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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

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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

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

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vibrations. The extensiveness of the CdSe data set offers the opportunity of checking the differences in the magnitudes of the cubic anharmonic parameters by refining them separately, from special groups of reflections.

Introduction

Cadmium selenide, like cadmium sulphide, is a semiconducting material which possesses the noncentrosymmetric hexagonal wurtzite structure (Zachariasen, 1926). The structure of CdSe is among the nearest to that of ideal wurtzite (Lawaetz, 1972). This material has been the subject of previous room-temperature Mo $K\alpha$ X-ray studies by Freeman, Mair & Barnea (1977) and Whiteley, Moss & Barnea (1978).

Freeman, Mair & Barnea (1977) collected integrated intensity data from two extended-face crystal specimens, one of which was used in the present study. In carrying out the least-squares refinement of their data these authors allowed the wurtzite position parameter u, the four conventional hexagonal temperature parameters [B_{11}(Cd), B_{33}(Cd), B_{11}(Se), B_{33}(Se)] and the scale factor to vary, *i.e.* they used the harmonic temperature factor [model I of Fakineos, Stevenson & Barnea (1982)]. They also paid particular attention to the CdSe Bijvoet ratios, which, because of the wavelengths of the K-absorption edges of Cd and Se (0·4641 and 0·9798 Å, respectively) relative to that of the incident beam (0·7107 Å), and the respective values of the atomic scattering factors, are typically very large. Indeed, we have observed that the Bijvoet-ratio magnitude for the 729/$72\bar{9}$ reflections exceeds 100%, in accord with theory.

Whiteley, Moss & Barnea (1977, 1978) have discussed the effects of anharmonicity on Bragg intensities in wurtzite structures, and refined a cubic anharmonic parameter from a set of seven CdSe anharmonic intensity ratios (AIR), collected with the same specimen used here. The anharmonic temperature factor used was that of model II (Fakineos, Stevenson & Barnea, 1982). Stevenson, Milanko & Barnea (1984) (the preceding article, hereafter referred to as SMB) have pointed out that, in this case, the use of model II was, to some extent, justifiable.

The present study of CdSe involves the analysis of a more extensive data set than in the previous studies. The structure-factor models used are more sophisticated and significant multiple diffraction effects have been avoided. Allowance has also been made for extinction and thermal diffuse scattering (TDS) effects.

The interpretation of anharmonic effects in the present study is based, as in SMB, on the use of the one-particle potential (OPP) within the framework of Dawson's (1967) generalized structure-factor formulation. The Debye temperature for CdSe has been reported as 181 K (Cline, Dunegan & Henderson, 1967) and so the classical form of the OPP temperature factor is valid. The temperature-factor models described by SMB for CdS will also be used here for CdSe. The effects of cubic anharmonicity on the wurtzite position parameter u for CdSe are of particular interest and will be seen to confirm the conclusions reached by SMB on the basis of the CdS analysis.

1. Experimental

The extended-face crystal technique (*e.g.* Mair, Prager & Barnea, 1971*a*, *b*) was used to measure integrated intensities with Mo $K\alpha$ X-radiation at 293 (2) K. The properties and preparation of the CdSe single crystal used in this work have been described in detail by Freeman, Mair & Barnea (1977) (specimen No. 2), the crystal face being parallel to the (110) planes. This specimen was also used by Whiteley, Moss & Barnea (1978) (hereafter referred to as WMB).

The experimental conditions under which the integrated intensities were collected are identical to those used by SMB for CdS, with one exception. It was necessary to replace the X-ray tube (and change generator settings) at one point during the data collection. The data were placed on the same relative scale by determining the appropriate factor from a set of measurements collected with both X-ray tubes. This procedure was further checked by allowing two scale factors to vary during the least-squares analysis of the data, one for each data subset. The largest difference between the refined values of these scale factors was less than $\frac{1}{3}$ of their e.s.d.'s. The data set consists of 270 independent reflections. The intensities were measured in positions no more than 2° in azimuth from the symmetric aspects (SMB).

Significant multiple diffraction peaks were avoided by carrying out azimuthal scans for each reflection, as discussed by SMB. Fig. 1(*a*) shows such an azimuthal scan for the $33\bar{4}$ reflection from $\psi = -0{\cdot}1$ to $\psi = -4{\cdot}0°$ (left to right) in steps of 0·1°, where ψ is the azimuthal angle. At each step an ω-2θ scan has been carried out. The highest peak in this scan ($\psi = -3{\cdot}0°$) has a maximum count rate of approximately 400 counts s^{-1}. In the absence of multiple diffraction, the azimuthal scan will show a smooth variation of intensity with ψ (the variation being due to absorption effects) and a constant ratio of the $K\alpha_1$ and $K\alpha_2$ components, as shown in Fig. 1(*b*) for the 705 reflection in CdS (SMB), from $\psi = -0{\cdot}2$ to $\psi = -2{\cdot}0°$. The maximum count rate in Fig. 1(*b*) is approximately 6000 counts s^{-1}. In Fig. 1(*a*), between $\psi = -1{\cdot}3$ and $\psi = -2{\cdot}2°$, multiple-diffraction effects have so enhanced the $K\alpha_2$ component that it has a larger peak count rate than the $K\alpha_1$ component.

The average % deviation in intensity of a reflection from the mean value of the set of symmetrically equivalent reflections measured for all the CdSe data was 0·6%, indicating that internal consistency was rather good. The histogram of the % deviation for CdSe is similar to that given by SMB for CdS.

Reference reflections were measured at regular intervals throughout the data collection to monitor fluctuations in the system and some corrections were made to allow for the observed presence of long-term variations in the incident-beam flux and/or the sensitivity of the detection system.

2. Analysis

The CdSe data set was analysed by a least-squares refinement program, in the manner described by SMB for CdS. In addition to the four temperature-factor models discussed by SMB (I, II, III and III′) two other models are investigated, a result of the extensiveness of the data set. These two additional models will be discussed in § 3, and refinements of special data subsets, which can be used to determine differences in the magnitudes of the cubic anharmonic parameters, are considered in § 5.

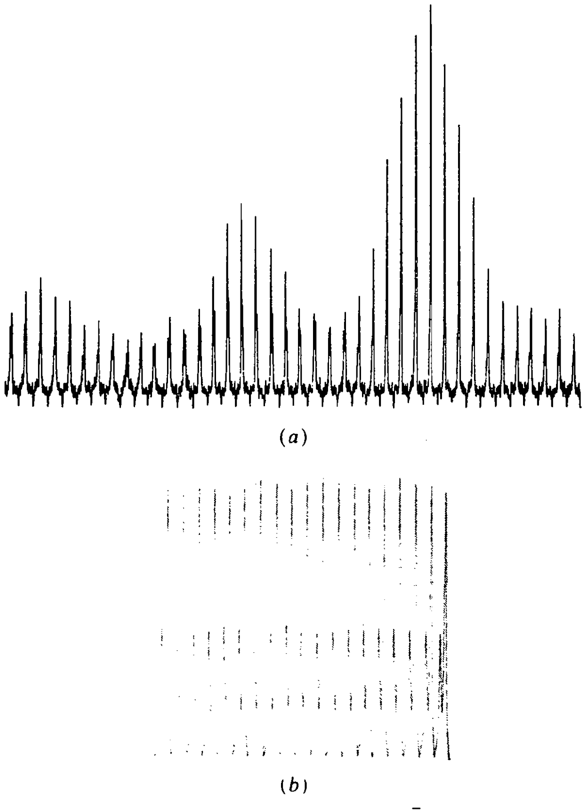

Fig. 1. (*a*) An azimuthal (ψ) scan for the $33\bar{4}$ reflection in CdSe, from −0·1 to −4·0° (left to right) in steps of 0·1°. Significant multiple-diffraction effects are evident. (*b*) An azimuthal scan for the 705 reflection in CdS (SMB), from −0·2 to −2·0°. No significant multiple-diffraction effects can be seen.

The elastic constants of Berlincourt, Jaffe & Shiozawa (1963) were used in the calculation of the one-phonon TDS correction factors α. The lattice parameters used were $a = 4{\cdot}299$ and $c = 7{\cdot}010$ Å (National Bureau of Standards, 1957). The largest anisotropies in the TDS corrections represented approximately 5% in α. The TDS corrections for CdSe were found to be quite large (Koto & Schulz, 1979), with the largest correction factor applied being 36%. As expected, the introduction of the TDS corrections resulted in an increase of the conventional hexagonal temperature parameters which amounted to about 8%.

The secondary-extinction factors y were calculated using Zachariasen's (1967) theory, with the effective domain radius r^* being refined. The results of a refinement in which the $\sin 2\theta$ factor (θ being the Bragg angle), omitted from the original expression for the diffraction cross-section in a perfect crystallite (Becker & Coppens, 1974), was included will be discussed in § 5. The largest extinction effects caused an 8% reduction of the kinematic intensity ($y \gtrsim 0{\cdot}92$). 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.

The other details of this analysis are as given in the previous article (SMB), to which the reader is referred.

3. The refined value of the *u* parameter

Table 1 shows the results of the different data refinements for CdSe, where R_H is Hamilton's R factor and GFIT is the goodness-of-fit parameter. Models I–III′ are as described by SMB. Model IV was discussed in the Appendix of Fakineos, Stevenson & Barnea (1982), and allows for the non-ideal nature of the structure and the anisotropy of the conventional hexagonal temperature parameters. Model IV involves, in part, the refinement of the cubic anharmonic parameter β_{332} from reflections with Miller indices *hk*0, whose structure factors are independent of the other anharmonic parameters, β_{313} and β_{337} (in the notation of WMB). In the case of CdS (SMB) there were too few *hk*0 reflections in the data set (five) to make use of model IV, but for CdSe we have 21 such reflections, enough to refine β_{332} reliably. Model IV′ is the same as model IV with the exception that the anharmonic parameters for Se are constrained to be zero (*cf.* models III and III′).

The other refined parameter values [B_{11}(Cd), B_{33}(Cd), B_{11}(Se), B_{33}(Se), the two scale factors and r^*] all agreed within one e.s.d. for the six models in Table 1. The largest correlation coefficients were for the interactions between the two scale factors and r^* (Lander & Mueller, 1970) and these never exceeded 0·85. The largest correlation coefficient involving u

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

Model	u	R_H(%)	GFIT
I	0·37625 (5)	1·363	1·737
II	0·37661 (4)	0·981	1·252
III	0·37596 (4)	0·941	1·201
III′	0·37598 (4)	0·926	1·181
IV	0·37586 (4)	0·937	1·196
IV′	0·37590 (4)	0·926	1·181

was 0·58 for interaction with the anharmonic parameter.

The only other value of the CdSe u parameter known to us is 0·37679 (12) (Freeman, Mair & Barnea, 1977), which is based on a harmonic refinement of the data and is somewhat larger than our $u_{\rm I}$ (u_X being the u parameter for model X). The value of $u_{\rm II}$ is, as can be predicted using the arguments in SMB, larger than $u_{\rm I}$ [$u_{\rm II}-u_{\rm I}\simeq 0{\cdot}00089$ according to the CdSe analogue of SMB's equation (8), *cf.* 0·00036 from Table 1]. The values of $u_{\rm III}$ and $u_{\rm III'}$ reflect the breakdown of the approximations made in deriving the constraints for model III (SMB) [CdSe does not possess the ideal wurtzite structure, B_{11}(Cd) and B_{33}(Cd) differ by approximately 2%, and B_{11}(Se) and B_{33}(Se) differ by approximately 1%]. These discrepancies are not serious enough to invalidate model III, but do show up as non-zero values of $u_{\rm III}-u_{\rm I}$ and $u_{\rm III'}-u_{\rm I}$, the signs of which, if not the magnitudes, are in accord with the expectations of Mair & Barnea (1975) [the values of u according to equations (5*a*) and (5*b*) of SMB (Keffer & Portis, 1957) are 0·3754 and 0·3748, respectively]. The value of u predicted by O'Keeffe & Hyde (1978) (see SMB) is 0·3756. The difference between $u_{\rm III}$ and $u_{\rm I}$ represents a sum of the differences between the time-averaged and potential minimum positions for adjacent Cd and Se atoms along the c axis of 0·0020 Å at room temperature [*cf.* 0·0022 Å for CdS (SMB)].

The ratios $R_H({\rm I})/R_H({\rm II})$, $R_H({\rm II})/R_H({\rm III})$ and $R_H({\rm III})/R_H({\rm III'})$, 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 model III and suggest that the Se atoms do not undergo significant cubic anharmonic thermal vibrations at room temperature, the latter also being reflected by $R_H({\rm IV})/R_H({\rm IV'})$. At this stage there is no definite evidence to support the use of model IV in preference to model III [as tested by $R_H({\rm III})/R_H({\rm IV})$]. More stringent tests, with structures further removed from that of ideal wurtzite, would be necessary in order to resolve the question of the usefulness of model IV. It is, however, interesting to note that $u_{\rm IV}$ and $u_{\rm IV'}$ are slightly closer to the values predicted by Keffer & Portis (1957) and O'Keeffe & Hyde (1978), and mentioned above.

The refined value of the anharmonic parameter for model II was $0{\cdot}75\,(5)\times10^{-20}\,{\rm J\,Å^{-3}}$ (in reasonable agreement with the values, given in § 4, from the refinement of AIR), whereas for model III $|\beta_{332}| = 0{\cdot}81\,(5)\times10^{-20}\,{\rm J\,Å^{-3}}$ and for model III′ $|\beta_{332}|_{\rm Cd} = 1{\cdot}15\,(7)\times10^{-20}\,{\rm J\,Å^{-3}}$. The values of the anharmonic parameters for model IV are: $|\beta_{332}| = 0{\cdot}90\,(8)\times10^{-20}$, $|\beta_{337}| = 1{\cdot}05\,(10)\times10^{-20}$, $\beta_{313,{\rm Cd}} = 0{\cdot}18\,(10)\times10^{-20}$ and $\beta_{313,{\rm Se}} = -0{\cdot}16\,(10)\times10^{-20}\,{\rm J\,Å^{-3}}$. The values of the anharmonic parameters for model IV′ are: $|\beta_{332}|_{\rm Cd} = 1{\cdot}27\,(11)\times10^{-20}$, $|\beta_{337}|_{\rm Cd} = 1{\cdot}53\,(14)\times10^{-20}$ and $\beta_{313,{\rm Cd}} = 0{\cdot}21\,(15)\times10^{-20}\,{\rm J\,Å^{-3}}$. It should be noted that the values of β_{313} obtained for models IV and IV′ have the opposite signs to those expected. This is due primarily to the sensitivity of these values to the anisotropy of the conventional hexagonal temperature parameters and the non-ideal nature of the structure. It is seen that these parameter values are relatively close to zero, especially when the size of the associated e.s.d. is considered.

4. Consequences of anharmonic thermal vibrations

Table 2 shows our experimental values of 18 CdSe AIR (WMB), together with the calculated values obtained from a least-squares refinement of the AIR (A). The value of the only refined parameter, the anharmonic parameter, was $0{\cdot}90\,(3)\times10^{-20}\,{\rm J\,Å^{-3}}$ (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 values of GFIT and R_H were 1·211 and 0·268, respectively. The calculated values of the AIR from the full refinement discussed in §§ 3 and 5 (model III) are also given in Table 2 (B).

Table 2. *The observed and calculated AIR*(%) *for* $70l/53l$ *pairs of reflections in* CdSe, *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 §§ 3 and 5 (B).

l	Observed	Calculated (A)	Calculated (B)
0	−13·7 (1·3)	−11·7	−10·6
1	4·4 (1·9)	5·0	4·5
$\bar{1}$	4·9 (1·7)	4·3	3·9
2	−15·6 (1·7)	−12·0	−10·7
$\bar{2}$	−8·4 (1.8)	−12·2	−10·9
3	3·0 (1·3)	3·9	3·5
$\bar{3}$	3·8 (1·2)	3·9	3·5
5	1·1 (1·3)	3·8	3·4
$\bar{5}$	2·2 (1·3)	3·9	3·5
6	−11·3 (2·8)	−12·2	−11·1
$\bar{6}$	−13·1 (2·5)	−12·0	−10·9
7	3·3 (2·5)	4·0	3·5
$\bar{7}$	9·6 (3·2)	4·4	3·8
8	−13·0 (2·5)	−11·6	−10·4
$\bar{8}$	−7·2 (2·5)	−11·6	−10·4
$\bar{9}$	6·2 (3·2)	4·1	3·8
11	3·6 (2·4)	3·8	3·4
$\overline{11}$	3·5 (2·4)	3·8	3·4

The seven observations of AIR common to Table 2 and WMB show reasonable agreement in general, although the values with Miller index $l = -2$ do have a large discrepancy. A least-squares refinement of 15 AIR, having removed the three AIR for which $l = -2$, -7 and -8, produced a refined anharmonic parameter value of 0·97 (3) × 10^{-20} J Å^{-3}, with R_H being 0·207. The refined anharmonic parameter value of WMB was 1·3 (1) × 10^{-20} J Å^{-3}. This larger value can be attributed to the other parameter values used [B_{11}(Cd), B_{33}(Cd), B_{11}(Se), B_{33}(Se) and u]. If the values used by WMB [those of Freeman, Mair & Barnea (1977)] are used in this analysis we obtain refined anharmonic parameter values of 1·13 (4) × 10^{-20} (18 AIR) and 1·22 (4) × 10^{-20} J Å^{-3} (15 AIR).

The results in Table 2 represent irrefutable evidence of anharmonic thermal vibration of the Cd and/or Se atoms at room temperature, as was the case for CdS (SMB).

5. Results

A table showing the observed and calculated (model III) structure factors, $|F_{oi}|$ and $|F_{ci}|$ respectively, for CdSe after least-squares refinement, together with the $E_i = 100\sigma(|F_{oi}| - |F_{ci}|)/|F_{oi}|$ [where $\sigma(X)$ is the standard deviation for the quantity X], and the secondary extinction and TDS correction factors is available.* The reflections have Bragg angles which range between 15 and 61° with Mo $K\alpha$ radiation. Table 3 contains the final parameter values corresponding to model III. The average difference between the 77 observed structure-factor values given by Freeman, Mair & Barnea (1977) (specimen No. 2)† and the corresponding values‡ obtained here is 1·4%.

The four conventional hexagonal temperature-parameter values of Freeman, Mair & Barnea (1977) [B_{11}(Cd) = 1·46 (2), B_{33}(Cd) = 1·77 (5), B_{11}(Se) = 1·21 (2) and B_{33}(Se) = 0·96 (8) Å^2] are, allowing for the absence of TDS corrections, in reasonable accord with the values in Table 3, with B_{11}(Cd) and B_{11}(Se) showing the best agreement. The only other values of the conventional hexagonal temperature parameters for CdSe known to us are those of Sirota & Yanovich (1972), which were obtained for a temperature of 330 K using a powder specimen. These values are all larger than those in Table 3, especially B_{33}(Se) [B_{11}(Cd) = 1·71, B_{33}(Cd) = 2·23, B_{11}(Se) = 2·00 and B_{33}(Se) = 3·38 Å^2]. Sakata, Stevenson & Harada (1983) showed that using the TDS corrections of Harada & Sakata (1974) and Sakata & Harada (1976), based on the spherical-volume approximation (SVA), did not significantly affect the value of $\bar{B}_{\text{CdSe}}$ (see SMB). The value of $\bar{B}_{\text{CdSe}}$ is 1·474 (4) Å^2, *cf.* 1·38 Å^2 using Stevenson & Harada's (1983) equation (26). The fact that the heavier of the two atomic species has the larger temperature parameters for CdSe (Table 3) has been discussed by SMB in relation to CdS.

Table 3. *The refined parameter values for* CdSe, *using model* III

B_{11}(Cd)	1·595 (4) Å^2
B_{33}(Cd)	1·627 (8) Å^2
B_{11}(Se)	1·273 (5) Å^2
B_{33}(Se)	1·284 (10) Å^2
u	0·37596 (4)
Scale (1)	2·748 (7) × 10
Scale (2)	2·747 (6) × 10
r^*	2·7 (3) × 10^3 Å
$\lvert\beta_{332}\rvert$	0·81 (5) × 10^{-20} J Å^{-3}
R_H	0·941%
GFIT	1·201

The value of the X-ray Debye temperature for CdSe can be determined from the values of the four conventional hexagonal temperature parameters in Table 3, as discussed by SMB. The value so obtained is 155 K, *cf.* 181 K (Cline, Dunegan & Henderson, 1967) and 185 K (Singh & Varshni, 1982). Allowing for the effects of dispersion on these two theoretical Debye-temperature values, as in SMB, yields 154 and 157 K, in excellent, if fortuitous (see SMB), agreement with the value obtained in the present case.

Predictably, the inclusion of quartic anharmonic effects in the temperature-factor models made no difference, and the associated quartic anharmonic parameter values were zero (within the e.s.d.).

The extinction effects in the CdSe data set, although larger than those seen for CdS (SMB), are still quite small. A refinement was also carried out (model III) which incorporated the $\sin 2\theta$ factor omitted from the original expression for the diffraction cross-section in a perfect crystallite (Becker & Coppens, 1974). It was assumed that the specimen was a type II crystal† (Zachariasen, 1967) and thus r^* was replaced by $r \sin 2\theta$, where r is the perfect-crystal domain radius. The refined value of r was 4·1 (4) × 10^3 Å and R_H and GFIT were 0·922% and 1·173 respectively (*cf.* 0·941% and 1·201, respectively, without the $\sin 2\theta$ factor). The largest change in the

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39302 (6pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† It should be noted that all the values of the Miller index h for Freeman, Mair & Barnea's (1977) specimen No. 1 data should be positive, *e.g.* $\bar{4}21$ should read 421, the former being a forbidden reflection (even if cubic anharmonicity is considered).

‡ In order to make the comparison valid the structure-factor values used from the present analysis were of the form $|F_{oi}|(1 + \alpha_i)^{1/2}$, where the $|F_{oi}|$ are from a harmonic treatment of the data and α_i is the TDS correction factor for the ith observation.

† A refinement without this assumption, allowing the extinction parameters r and g (Zachariasen, 1967) to vary, produced a rather large value of g, which was consistent with the characteristics of a type II crystal.

values of the eight other refined parameters was less than 0·3%, and all changes were less than one e.s.d.

The extensiveness of the CdSe data set offers the opportunity of checking the differences in the magnitudes of the cubic anharmonic parameters, as predicted in model III. This is achieved by refining special groups of reflections, for which the structure factor is independent of certain anharmonic parameters. A refinement of 21 *hk*0 reflections, whose structure factors only depend on β_{332}, yielded $|\beta_{332}| = 0{\cdot}90\,(8)\times10^{-20}$ J Å^{-3}. A refinement of 72 *hkl* reflections ($h+2k=3m$, $l=2n$, where m and n are integers), whose structure factors are independent of β_{332}, yielded $|\beta_{313}| = |\beta_{337}| = 0{\cdot}50\,(14)\times10^{-20}$ J Å^{-3} (model II) and $|\beta_{337}| = 1{\cdot}17\,(27)\times10^{-20}$ J Å^{-3} (model III). Using this last result and the value of $|\beta_{332}|$ above gives $|\beta_{337}/\beta_{332}| = 1{\cdot}3\,(3)$, in good agreement with the predicted value of $2^{1/2}$ (model III). The somewhat large e.s.d. for $|\beta_{337}/\beta_{332}|$ is due primarily to the e.s.d. for $|\beta_{337}|$, which reflects its interaction with the u parameter (correlation coefficient = 0·78). The *hk*0 reflections, from which $|\beta_{332}|$ is determined, have structure factors which are independent of u.

Attempts were made to refine the anomalous-dispersion corrections from 113 CdSe Bijvoet ratios. 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). The refined parameter values were $f'_{\rm Cd} = -0{\cdot}89\,(13)$, $f''_{\rm Cd} = 1{\cdot}28\,(1)$, $f'_{\rm Se} = -0{\cdot}03\,(7)$ and $f''_{\rm Se} = 2{\cdot}19\,(4)$ [*cf.* −1·005, 1·202, −0·178 and 2·223 from Cromer & Liberman (1970) respectively], where $f'_X(f''_X)$ is the real (imaginary) dispersion correction for atomic species X, and the e.s.d.'s include the effect of the uncertainty in the u parameter (Freeman, Mair & Barnea, 1977). The results for CdSe are in better agreement with Cromer & Liberman (1970) than the CdS results (SMB) were, which can be attributed to the relative sizes of the two data sets and the magnitudes of the Bijvoet ratios involved. Only six of the 113 CdSe Bijvoet ratios measured have the sign incorrectly determined, all of these having $|l| = 8$. [Bijvoet ratios for reflections with $l = 4n$, where n is an integer, are zero for ideal wurtzite in the harmonic approximation (in all cases considered bonding effects can be neglected). The largest calculated Bijvoet-ratio magnitude with $|l| = 8$ (model III) is only 1·96%. Bijvoet ratios for reflections with $|l| = 4$ will be discussed in § 6.] The largest calculated Bijvoet-ratio magnitude (model III) is 74·43% ($537/53\bar{7}$).

6. *hk*4/*hk*$\bar{4}$ Bijvoet ratios

The observation of non-zero Bijvoet ratios in the set of reflections with $l = 4n$ is evidence of the non-ideal nature of the structure and/or the presence of anharmonicity. In the case of CdS (SMB) only four Bijvoet ratios were measured with $l = 4n$, and of these the largest calculated magnitude was only 0·61% ($224/22\bar{4}$), the other three having $|l| = 8$. For CdSe the 15 $|l| = 8$ Bijvoet ratios measured have calculated magnitudes less than 2%, but the $|l| = 4$ Bijvoet-ratio magnitudes are quite large [the largest of the four measured having a calculated value of 18·57% ($224/22\bar{4}$)]. In fact, the $hk4/hk\bar{4}$ Bijvoet ratios for CdSe (with Mo $K\alpha$ radiation) are generally quite large due to a fortuitous combination of circumstances (the atomic species present, the wavelength used, the value of l, *etc.*). These $hk4/hk\bar{4}$ Bijvoet ratios are very sensitive to the u parameter and the cubic anharmonic parameter(s) in general (WMB discussed the remarkable sensitivity of the $224/22\bar{4}$ Bijvoet ratio to $\beta = |\beta_{313}| = |\beta_{337}|$).*

In this section we report on the refinement of five $hk4/hk\bar{4}$ Bijvoet ratios, measured specifically for the purpose of obtaining the values of the u parameter and the cubic anharmonic parameter(s). The experimental conditions under which these measurements were made were the same as those for the main data collection (see § 1 and SMB). The five Bijvoet ratios measured were selected so that $h+2k=3m$, which eliminates their dependence on β_{332}. The observed values are listed in the second column of Table 4 (ignoring, for the moment, the third, fourth and fifth columns), with the $224/22\bar{4}$ value showing excellent agreement with the value of WMB, namely 16·2 (2·3)%. The constituent reflections of each Bijvoet ratio were measured several times (to improve counting statistics), as were equivalent reflections where available (the reflections of the form *hhl* had no equivalent reflections which could be measured reliably). The associated e.s.d.'s are based on counting and population statistics.

The Bijvoet ratio for $hk4/hk\bar{4}$ reflections, with $h+2k=3m$, can be given by

$$B = \frac{4T_{c,A}T_{c,B}(f'_{c,A}f''_B - f'_{c,B}f''_A)(8\pi\Delta u - \tau_{a,AB})}{[(f'^2_{c,A}+f''^2_A)T^2_{c,A} + (f'^2_{c,B}+f''^2_B)T^2_{c,B} - 2T_{c,A}T_{c,B}(f'_{c,A}f'_{c,B}+f''_Af''_B)]} \qquad (1)$$

where

$$\Delta u = u - 3/8 \qquad (2a)$$

and

$$\tau_{a,AB} = \frac{T^{(2)}_{a,A}}{T_{c,A}} - \frac{T^{(2)}_{a,B}}{T_{c,B}}. \qquad (2b)$$

---

* We note that the horizontal axis in Fig. 2 of WMB should be in units of $\beta(\times10^{-13}$ erg Å$^{-3})$ (10^{-20} J Å^{-3}), not β ($\times10^{-12}$ erg Å^{-3}) (10^{-19} J Å^{-3}).

Table 4. *The observed and calculated* (*model* III) CdSe *Bijvoet ratios* (%) *for* $hk4/hk\bar{4}$ *reflections* ($h+2k=3m$, *where* m *is an integer*)

B_u and B_{anh} are calculated using (1)-(3) with the constraints of model III (see text).

$hk4/hk\bar{4}$	Observed	Calculated	B_u	B_{anh}
$114/11\bar{4}$	7·8 (1·5)	7·9	7·8	0·1
$304/30\bar{4}$	17·1 (2·1)	14·5	12·9	1·7
$224/22\bar{4}$	16·0 (1·6)	17·5	14·8	2·9
$414/41\bar{4}$	23·6 (2·4)	23·7	17·4	6·7
$334/33\bar{4}$	27·5 (3.0)	26·6	18·0	9·2

In (1), $T_{c,X}$ represents the harmonic temperature factor for atomic species X, and $f'_{c,X}$ is the sum of the free-atom spherical scattering factor for atomic species X and f'_X. In (2*b*), $T^{(2)}_{a,X}$ is that part of the cubic anharmonic temperature factor which contains β_{313} and β_{337}, without i, for atom $X(1)$ (see WMB). In deriving (1) terms containing $T^{(2)}_{a,A}$, $T^{(2)}_{a,B}$, $T^{(2)2}_{a,A}$, $T^{(2)2}_{a,B}$, $\Delta u T^{(2)}_{a,A}$, $\Delta u T^{(2)}_{a,B}$ and $(\Delta u)^2$ were neglected. When evaluating (1), and in particular $\tau_{a,AB}$, $l=4$ should be used. Given that the imaginary dispersion corrections are non-zero, (1) is non-zero if (and only if) $8\pi\Delta u-\tau_{a,AB}\neq 0$. For the Bijvoet ratios considered in Table 4 $\tau_{a,\text{CdSe}}<0$ (as calculated with the constraints of model III), and $\Delta u>0$ for CdSe, so that the last factor in the numerator of (1) is significantly different from zero. (In the case of model II, for Table 4, $\tau_{a,\text{CdSe}}>0$ and Δu is correspondingly larger than the value for model III.)

A least-squares refinement program was written to analyse the Bijvoet-ratio data. The only parameters which need to be refined are u and the cubic anharmonic parameter (for the different temperature-factor models). The four conventional hexagonal temperature-parameter values are now well known and essentially independent of the temperature-factor model used. No allowance was made for the presence of extinction because these Bijvoet ratios are not sensitive to such effects, and $y>0·99$ in all cases. The results of the refinements are given in Table 5 and the calculated Bijvoet ratios corresponding to model III are listed in the third column of Table 4. Model $\underline{\text{III}}$ constrains the cubic anharmonic parameter for model III ($|\beta_{337}|$) to the value obtained from the main analysis (§§ 3 and 5). The u parameter values show the trends discussed in § 3 and agree within one e.s.d. with the values in Table 1. The size of the e.s.d.'s for the refined cubic anharmonic parameter values renders their comparison with other values inconclusive.

In order to illustrate the relative contributions of the non-ideality of the structure and the anharmonicity of thermal vibrations to the Bijvoet ratios in Table 4, (1) was divided into two terms:

$$B=B_u+B_{\text{anh}}, \tag{3}$$

where B_u (B_{anh}) is calculated by setting $\tau_{a,AB}$ (Δu) $=0$ in (1). The fourth and fifth columns in Table 4 contain

Table 5. *The results of the least-squares refinements for the data in Table* 4

$\beta=|\beta_{313}|=|\beta_{337}|$ for model II and $\beta=|\beta_{337}|$ for models III and $\underline{\text{III}}$.

Model	u	β ($\times 10^{-20}$ J Å^{-3})	Correlation coefficient	R_H (%)
I	0·37616 (9)	-	-	14·6
II	0·37660 (19)	0·60 (25)	0·95	8·3
III	0·37592 (11)	1·01 (41)	0·85	8·3
$\underline{\text{III}}$	0·37589 (5)	$\underline{1·15}$	-	8·5

the calculations (model III) of B_u and B_{anh} respectively, using the appropriate u and β values from Table 5. Small discrepancies between the calculated Bijvoet ratios (third column) and the sums of the values of B_u and B_{anh} in Table 4 can be attributed to the approximations made in deriving (1) (since the least-squares program involves the calculation of $|F|^2$ values initially). Clearly, B_{anh} becomes an increasingly important component of B as θ increases in Table 4, although B_u still dominates. In the case of model II, B_u is approximately 75% larger than in Table 4 and B_{anh} ranges from $-4·0\%$ ($334/33\bar{4}$) to $-7·9\%$ ($224/22\bar{4}$), the sums of the values of B_u and B_{anh} agreeing with those in Table 4. It should be noted that $|\tau_{a,\text{CdSe}}|$ increases with increasing θ in Table 4 for model III, whereas it decreases for model II.

The difficulty experienced in obtaining β values (as opposed to u values) from the observed Bijvoet ratios in Table 4 is readily understood when consideration is given to the relative contributions of B_u and B_{anh}.

The fact that it has proved possible to refine reliable values of u from five Bijvoet-ratio measurements is rather fortuitous, and the procedure has limited general applicability. The dependence of this procedure on the presence of anomalous scattering further limits its use in the case of neutron studies (see Peterson & Smith, 1961).

7. Comparison with CdS

The studies of CdSe and CdS, presented here and in the previous article (SMB) respectively, have revealed a similarity between the refined values of the cubic anharmonic parameters for these materials [*e.g.* $|\beta_{332}|_{\text{CdS}}=0·88\ (6)\times 10^{-20}$ and $|\beta_{332}|_{\text{CdSe}}=0·81\ (5)\times 10^{-20}$ J Å^{-3}, for model III]. We are not aware of any other materials with the wurtzite structure for which anharmonic-parameter determinations have been made. The most reliable values of u obtained are 0·37715 (8) for CdS and 0·37596 (4) for CdSe, determined using model III.

In the case of CdSe it appears that the Se atoms do not undergo significant cubic anharmonic thermal vibrations at room temperature, whereas the assumption that $|\beta_{332}|_{\text{S}}=0$ in model III for CdS (SMB) resulted in a decrease of R_H which was '*not significant*'.

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Order–Disorder in the α'-(Ca, Sr)$_2$SiO$_4$ Solid Solution: a Structural and Statistical-Thermodynamic Analysis

BY MICHELE CATTI

Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via Golgi 19, 20133 *Milano, Italy*

GIUSEPPE GAZZONI

CNR III *Sezione Centro Nazionale di Cristallografia, c/o Dipartimento di Scienze della Terra,*
Via S. Massimo 22, 10123 *Torino, Italy*

AND GABRIELLA IVALDI

Dipartimento di Scienze della Terra, Università di Torino, Via S. Massimo 22, 10123 *Torino, Italy*

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Abstract

X-ray data were collected by single-crystal diffractometry (Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å) from the four compounds $Ca_{0.5}Sr_{1.5}SiO_4$, $CaSrSiO_4$, $Ca_{1.5}Sr_{0.5}SiO_4$ and $Ca_{1.8}Sr_{0.2}SiO_4$ [orthorhombic, space group *Pmnb* (non-standard setting of *Pnma*); crystal data range from $a = 5{\cdot}647\,(1)$, $b = 7{\cdot}037\,(1)$, $c = 9{\cdot}644\,(2)$ Å, $V = 383{\cdot}2$ Å^3, $M_r = 243{\cdot}552$, $D_x = 4{\cdot}221$ Mg m^{-3}, $Z = 4$, $\mu(\text{Mo } K\alpha) = 21{\cdot}2$ mm^{-1}, $F(000) = 452$ for $Ca_{0.5}Sr_{1.5}SiO_4$ to $a = 5{\cdot}5555\,(9)$, $b = 6{\cdot}8010\,(7)$, $c = 9{\cdot}317\,(2)$ Å, $V = 352{\cdot}0$ Å^3, $M_r = 181{\cdot}750$, $D_x = 3{\cdot}429$ Mg m^{-3}, $Z = 4$, $\mu(\text{Mo } K\alpha) = 6{\cdot}0$ mm^{-1}, $F(000) = 358{\cdot}4$ for $Ca_{1.8}Sr_{0.2}SiO_4$] synthesized by flux-growth crystallization. Least-squares refinements were based on the positionally disordered structure model of α'-Sr_2SiO_4, with atoms statistically distributed between mirror-related positions. Independent observations and final *R* values ranged from 826 to 1030 and from 0·030 to 0·052, respectively. An ordered model with most atoms on the (100) mirror plane (low-K_2SO_4 structure type) gave unsatisfactory results, particularly for the Ca-rich terms. The tilt of the SiO_4 group with respect to the (100) plane and its distortion from *m* symmetry increase with the Ca/Sr ratio, showing that positional