beta_{332}| = |\beta_{337}|$; III: $|\beta_{313}| = 0$, $|\beta_{337}| = 2^{1/2}|\beta_{332}|$]. Model I is harmonic, model II is that used by WMB and model III is a more realistic set of constraints, based on the use of certain physical properties which impose restrictions on the form of the OPP. The relative signs for the anharmonic parameters are given by WMB and Fakineos, Stevenson & Barnea (1982). Models II and III involve the refinement of the four conventional hexagonal temperature parameters and one anharmonic parameter (attempts to refine separate anharmonic parameters for each atomic species resulted in large correlation between these parameters).

2. Experimental

The extended-face crystal technique (*e.g.* Mair, Prager & Barnea, 1971a, b) was used to measure integrated intensities for 118 independent reflections with Mo $K\alpha$ X-radiation at 293 (2) K. The flat face of the large CdS single crystal used has been ground, etched and polished parallel to the (100) planes. The crystal was mounted on a Philips PW1100/20 computer-controlled four-circle X-ray diffractometer. An NaI(Tl) scintillation detector was employed in conjunction with pulse-height analysis, and measurements were carried out using ω–2θ scans of width 3°θ starting 1·5°θ below the peak maximum. Background was measured from stationary counts at both limits of the scan. The rectangular detector aperture was 1·5 by 2°. The Mo $K\alpha$ radiation was selected by a graphite (002) flat-crystal monochromator and then passed through an incident-beam collimator of 0·5 mm diameter.

Significant multiple-diffraction effects were avoided by rotating the crystal about the scattering vector of a given reflection, to a position about which the Bragg intensities showed no irregularities (Prager, 1971; Post, 1976). All measurements were carried out in two aspects (generally asymmetric) and averaged, a procedure which provides an experimental correction for absorption (Mair, Prager & Barnea, 1971a). The intensities were measured in positions no more than 1·5° in azimuth from the symmetric aspects.

The internal consistency of the measured integrated Bragg intensities was judged by the agreement between symmetrically equivalent reflections, each having been measured several times. Fig. 1 shows a

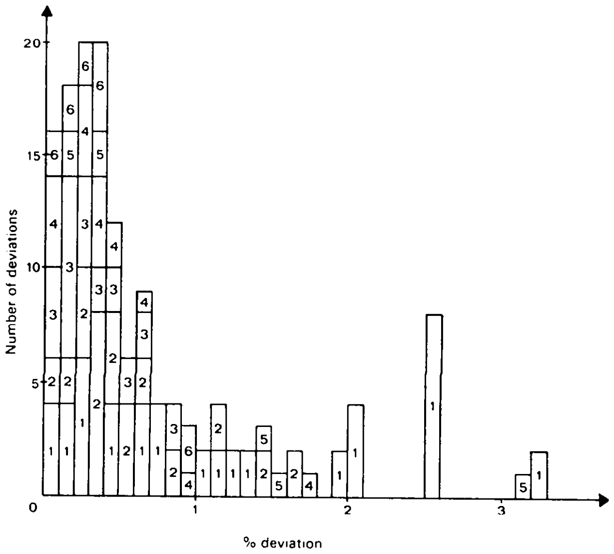

Fig. 1. Histogram of the % deviation in intensity of a reflection from the mean value of the set of symmetrically equivalent reflections measured, for CdS. The measurements have been subdivided into six equal groups according to the magnitudes of the structure factors, the smallest being in group 1. The ratio of the largest and smallest structure factors is approximately ten.

histogram of the % deviation in intensity of a reflection from the mean value of the set of equivalent reflections measured. The average deviation, for all the CdS measurements, was 0·7%. The implications of Fig. 1 with regard to the accuracy of extended-face crystal measurements of structure factors will be discussed elsewhere. We note that almost 80% of the data presented in Fig. 1 have deviations of less than 1% and that the data with deviations above 1% consist primarily of those reflections for which counting statistics are important.

3. Analysis

The data set was analysed by a least-squares refinement program, which uses the IMSL (1975) library subroutine *ZXSSQ* to minimize the difference between observed and calculated structure factors. The quantity minimized is

$$S=\sum_i w_i(|F_{oi}|-|F_{ci}|)^2, \qquad (4)$$

where w_i is the weight given to $(|F_{oi}|-|F_{ci}|)$, $|F_{oi}|$ and $|F_{ci}|$ being the observed and calculated absolute values of the structure factor corresponding to the *i*th observation, respectively.

The following parameters can be refined: B_{11}(Cd), B_{33}(Cd), B_{11}(S), B_{33}(S), u, the scale factor, the extinction parameter r^*, two anharmonic parameters (one for each atomic species) and the four anomalous-dispersion corrections. The two anharmonic parameters can be specified in accordance with the models mentioned in § 1. However, attempts to refine the two anharmonic parameters produced large correlations between them. Consequently, no distinction is made in this analysis between the magnitudes of these two parameters (with one exception in § 4), *i.e.* only one anharmonic parameter was refined.

The observed intensities were corrected for anisotropic one-phonon thermal diffuse scattering (TDS) effects (Kurittu & Merisalo, 1977; Merisalo & Kurittu, 1978), before averaging symmetrically equivalent reflections. The elastic constants of Berlincourt, Jaffe & Shiozawa (1963) were used. The largest anisotropies in the TDS correction factors (α) represented approximately 3%. The TDS corrections for CdS were found to be quite large (Koto & Schulz, 1979), the largest correction factor applied being 29%. As expected, the introduction of the TDS corrections resulted in an increase in the conventional hexagonal temperature parameters, which amounted in our case to about 6%.

The Bragg intensities were then corrected for Lorentz and polarization effects, the latter including the effect of the monochromator (Azaroff, 1955), which was assumed to follow kinematic theory (see also Freeman, Mair & Barnea, 1977). The square roots of the corrected intensities were then divided by the refined scale factor to yield the $|F_{oi}|$.

The kinematic structure factors were calculated using the relativistic Hartree–Fock spherical atomic scattering factors of Doyle & Turner (1968) and the anomalous-dispersion corrections of Cromer & Liberman (1970) (in general, the latter were not refined). The lattice parameters used were $a=4{\cdot}136$ and $c=6{\cdot}713$ Å (National Bureau of Standards, 1955). The secondary-extinction factors, y, were calculated using Zachariasen's (1967) theory. The effective domain radius r^* was refined. The possibility of using other models for extinction was not pursued since the largest extinction effects caused only a 3% reduction of the kinematic intensity ($y\gtrsim 0{\cdot}97$). The products of the calculated kinematic structure factors and the square roots of the extinction factors yielded the $|F_{ci}|$. Refinements of the data with the most extinguished reflections removed showed virtually no change in the thermal parameters or u and led us to believe that extinction did not affect the results.

Correlation matrices were calculated in order to assess the interactions of the refined parameters (Geller, 1961; Rollett, 1965). Hamilton's R factor (R_H), the goodness-of-fit parameter (GFIT) and the e.s.d. for refined parameter values were also calculated.

The weights w_i appearing in (4) were

$$w_i=[\sigma^2(|F_{oi}|)+\sigma^2(|F_{ci}|)]^{-1},$$

where $\sigma^2(X)$ is the variance for quantity X. The calculation of $\sigma^2(|F_{oi}|)$ involves the inclusion of a variety of error sources such as counting statistics, population statistics and the estimated error in the TDS correction. $\sigma^2(|F_{ci}|)$ is due to the uncertainty in the extinction correction. The correctness of the weighting scheme was checked by evaluating GFIT in groups of increasing $|S|$ (Rollett, 1965). None of the results were found to be crucially dependent on the weighting.

4. The refined value of the *u* parameter

The nearest-neighbour environment of each atom in the ideal wurtzite structure is tetrahedral with $u=\frac{3}{8}$ and $c/a=(\frac{8}{3})^{1/2}$. If the structure is not ideal, nearest-neighbour atoms will form distorted tetrahedra. The change in c/a (from the ideal value) will be accompanied by a change in u. Keffer & Portis (1957) (see also Jeffrey, Parry & Mozzi, 1956) have derived expressions for u, on the assumption that the bond-stretching constants are much larger than the bond-bending constants:

$$u=\tfrac{1}{4}+\tfrac{1}{3}(a/c)^2, \qquad (5a)$$

and *vice versa*:

$$u=\tfrac{1}{2}-(\tfrac{1}{24})^{1/2}a/c. \qquad (5b)$$

Both ($5a$) and ($5b$) tend to underestimate the existing observed values of u which, with only one exception to our knowledge (ZnO; Kihara & Donnay, 1981), are based on harmonic refinements of the data. The value of u given by ($5a$) is always closer to the observed value and the difference between the two has been attributed to anharmonicity by Mair & Barnea (1975).

All the observed values of u known to us are for compounds with $c/a < (\frac{8}{3})^{1/2}$, with the exception of AgI [Burley (1963); $u = 0{\cdot}3747\,(15)$]. If $c/a = (\frac{8}{3})^{1/2}$ both ($5a$) and ($5b$) give $u = \frac{3}{8}$, and it can be argued that in an ideal wurtzite anharmonicity will not affect the u parameter because its effect along the c-axis bond is exactly compensated by the combined effect it has along the other three tetrahedral bonds about a given atom. This is demonstrated in the case of AgI, which is very close to being an ideal wurtzite and for which ($5a$) gives the observed value of u. When $c/a > (\frac{8}{3})^{1/2}$ the value of u given by ($5b$) is greater than that given by ($5a$) and we suggest that both these values will be greater than any observed values derived from harmonic treatments of the data for such compounds, with the difference still attributable to anharmonicity. The sign and magnitude of the difference between the predicted and observed (harmonic) values of u depend on the forces binding the atoms in the solid, with the relative strength of the Coulomb interaction and the short-range interactions being an important consideration (Mair & Barnea, 1975).

O'Keeffe & Hyde (1978) have pointed out that compounds which exist in both the wurtzite and zinc blende modifications have, for the wurtzite phase, $c/a \gtrsim (\frac{8}{3})^{1/2}$. For compounds which have only the wurtzite phase, $c/a < (\frac{8}{3})^{1/2}$ (see also Lawaetz, 1972), in accord with the lack of polytypism in CdS and CdSe for example.

Stevenson (1983) has reviewed the findings of other authors with regard to the values of u and c/a in wurtzite structures and has discussed the wide range of lattice-parameter values (and in particular c/a values) which exist in the literature for CdS, giving several justifications for the choice made here.

Ibers (1959) (see also Busing & Levy, 1964) pointed out that the assumption of harmonic thermal vibrations could lead to erroneous atomic position parameters. If the atoms within a structure are vibrating in harmonic potential wells the positions determined by the potential minimum and the time-averaged positions would coincide. When cubic terms in the displacements are introduced this may no longer be the case because the potential is asymmetric. Mair & Wilkins (1981) have recently given theoretical consideration to atomic position parameters as determined by X-ray or neutron diffraction. They discuss the difference between atomic positions determined from the minimum of the potential and the time-averaged or thermodynamic equilibrium positions. The two sets of atomic positions differ only if they are not completely determined by symmetry. This, necessarily, restricts the atomic sites for which such a difference can occur to those of a set of ten point symmetries, of which $3m$ (for wurtzite) is a member. The closely related zinc blende structure, for example, has a point symmetry of $\bar{4}3m$, which is not a member of this set.

In developing the OPP it is possible to expand about either set of atomic positions. If the expansion is made about the time-averaged positions a first-order term does occur, whereas there is no first-order term for an expansion about the positions of the potential minimum (Mair & Wilkins, 1981). Mair & Wilkins have also shown that it is not possible to refine simultaneously both for the effect of the coefficient of the first-order term in the temperature factor and for the equilibrium position. The anharmonic refinements (models II and III) carried out in this paper will thus yield atomic positions defining the minimum of the potential. (WMB expanded the OPP about the time-averaged positions, a choice partly dictated by the values of position and thermal parameters available. They found, by projection analysis, that the first-order term in their temperature factor could, in fact, be neglected.) Mair & Wilkins (1981) have indicated that a conventional harmonic refinement (model I) will yield atomic positions which closely approximate the time-averaged positions. The size of the difference between the u parameters obtained from model I and models II and III will depend on the extent of the anharmonicity, the anharmonic model used and the deviation of the structure from that of ideal wurtzite.

Fakineos, Stevenson & Barnea (1982) have given the following expression for the expectation value of z, the component along the c axis of an atom's displacement from the corresponding position defined by the potential minimum:

$$\langle z\rangle = -B_{33}[(2B_{11}+3B_{33})\beta_{313} - 3(B_{11}-B_{33})\beta_{337}]/64\pi^4 k_B T, \qquad (6)$$

where k_B is Boltzmann's constant and T is the temperature. Equation (6) is valid for the four atoms in the unit cell and is the same for atoms of the same species. If the constraints between the anharmonic parameters of model II are substituted in (6) we get

$$\langle z\rangle = \pm 5B_{11}B_{33}|\beta_{332}|/64\pi^4 k_B T, \qquad (7)$$

where the '+' is for Cd atoms and the '−' for S atoms.*

---

* The absolute signs of the anharmonic parameters for CdS can be ascertained from refinements using model II or from the predictions of model III.

From (7) we obtain the following approximation:

$$u_{\mathrm{II}} - u_{\mathrm{I}} = 5[B_{11}(\mathrm{Cd})B_{33}(\mathrm{Cd}) + B_{11}(\mathrm{S})B_{33}(\mathrm{S})]|\beta_{332}|/64\pi^4 k_B Tc, \quad (8)$$

where u_X refers to the value of u obtained in model X. Clearly, the right-hand-side of (8) is positive and so u_{II} is predicted to be greater than u_{I} for CdS, in contrast to the expectations of Mair & Barnea (1975). If the more realistic constraints of model III are substituted in (6), along with $B_{11} = B_{33}$, which was assumed when deriving these constraints, then $\langle z \rangle = 0$ for all atoms and $u_{\mathrm{III}} \simeq u_{\mathrm{I}}$, as discussed earlier in connection with (5*a*) and (5*b*). Any sizable differences between u_{I} and u_{III} can be attributed to a breakdown of the assumptions made when deriving the constraints ($B_{11} = B_{33}$, and that the structure is ideal wurtzite). Whether $u_{\mathrm{III}} - u_{\mathrm{I}}$ is positive or negative is determined by the nature of the deviation of the structure from the ideal. In accordance with the expectations of Mair & Barnea (1975) we would expect $u_{\mathrm{III}} - u_{\mathrm{I}}$ to be negative for CdS.

Table 1 shows the results of the different data refinements for CdS.† As mentioned previously, in our attempts to refine two anharmonic parameters, to distinguish between the atomic species, we encountered a large correlation between them. We did, however, observe that the anharmonic parameter for S was close to zero, with a considerable e.s.d. [$|\beta_{332}|_{\mathrm{Cd}} = 0{\cdot}97\,(9) \times 10^{-20}$ J Å^{-3} and $|\beta_{332}|_{\mathrm{S}} = 0{\cdot}03\,(56) \times 10^{-20}$ J Å^{-3} with the constraints of model III, *cf.* $|\beta_{332}| = 0{\cdot}88\,(6) \times 10^{-20}$ J Å^{-3} when no distinction between Cd and S is made]. This observation is similar to those made for the halide atoms in CuCl (Sakata, Hoshino & Harada, 1974) and CuBr (Harada, Suzuki & Hoshino, 1976). Consequently, a refinement was carried out with the constraints of model III, allowing $|\beta_{332}|_{\mathrm{Cd}}$ to vary and constraining $|\beta_{332}|_{\mathrm{S}}$ to be zero. This model is denoted III′ in Table 1, and the refined value of $|\beta_{332}|_{\mathrm{Cd}}$ was $0{\cdot}97\,(7) \times 10^{-20}$ J Å^{-3}.

The other refined parameter values [B_{11}(Cd), B_{33}(Cd), B_{11}(S), B_{33}(S), the scale factor and r^*] all agreed within one e.s.d. for the four models in Table 1. The refined value of the anharmonic parameter for model II was $0{\cdot}85\,(6) \times 10^{-20}$ J Å^{-3}. The largest correlation coefficients were for the interactions between B_{11}(Cd), the scale factor and r^* (Lander & Mueller, 1970) and these never exceeded 0·89. The largest correlation coefficient involving u was 0·28 for interaction with the anharmonic parameter. The ratios $R_H(\mathrm{I})/R_H(\mathrm{II})$ and $R_H(\mathrm{II})/R_H(\mathrm{III})$, where $R_H(X)$ is R_H for model X, correspond to a rejection of the appropriate hypotheses at the 0·5% significance level (Hamilton, 1965), which is '*highly significant*' (Hamilton, 1964). Thus, the results support the use of the constraints between the anharmonic parameters derived by Fakineos, Stevenson & Barnea (1982), *i.e.* model III. The ratio $R_H(\mathrm{III})/R_H(\mathrm{III'})$ corresponds to a rejection of the appropriate hypothesis at the 25% significance level, which is '*not significant*'.

Table 1. *The refined values of the* CdS *u parameter for different temperature-factor models*

Model	u	R_H(%)	GFIT
I	0·37748 (13)	1·127	1·635
II	0·37771 (8)	0·696	1·017
III	0·37715 (8)	0·665	0·969
III′	0·37725 (8)	0·658	0·959

The value of u_{I} in Table 1 is in excellent agreement with the value cited by Mair & Barnea (1975), namely 0·3775 (3). The value of u_{II} is, as predicted by (8), larger than u_{I} [$u_{\mathrm{II}} - u_{\mathrm{I}} \simeq 0{\cdot}00081$ according to (8), *cf.* 0·00023 from Table 1]. The values of u_{III} and $u_{\mathrm{III'}}$ reflect, according to (6), the breakdown of the approximations made in deriving the constraints for model III. Indeed, the CdS structure is not ideal, B_{11}(Cd) and B_{33}(Cd) differ by approximately 4% and B_{11}(S) and B_{33}(S) differ by approximately 1%; this is not serious enough to invalidate model III, but does show up as non-zero values of $u_{\mathrm{III}} - u_{\mathrm{I}}$ and $u_{\mathrm{III'}} - u_{\mathrm{I}}$, the signs of which are in accord with the expectations of Mair & Barnea (1975). Fakineos, Stevenson & Barnea (1982) have suggested a method to obviate the need to make these approximations but unfortunately it relies, in part, on the refinement of a set of *hk*0 reflections (*h*, *k* and *l* being the Miller indices of a reflection), of which there are too few for this CdS data set [the method will be demonstrated for CdSe in the following article (Stevenson & Barnea, 1984)]. The values of u according to (5*a*) and (5*b*) are 0·3765 and 0·3742, respectively, both of which still underestimate u_{III} and $u_{\mathrm{III'}}$. The value of u predicted by O'Keeffe & Hyde (1978) [their equation (8) with $p = -0{\cdot}31$] is 0·3777. The difference between u_{III} and u_{I} represents a sum of the differences between the time-averaged and potential minimum positions for adjacent Cd and S atoms along the c axis of 0·0022 Å at room temperature.

5. Consequences of anharmonic thermal vibrations

WMB have discussed the appearance of certain harmonically forbidden reflections due to the anharmonicity of thermal vibrations (*i.e.* due to one third-order antisymmetric temperature-factor term in particular). They found that the reliable observation of these reflections in CdSe at room temperature was precluded by the lack of intensity. We have similar experiences with CdS at room temperature; here the lack of intensity was accompanied by a large

---

† Inconsequential differences between the results quoted for CdS by Fakineos, Stevenson & Barnea (1982) and in this paper are due to the symmetrically equivalent reflections having been treated separately in the earlier analysis.

Table 2. *The observed and calculated AIR* (%) *for* $70l/53l$ *pairs of reflections in* CdS, *where* l *is the third Miller index*

The calculated values come from a least-squares refinement of the AIR (*A*) and from one of the full refinements discussed in §§ 4 and 6 (*B*).

l	Observed	Calculated (*A*)	Calculated (*B*)
0	−14·6 (1·4)	−11·4	−9·4
1	2·0 (1·4)	4·5	3·7
$\bar{1}$	3·3 (1·4)	4·6	3·8
2	−9·7 (2·2)	−12·2	−10·1
$\bar{2}$	−13·3 (2·2)	−12·1	−10·0
3	4·2 (1·4)	3·8	3·1
$\bar{3}$	4·0 (1·4)	3·8	3·2
5	3·6 (1·4)	3·8	3·1
$\bar{5}$	5·4 (1·4)	3·8	3·1
6	−9·4 (2·4)	−12·5	−10·2
$\bar{6}$	−12·5 (2·5)	−12·6	−10·3
7	5·5 (2·3)	4·4	3·7
$\bar{7}$	3·9 (2·3)	4·3	3·6
8	−10·0 (2·4)	−11·4	−9·4
$\bar{8}$	−8·7 (2·4)	−11·4	−9·4
9	5·9 (2·5)	4·7	3·9
$\bar{9}$	2·7 (2·5)	4·8	3·9
11	7·9 (2·3)	3·8	3·1
$\overline{11}$	7·3 (2·3)	3·9	3·2

contribution of TDS from optic modes (Maradudin, Montroll & Weiss, 1963). However, such harmonically forbidden reflections have been reliably observed with X-rays at room temperature for h.c.p. zinc (Merisalo, Järvinen & Kurittu, 1978) and h.c.p. cadmium (Merisalo, Peljo & Soininen, 1978).

WMB also reported on the intensity differences which occur, as a result of the presence of one of the third-order temperature-factor terms, for non-symmetry-related reflections occurring at the same Bragg angle. Table 2 shows our experimental values of 19 anharmonic intensity ratios (AIR) (WMB), together with the calculated values obtained from a least-squares refinement in which the weighted sum of squared differences between observed and calculated AIR was minimized (*A*). The minimization was carried out by varying only the anharmonic parameter, whose refined value was $1{\cdot}07\,(3)\times10^{-20}$ J Å^{-3} (model II). The values of the four conventional hexagonal temperature parameters and u were taken from the corresponding refinement (model II) of the full data set. The e.s.d.'s for the observed AIR in Table 2 are based on population and counting statistics and their squared reciprocals are the weights used in the refinement program. The values of GFIT and R_H were 1·107 and 0·263, respectively; the value of the latter was large because we were refining ratios. TDS and extinction corrections proved to be unnecessary, owing to the insensitivity of the AIR to such effects, in this case. The calculated values of the AIR from the full refinement discussed in §§ 4 and 6 (model III) are also given in Table 2 (*B*).

Since the AIR are zero in the harmonic approximation (model I), the results in Table 2 represent irrefutable evidence of anharmonic thermal vibration of the Cd and/or S atoms at room temperature. Refinement of the AIR in accordance with model III produced virtually no changes. This was expected, since the intensity differences are due to the temperature-factor term containing β_{332}. Thus the use of model II for the refinement of CdSe AIR is not without some justification (WMB).

It is also interesting that, for ideal wurtzite ($u=\frac{3}{8}$), the Bijvoet ratios for reflections with $l=4n$ (where n is an integer) are zero in the harmonic approximation (remembering that bonding effects can be neglected here). The observation of non-zero Bijvoet ratios in this family of reflections is then evidence of the non-ideal nature of the structure and/or the presence of anharmonicity.

6. Results

Table 3 shows the observed and calculated (model III) structure factors for CdS after least-squares refinement, together with the $E_i=100\sigma(|F_{oi}|-|F_{ci}|)/|F_{oi}|$ and the secondary extinction and TDS correction factors. The reflections have Bragg angles which range between 21 and 65° with Mo $K\alpha$ radiation. Table 4 contains the final parameter values corresponding to Table 3. Table 5 shows other experimental determinations of the four conventional hexagonal temperature parameters. The temperature parameters of Fakineos and Castles are artificially reduced, perhaps by 5%, since no TDS corrections were made. Allowing for this their values are in reasonable agreement with those in Table 4, with the exception of Fakineos's B_{33}(S) value. The values of Bocchi & Ghezzi (1975) are all appreciably and unaccountably larger. The '*overall*' temperature-parameter value for CdS ($\bar{B}_{\rm CdS}$; the weighted average of the four conventional hexagonal temperature parameters) is 1·343 (3) Å^2. Hewat's (1970) lattice-dynamical treatment yields a value of 1·1 Å^2 and the approximation given by Stevenson & Harada (1983) [their equation (26)] yields 1·29 Å^2 [the value given by Stevenson & Harada (1983) contains an error; see Stevenson & Harada (1984)]. The value of $\bar{B}_{\rm CdS}$ calculated using equations (3.1) of Hewat (1972) is 1·01 Å^2. The elastic constants used were those of Berlincourt, Jaffe & Shiozawa (1963) and the average value of ω_0^{-2} (where ω_0 is the zone-centre frequency determined by Raman scattering) was calculated using the data of Tell, Damen & Porto (1966) and Brafman & Mitra (1968).

The e.s.d.'s for the conventional temperature-parameter values in Table 4 show that the parameter values for S are more difficult to determine than those for Cd. This is due to the appreciable difference between the scattering powers of the two atomic species. The fact that the heavier of the two atomic species has the larger temperature parameters is not surprising given that we are operating above the

Table 3. *The observed and calculated (model* III*) structure factors, the* $E_i = 100\sigma(|F_{oi}| - |F_{ci}|)/|F_{oi}|$, *and the extinction and TDS correction factors for* CdS

h	k	l	$\|F_{oi}\|$	$\|F_{ci}\|$	E_i	y	α
2	2	2	34·31	34·26	0·79	0·970	0·044
2	2	$\bar{2}$	35·12	34·89	0·65	0·969	0·044
3	1	1	22·97	22·97	0·60	0·986	0·044
3	1	$\bar{1}$	22·43	22·45	0·59	0·987	0·044
2	1	$\bar{5}$	33·68	33·95	0·64	0·971	0·047
3	1	3	31·35	31·34	0·63	0·977	0·054
3	1	$\bar{3}$	31·05	31·01	0·63	0·977	0·054
4	0	1	19·85	19·86	0·55	0·991	0·058
4	0	$\bar{1}$	19·29	19·37	0·55	0·991	0·058
2	2	4	18·83	18·68	0·53	0·992	0·058
2	2	$\bar{4}$	18·90	18·74	0·53	0·992	0·058
4	0	3	27·42	27·54	0·71	0·983	0·068
4	0	$\bar{3}$	26·97	27·22	0·61	0·984	0·068
3	0	6	25·22	25·36	0·61	0·986	0·070
3	0	$\bar{6}$	24·63	24·77	0·61	0·987	0·069
3	2	1	17·36	17·30	0·73	0·993	0·071
3	2	$\bar{1}$	16·83	16·84	0·53	0·994	0·071
3	1	5	25·66	25·76	0·59	0·986	0·074
3	1	$\bar{5}$	25·91	26·03	0·59	0·985	0·074
3	2	2	12·53	12·48	0·65	0·997	0·076
3	2	$\bar{2}$	12·80	12·76	0·53	0·996	0·074
4	1	0	30·81	30·33	0·62	0·980	0·079
3	2	3	24·45	24·25	1·37	0·988	0·081
3	2	$\bar{3}$	24·09	23·96	0·85	0·988	0·082
4	1	2	22·89	22·92	0·55	0·989	0·085
4	1	$\bar{2}$	23·46	23·45	0·58	0·988	0·085
3	2	5	20·32	20·26	0·56	0·992	0·102
3	2	$\bar{5}$	20·51	20·48	0·55	0·991	0·103
3	1	7	12·57	12·56	0·65	0·997	0·106
3	1	$\bar{7}$	13·03	12·96	0·65	0·997	0·106
5	0	3	18·92	19·01	0·57	0·993	0·111
5	0	$\bar{3}$	18·72	18·76	0·53	0·993	0·110
3	3	2	18·23	18·07	0·53	0·993	0·114
3	3	$\bar{2}$	18·70	18·52	0·53	0·993	0·114
4	1	6	15·70	15·74	0·56	0·995	0·127
4	1	$\bar{6}$	15·31	15·32	0·53	0·995	0·127
3	2	7	10·11	10·06	0·65	0·998	0·134
3	2	$\bar{7}$	10·40	10·39	0·65	0·998	0·134
5	1	3	15·23	15·28	0·53	0·995	0·140
5	1	$\bar{3}$	15·07	15·07	0·55	0·995	0·140
4	2	5	14·36	14·35	0·65	0·996	0·146
4	2	$\bar{5}$	14·50	14·52	0·65	0·996	0·146
6	0	0	16·88	17·02	0·53	0·994	0·153
3	3	6	12·54	12·61	0·65	0·997	0·154
3	3	$\bar{6}$	12·21	12·26	0·65	0·997	0·154
4	3	1	8·58	8·65	0·67	0·999	0·159
4	3	$\bar{1}$	8·34	8·38	0·67	0·999	0·159
5	1	5	12·91	12·95	0·93	0·997	0·160
5	1	$\bar{5}$	13·07	13·11	0·79	0·997	0·160
4	2	6	6·16	6·13	0·89	0·999	0·160
4	2	$\bar{6}$	5·97	5·96	0·67	0·999	0·159
3	2	9	6·73	6·81	0·67	0·999	0·175
3	2	$\bar{9}$	6·53	6·60	0·67	0·999	0·174
5	1	7	6·58	6·59	0·78	0·999	0·189
5	1	$\bar{7}$	6·79	6·81	0·67	0·999	0·189
3	3	8	11·96	12·01	0·83	0·997	0·189
3	3	$\bar{8}$	12·09	11·98	1·11	0·997	0·189
6	1	3	9·78	9·74	0·65	0·998	0·193
6	1	$\bar{3}$	9·63	9·59	0·65	0·998	0·194
5	3	0	5·45	5·40	0·89	0·999	0·207
7	0	0	5·07	5·15	1·03	0·999	0·207
4	4	2	8·38	8·40	0·67	0·999	0·207
4	4	$\bar{2}$	8·59	8·63	0·75	0·998	0·207
5	2	6	8·19	8·19	0·67	0·999	0·207
5	2	$\bar{6}$	7·92	7·95	0·67	0·999	0·207
5	3	1	5·65	5·61	0·67	0·999	0·207
5	3	$\bar{1}$	5·35	5·43	1·21	0·999	0·208
7	0	1	5·71	5·72	0·67	0·999	0·209
7	0	$\bar{1}$	5·44	5·54	1·32	0·999	0·208
4	1	10	8·37	8·33	0·67	0·999	0·204
4	1	$\overline{10}$	8·50	8·55	0·67	0·999	0·205
6	1	5	8·30	8·31	0·67	0·999	0·211
6	1	$\bar{5}$	8·40	8·41	0·98	0·999	0·211
5	3	2	4·13	4·12	1·45	1·000	0·211
5	3	$\bar{2}$	4·26	4·23	1·94	1·000	0·211
7	0	2	3·94	3·91	1·36	1·000	0·212
7	0	$\bar{2}$	3·99	4·02	1·55	1·000	0·211
5	3	3	7·86	7·89	0·67	0·999	0·215
5	3	$\bar{3}$	7·73	7·78	0·67	0·999	0·217
7	0	3	8·02	8·02	0·67	0·999	0·217
7	0	$\bar{3}$	7·89	7·90	0·67	0·999	0·217
6	2	3	7·18	7·20	0·68	0·999	0·227
6	2	$\bar{3}$	7·12	7·09	0·68	0·999	0·227
5	3	5	6·78	6·75	0·68	0·999	0·231
5	3	$\bar{5}$	6·83	6·84	1·26	0·999	0·232
7	0	5	6·90	6·86	0·68	0·999	0·232
7	0	$\bar{5}$	7·02	6·94	1·55	0·999	0·232
6	1	7	4·24	4·26	0·85	1·000	0·234
6	1	$\bar{7}$	4·38	4·42	0·85	1·000	0·234
5	3	6	2·94	2·92	0·87	1·000	0·241
5	3	$\bar{6}$	2·88	2·83	0·87	1·000	0·242
7	0	6	2·80	2·77	0·87	1·000	0·241
7	0	$\bar{6}$	2·71	2·69	0·89	1·000	0·241
4	3	9	3·81	3·60	1·60	1·000	0·243
4	3	$\bar{9}$	3·54	3·49	1·61	1·000	0·243
5	4	1	3·75	3·72	1·55	1·000	0·246
5	4	$\bar{1}$	3·59	3·59	0·85	1·000	0·246
5	3	7	3·44	3·47	0·86	1·000	0·251
5	3	$\bar{7}$	3·58	3·60	0·86	1·000	0·252
7	0	7	3·53	3·54	0·86	1·000	0·251
7	0	$\bar{7}$	3·65	3·67	0·86	1·000	0·251
8	0	0	3·29	3·30	0·86	1·000	0·254
5	3	8	2·82	2·81	1·03	1·000	0·262
5	3	$\bar{8}$	2·77	2·81	0·87	1·000	0·262
7	0	8	2·69	2·69	0·87	1·000	0·261
7	0	$\bar{8}$	2·66	2·68	0·87	1·000	0·261
5	3	9	2·36	2·34	0·90	1·000	0·271
5	3	$\bar{9}$	2·25	2·26	0·90	1·000	0·271
7	0	9	2·43	2·39	0·87	1·000	0·270
7	0	$\bar{9}$	2·29	2·30	0·93	1·000	0·270
5	5	2	3·30	3·28	1·29	1·000	0·279
5	5	$\bar{2}$	3·41	3·39	0·95	1·000	0 .79
6	4	5	2·67	2·67	0·87	1·000	0·289
6	4	$\bar{5}$	2·69	2·71	0·87	1·000	0·284
5	3	11	2·50	2·52	0·87	1·000	0·282
5	3	$\overline{11}$	2·48	2·47	0·87	1·000	0·283
7	0	11	2·60	2·56	0·87	1·000	0·282
7	0	$\overline{11}$	2·57	2·51	1.05	1.000	0.282

Table 4. *The refined parameter values for* CdS, *using model* III

B_{11}(Cd)	1·376 (3) Å^2
B_{33}(Cd)	1·430 (5) Å^2
B_{11}(S)	1·136 (7) Å^2
B_{33}(S)	1·126 (20) Å^2
u	0·37715 (8)
Scale	8·20 (2) × 10
r^*	5·9 (17) × 10^2 Å
$\|\beta_{332}\|$	0·88 (6) × 10^{-20} J Å^{-3}
R_H	0·665%
GFIT	0·969

Table 5. *Other experimental values of the conventional hexagonal temperature parameters* (Å^2) *for* CdS

	Bocchi & Ghezzi (1975)	A. Fakineos (private communication)	J. Castles (private communication)
B_{11}(Cd)	1·89 (3)	1·22	1·24
B_{33}(Cd)	2·25 (3)	1·46	1·28
B_{11}(S)	1·29 (6)	1·05	0·99
B_{33}(S)	1·53 (6)	0·70	1·01

Debye temperature (Huiszoon & Groenewegen, 1972) and that the unit cell is reasonably large (Scheringer, 1973).

The value of the X-ray Debye temperature for CdS can be determined from the values of the four conventional hexagonal temperature parameters in Table 4, by using the familiar expression relating the temperature parameter and the Debye temperature for cubic crystals consisting of one kind of atom only (see, for example, Abrahams & Bernstein, 1969). The value thus obtained is 187 K, *cf.* 216 K (Cline, Dunegan & Henderson, 1967) and 223 K (Singh & Varshni, 1982). These two theoretical values of the Debye temperature, calculated from elastic constants, do not allow for dispersion. The effects of dispersion can be included by lowering the theoretical values by a factor $(2\ln 2)^{-1/2}$ (Hewat, 1972; Singh & Varshni, 1982), to yield 183 and 189 K, in excellent agreement with the value obtained in the present case. This agreement may, however, be somewhat fortuitous because of the optic-mode component in the refined values of the conventional hexagonal temperature parameters. It is interesting to note that the temperature parameters of Bocchi & Ghezzi (1975) yield a Debye temperature of 157 K, in good accord with their own determinations and significantly lower than the theoretical values quoted above.

The value of $|\beta_{332}|$ in Table 4 is consistent with that obtained from the corresponding refinement of AIR [1·06 (3) × 10^{-20} J Å^{-3}], as discussed in § 5. This value can also be compared with the value of $|\beta_{332}|$ for CdSe at room temperature (model III) which is 0·81 (5) × 10^{-20} J Å^{-3} (Stevenson & Barnea, 1984). The refined value of r^* in Table 4 would be considered small by most standards.

Fig. 2(*a*) [3(*a*)] demonstrates the effect of anharmonic thermal vibrations on the probability density function in the (001)[(110)] plane for a Cd atom. Fig. 2(*b*) [3(*b*)] gives the atomic arrangement in this plane. The contours of equal probability are circular in the harmonic approximation for the basal plane [Fig. 2(*a*)], and are slightly elliptical in Fig. 3(*a*) because of the anisotropy of the conventional hexagonal temperature parameters [B_{11}(Cd) ≠ B_{33}(Cd)]. Figs. 2(*b*) and 3(*b*) can be used to explain why the Cd atom vibrates preferentially in certain directions (where there are 'holes' in the atomic arrangement) and less in others (where atoms are in close proximity).

Attempts to refine the anomalous-dispersion corrections in conjunction with the other parameters proved to be unsuccessful owing to large correlations,

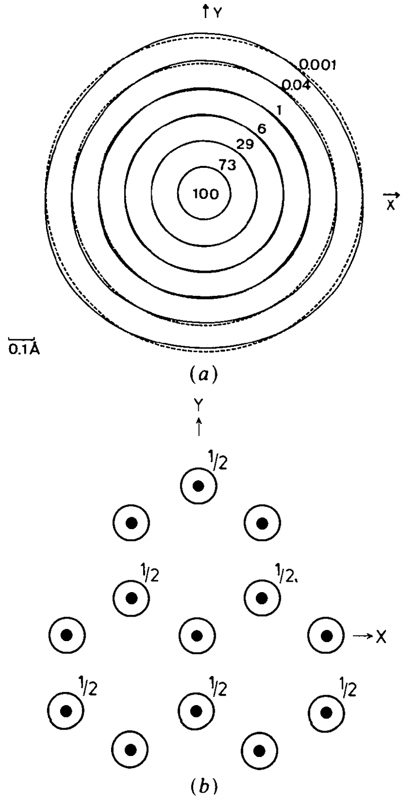

Fig. 2. (*a*) The probability density function in the (001) plane for a Cd atom at 293 K. The solid lines are anharmonic contours and the broken lines are harmonic contours (scaled to 100 units at the centre) describing the probability density function produced by thermal motion. The harmonic contours are isotropic because B_{11}(Cd) = B_{22}(Cd). (*b*) The atomic arrangement in the (001) plane. The small solid circles represent Cd atoms. The larger open circles represent S atoms displaced out of the page (along the *c* axis) by *u* relative to the Cd atoms below them. Those pairs of atoms labelled '½' are displaced a further *c*/2 out of the page. The central Cd atom is the one in question.

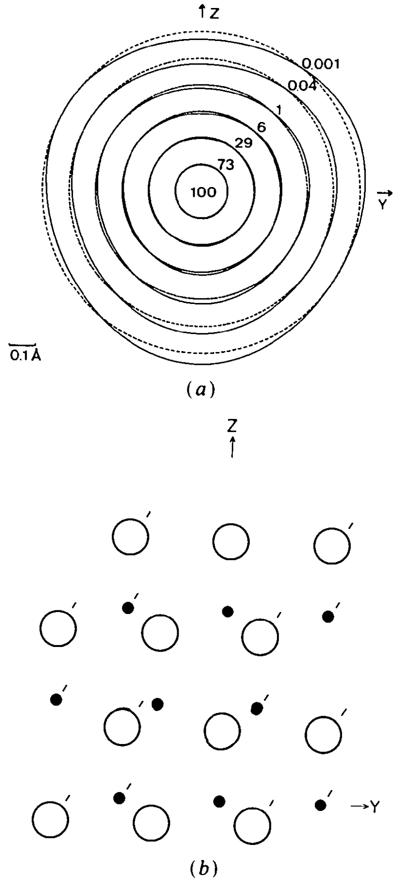

Fig. 3. (*a*) The probability density function in the (110) plane for a Cd atom at 293 K. The harmonic contours are anisotropic because B_{11}(Cd) ≠ B_{33}(Cd). (*b*) The atomic arrangement in the (110) plane. The 'primed' atoms indicate that there is one atom of that species $6^{1/2}c/8$ above the plane of the page and one $6^{1/2}c/8$ below. The Cd atom which is in the plane of the page in the lower (or upper) row is the one in question.

especially between the real dispersion corrections and the conventional hexagonal temperature parameters. Similar experiences have been reported by other authors, *e.g.* Cromer, Larson & Roof (1964) for $UMoC_2$. Attempts were also made to refine the dispersion corrections from observed Bijvoet ratios (Zachariasen, 1965; Freeman, Mair & Barnea, 1977). Large correlations precluded the simultaneous refinement of all four dispersion corrections, but the corrections for either atomic species could be ascertained separately (Freeman, Mair & Barnea, 1977) and showed approximate agreement with the values of Cromer & Liberman (1970) in the case of the imaginary corrections. The refined values of the real dispersion corrections, however, showed large discrepancies with those of Cromer & Liberman (1970), highlighting the extreme sensitivity of these quantities to the quality of the data. In general, the observed and calculated Bijvoet ratios displayed good agreement. Indeed, of the 56 CdS Bijvoet ratios measured only one has the sign incorrectly determined (the largest calculated Bijvoet-ratio magnitude in Table 3 being only 7·35%).

7. Discussion

In this paper we have shown that the anharmonicity of thermal vibrations can be determined from accurate X-ray intensity measurements collected with the wurtzite CdS at room temperature. The way in which the associated cubic anharmonic parameters are related is of considerable importance, especially for the determination of the *u* parameter. Constraining all the cubic anharmonic parameters to be equal in magnitude (model II) misrepresents the OPP and leads to an erroneous value for *u*. The most reliable value of *u* obtained for CdS is 0·37715 (8), determined using model III.

In the case of a more extensive data set it is also possible to test the differences in the magnitudes* of the anharmonic parameters as predicted, for example, in model III by refining special groups of reflections [*hk*0 reflections have structure factors which are independent of both β_{313} and β_{337}; *hkl* reflections with $h+2k=3m$ and $l=2n$ (where *m* and *n* are integers) have structure factors which are independent of β_{332}]. Such refinements will be discussed by Stevenson & Barnea (1984), for CdSe.

The results described in this paper for CdS should prove instructive for future studies involving other wurtzites, of which there are several interesting examples [Lawaetz (1972) lists 20 wurtzite structures; see also, O'Keeffe & Hyde (1978)].

The observed differences between time-averaged atomic positions and those defining the minimum of the potential have been shown to be significant, and will be larger for less highly symmetric crystals (for sites with the appropriate point symmetries), at higher temperatures and in the presence of larger anharmonic effects.

The results of this work have shown that it is feasible to study the effects of anharmonic thermal vibrations with X-rays and, indeed, the neglect of anharmonicity in X-ray studies requires justification. Further work may utilize neutron techniques which are particularly well suited to temperature-dependent studies. Synchrotron radiation and the increasing intensities available from γ-ray sources will facilitate the collection of extensive sets of very accurate high-angle data, where anharmonic effects are greatest. They will also enable studies to be carried out with crystals of lower symmetry, where more anharmonic parameters are required to specify the temperature-factor models. High-temperature work may also necessitate the refinement of quartic anharmonic parameters (*e.g.* Moss, McMullan & Koetzle, 1980).

We are grateful to G. J. McIntyre for supplying us with a listing of the program used to obtain the vectors necessary for the calculation of the anisotropic TDS corrections. We also thank A. Fakineos for the initial impetus he gave this work. Two of the authors (AWS and MM) gratefully acknowledge the financial support of a Commonwealth Postgraduate Research Award and a Melbourne University Research Grant, respectively. This work was supported by the Australian Research Grants Scheme.

References

ABRAHAMS, S. C. & BERNSTEIN, J. L. (1969). *Acta Cryst.* B**25**, 1233-1236.

ALBANESE, G., DERIU, A. & GHEZZI, C. (1976). *Acta Cryst.* A**32**, 904-909.

AZAROFF, L. V. (1955). *Acta Cryst.* **8**, 701-704.

BERLINCOURT, D., JAFFE, H. & SHIOZAWA, L. R. (1963). *Phys. Rev.* **129**, 1009-1017.

BOCCHI, C. & GHEZZI, C. (1975). *J. Phys. Chem. Solids*, **36**, 421-426.

BRAFMAN, O. & MITRA, S. S. (1968). *Phys. Rev.* **171**, 931-934.

BURLEY, G. (1963). *J. Chem. Phys.* **38**, 2807-2812.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142-146.

CLINE, C. F., DUNEGAN, H. L. & HENDERSON, G. W. (1967). *J. Appl. Phys.* **38**, 1944-1948.

CROMER, D. T., LARSON, A. C. & ROOF, R. B. JR (1964). *Acta Cryst.* **17**, 272-276.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.

DAWSON, B. (1967). *Proc. R. Soc. London Ser. A*, **298**, 255-263.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390-397.

FAKINEOS, A., STEVENSON, A. W. & BARNEA, Z. (1982). *Aust. J. Phys.* **35**, 415-424.

FIELD, D. W. (1982). *Acta Cryst.* A**38**, 10-12.

FREEMAN, D. K., MAIR, S. L. & BARNEA, Z. (1977). *Acta Cryst.* A**33**, 355-359.

GELLER, S. (1961). *Acta Cryst.* **14**, 1026-1035.

---

* This phrase should be used instead of '*the degree of anisotropy*' [last paragraph on p. 421 of Fakineos, Stevenson & Barnea's (1982) paper].

Hamilton, W. C. (1964). *Statistics in Physical Science.* New York: Ronald Press.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502-510.

Harada, J., Suzuki, H. & Hoshino, S. (1976). *J. Phys. Soc. Jpn*, **41**, 1707-1715.

Hewat, A. W. (1970). PhD Thesis. Univ. of Melbourne.

Hewat, A. W. (1972). *J. Phys. C*, **5**, 1309-1316.

Huiszoon, C. & Groenewegen, P. P. M. (1972). *Acta Cryst.* **A28**, 170-172.

Ibers, J. A. (1959). *Acta Cryst.* **12**, 251-252.

IMSL (1975). Edition 5. IMSL Inc., Houston, Texas, USA.

Jeffrey, G. A., Parry, G. S. & Mozzi, R. L. (1956). *J. Chem. Phys.* **25**, 1024-1031.

Keffer, F. & Portis, A. M. (1957). *J. Chem. Phys.* **27**, 675-682.

Kihara, K. & Donnay, G. (1981). *Acta Cryst.* A37, C156.

Koto, K. & Schulz, H. (1979). *Acta Cryst.* **A35**, 971-974.

Kurittu, J. & Merisalo, M. (1977). *Report Series in Physics*, No. 132. Univ. of Helsinki.

Kurki-Suonio, K., Merisalo, M. & Peltonen, H. (1979). *Phys. Scr.* **19**, 57-63.

Lander, G. H. & Mueller, M. H. (1970). *Acta Cryst.* **B26**, 129-136.

Larsen, F. K., Lehmann, M. S. & Merisalo, M. (1980). *Acta Cryst.* **A36**, 159-163.

Lawaetz, P. (1972). *Phys. Rev. B*, **5**, 4039-4045.

Mair, S. L. & Barnea, Z. (1975). *Acta Cryst.* **A31**, 201-207.

Mair, S. L., Prager, P. R. & Barnea, Z. (1971*a*). *Nature (London) Phys. Sci.* **234**, 35.

Mair, S. L., Prager, P. R. & Barnea, Z. (1971*b*). *J. Appl. Cryst.* **4**, 169-171.

Mair, S. L. & Wilkins, S. W. (1976). *J. Phys. C*, **9**, 1145-1158.

Mair, S. L. & Wilkins, S. W. (1981). *Acta Cryst.* **A37**, 264-266.

Maradudin, A. A., Montroll, E. W. & Weiss, G. H. (1963). *Theory of Lattice Dynamics in the Harmonic Approximation.* New York: Academic Press.

Merisalo, M., Järvinen, M. & Kurittu, J. (1978). *Phys. Scr.* **17**, 23-25.

Merisalo, M. & Kurittu, J. (1978). *J. Appl. Cryst.* **11**, 179-183.

Merisalo, M. & Larsen, F. K. (1977). *Acta Cryst.* **A33**, 351-354.

Merisalo, M. & Larsen, F. K. (1979). *Acta Cryst.* **A35**, 325-327.

Merisalo, M., Peljo, E. & Soininen, J. (1978). *Phys. Lett. A*, **67**, 80-82.

Moss, B., McMullan, R. K. & Koetzle, T. F. (1980). *J. Chem. Phys.* **73**, 495-508.

Moss, G. R. (1977). PhD Thesis. Univ. of Melbourne.

National Bureau of Standards (1955). *Natl Bur. Stand. (US) Circ.* No. 539, Vol. 4, pp. 15-16.

Nizzoli, F. (1976). *J. Phys. C*, **9**, 2977-2986.

O'Keeffe, M. & Hyde, B. G. (1978). *Acta Cryst.* **B34**, 3519-3528.

Post, B. (1976). *Acta Cryst.* **A32**, 292-296.

Prager, P. R. (1971). PhD Thesis. Univ. of Melbourne.

Rollett, J. S. (1965). *Computing Methods in Crystallography.* Oxford: Pergamon Press.

Sakata, M., Hoshino, S. & Harada, J. (1974). *Acta Cryst.* **A30**, 655-661.

Scheringer, C. (1973). *Acta Cryst.* **A29**, 82-86.

Singh, D. & Varshni, Y. P. (1982). *Acta Cryst.* **A38**, 854-858.

Stevenson, A. W. (1983). PhD Thesis. Univ. of Melbourne.

Stevenson, A. W. & Barnea, Z. (1984). *Acta Cryst.* **B40**, 530-537.

Stevenson, A. W. & Harada, J. (1983). *Acta Cryst.* **A39**, 202-207.

Stevenson, A. W. & Harada, J. (1984). *Acta Cryst.* **A40**, 162.

Tanaka, K. & Marumo, F. (1983). *Acta Cryst.* **A39**, 631-641.

Tell, B., Damen, T. C. & Porto, S. P. S. (1966). *Phys. Rev.* **144**, 771-774.

Vahvaselkä, A. (1980). *Acta Cryst.* A36, 1050-1057.

Whiteley, B., Moss, G. & Barnea, Z. (1977). *Phys. Lett. A*, **60**, 429-430.

Whiteley, B., Moss, G. & Barnea, Z. (1978). *Acta Cryst.* **A34**, 130-136.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography.* Cambridge Univ. Press.

Zachariasen, W. H. (1965). *Acta Cryst.* **18**, 714-716.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558-564.

Zucker, U. H. & Schulz, H. (1982). *Acta Cryst.* **A38**, 568-576.

Acta Cryst. (1984). B40, 530-537

Anharmonic Thermal Vibrations and the Position Parameter in Wurtzite Structures.
II. Cadmium Selenide

By Andrew W. Stevenson* and Zwi Barnea

School of Physics, University of Melbourne, Parkville, Victoria 3052, Australia

(*Received* 30 *June* 1983; *accepted* 12 *March* 1984)

Abstract

A similar study to that described in the previous article [Stevenson, Milanko & Barnea (1984). *Acta Cryst.* **B40**, 521-530] for CdS is reported here for CdSe, which also possesses the hexagonal wurtzite structure. Intensity measurements have been carried out with an extended-face single crystal of CdSe using Mo $K\alpha$ X-radiation at room temperature. The analysis of the Bragg intensities reveals the presence of significant cubic anharmonic effects. The effects of anharmonicity on the wurtzite position parameter u are described. The dependence of the CdS u parameter on the temperature-factor model used in the analysis (Stevenson, Milanko & Barnea, 1984) is also demonstrated in the present case for CdSe. The most reliable determination of the CdSe position parameter, with allowance for cubic anharmonicity, is 0·37596 (4). The observation of several sizable anharmonic intensity ratios [Whiteley, Moss & Barnea (1978). *Acta Cryst.* **A34**, 130-136] demonstrates the possibility of measuring the anharmonicity of thermal

---

* Present address: CSIRO Division of Chemical Physics, PO Box 160, Clayton, Victoria 3168, Australia.

0108-7681/84/060530-08$01.50