

Table 8. *Strength of linkage between journals in crystallography and other disciplines*

Link to	Strength
Chemistry	Strong
Physics	↓
Multidisciplinary	↓
Materials science	↓
{ Mineralogy }	↓
{ Metallurgy }	↓
Biology	Weak

number of journals with only a few citations each could not be classified because they were not listed separately by JCR, but were combined into an 'all others' category.

Fig. 7 shows the citation linkages between crystallography and six other disciplines. The linkage to multidisciplinary journals, such as *Science* and *Nature*, is also shown. The number of citations associated with each link is also indicated. Table 8 ranks the linkages shown in Fig. 7, from the strongest (to chemistry) to the weakest (to biology). The links to chemistry are about an order of magnitude stronger than those to mineralogy, materials science, metallurgy, and biology, confirming the conclusions of Fig. 6.

Bibliometric and citation data usually do not change rapidly with time; brief checks of available 1978 data show that this is the case with the crystallographic literature.

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Anharmonic Temperature Factors of Zinc Selenide Determined by X-ray Diffraction from an Extended-Face Crystal

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Abstract

Generalized structure factor expressions are derived for the zinc blende structure. Inclusion of dispersion correc-

tions is shown to give rise to the breakdown of Friedel's law for all-even-index reflections, an effect due to the presence of bonding or anharmonicity. X-ray intensity measurements from an extended-face crystal are interpreted within the generalized structure factor formalism to yield the B factors $B_{zn} = 1.020 \pm 0.005 \text{ \AA}^2$ and $B_{se} = 0.739 \pm 0.008 \text{ \AA}^2$ and an effective cubic anharmonic thermal parameter $\mathcal{B}_{znse} = \beta_{zn}/\alpha_{zn}^3 -$

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$\beta_{\text{Se}}/\alpha_{\text{Se}}^3 = -(6.8 \pm 1.1) \times 10^{36} \text{ J}^{-2} \text{ \AA}^3$ at 296 K. These are compared with values for other zinc blende compounds and with theoretically calculated B factors.

Introduction

In interpreting X-ray diffraction intensity data it is common to assume that the thermal vibrations of the atoms are harmonic and constrained in such a way that the time-averaged probability function for the position of an atom is a Gaussian function of the displacement from its equilibrium position. Contours of equal probability are then ellipsoids or, in the case of cubic crystals, spheres. However, in a crystal the neighbours of an atom will of necessity be arranged with a particular symmetry which one would expect to be reflected in the thermal vibrations. The thermal motion will then be modified in such a way that the atom will spend more time in regions of low potential. This gives rise to anharmonic components in the thermal vibrations. The contributions of these anharmonic components to the Bragg intensities were, as far as we know, first considered by Dawson, Hurley & Maslen (1967).

Most early studies of anharmonicity were carried out by neutron diffraction. Some X-ray studies, namely of CaF_2 (Cooper, 1970; Strock & Batterman, 1972), Mg_2Si (Cooper & Panke, 1970), AuGa_2 (Hollenberg & Batterman, 1974), sodium (Field & Medlin, 1974), germanium (Mair & Barnea, 1975), CdSe (Whiteley, Moss & Barnea, 1977), CuCl (Valvoda & Ječný, 1978), white tin (Merisalo & Järvinen, 1978), zinc (Merisalo, Järvinen & Kurittu, 1978) and cadmium (Merisalo, Peljo & Soininen, 1978) are also reported in the literature. All these, with the exceptions of CdSe and CuCl , are centrosymmetric.

In this paper we report a room-temperature X-ray study of zinc selenide, a crystal with the non-centrosymmetric zinc blende structure. Firstly, we present the generalized structure factor expressions. The inclusion of anomalous dispersion corrections complicates these somewhat and gives rise to a Bijvoet-type asymmetry which arises through the simultaneous presence of both anharmonicity or bonding and dispersion. The experimental intensities are interpreted within the framework of this structure factor formalism and provide information about anharmonicity and to a lesser extent bonding. The cubic anharmonic parameter is then compared with those available for two other related zinc blende compounds studied by neutron diffraction (Cooper, Rouse & Fuess, 1973).

Other compounds with the zinc blende structure, in which vibrational anharmonicity has been investigated, are CuCl in both a room-temperature X-ray study (Valvoda & Ječný, 1978) and a multi-temperature neutron study (Sakata, Hoshino & Harada, 1974) and CuBr in a high-temperature neutron study (Harada, Suzuki & Hoshino, 1976).

Theory

Following Dawson's (1967) formalism the generalized structure factor $F(\mathbf{S})$ is expressed as

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

Here \mathbf{S} is the scattering vector and $f_j(\mathbf{S})$ and $T_j(\mathbf{S})$ are the atomic scattering factor and temperature factor[†] respectively of the j th atom whose position with respect to the origin is \mathbf{r}_j .

In general, both the at-rest charge distribution and nuclear smearing function may be non-centrosymmetric and hence $f_j(\mathbf{S})$ and $T_j(\mathbf{S})$ may be complex:

$$\begin{aligned} f_j(\mathbf{S}) &= f_{c,j}(\mathbf{S}) + if_{a,j}(\mathbf{S}), \\ T_j(\mathbf{S}) &= T_{c,j}(\mathbf{S}) + iT_{a,j}(\mathbf{S}), \end{aligned}$$

where the subscripts c and a refer to the centrosymmetric and antisymmetric components respectively. For X-rays we also include the effects of anomalous dispersion:

$$f_j(\mathbf{S}) = f_{c,j}(\mathbf{S}) + if_{a,j}(\mathbf{S}) + f'_j + if''_j,$$

where f'_j and f''_j are the real and imaginary dispersion corrections of atom j . Since f'_j has the same centrosymmetric properties as $f_{c,j}(\mathbf{S})$ we can combine them in a single term $f'_{c,j}(\mathbf{S})$. We then have

$$f_j(\mathbf{S}) = f'_{c,j}(\mathbf{S}) + if_{a,j}(\mathbf{S}) + if''_j.$$

Introducing the appropriate quantities in terms of real and imaginary parts, we find that the generalized structure factor is [suppressing (\mathbf{S})]

$$\begin{aligned} F = \sum_j \{ & (f'_{c,j} T_{c,j} - f''_j T_{a,j} - f_{a,j} T_{a,j}) \cos 2\pi \mathbf{S} \cdot \mathbf{r}_j \\ & - (f''_j T_{c,j} + f_{a,j} T_{c,j} + f'_{c,j} T_{a,j}) \sin 2\pi \mathbf{S} \cdot \mathbf{r}_j \} \\ & + i \{ (f''_j T_{c,j} + f_{a,j} T_{c,j} + f'_{c,j} T_{a,j}) \cos 2\pi \mathbf{S} \cdot \mathbf{r}_j \\ & + (f'_{c,j} T_{c,j} - f''_j T_{a,j} - f_{a,j} T_{a,j}) \sin 2\pi \mathbf{S} \cdot \mathbf{r}_j \}. \end{aligned} \quad (2)$$

The atomic positions for XY compounds having the zinc blende structure are

$$\begin{aligned} X: & 000 + \text{equivalent f.c.c. sites,} \\ Y: & \frac{1}{4}\frac{1}{4}\frac{1}{4} + \text{equivalent f.c.c. sites.} \end{aligned}$$

The site symmetry of all atoms is $\bar{4}3m$, but the tetrahedra about the X sites have opposite orientation to those about the Y sites.

Using (2) and the positions of the atoms X and Y , we can obtain the square of the scattering amplitude, $F_{hkl} F_{hkl}^*$. For the various types of reflections allowed in the zinc blende structure we find: for reflections

[†] Following Willis & Pryor (1975), p. 81, we use 'Debye-Waller factor' to denote the reduction in intensity of the reflection caused by thermal vibration and 'temperature factor' as the corresponding quantity multiplying the atomic scattering factor.

with $h + k + l = 4n$ (upper sign) and reflections with $h + k + l = 4n + 2$ (lower sign),

$$F_{hkl} F_{hkl}^* = 16(f_{c,x}'^2 + f_{a,x}'^2 + f_x''^2 + 2f_x'' f_{a,x}') (T_{c,x}^2 + T_{a,x}^2) + 16(f_{c,y}'^2 + f_{a,y}'^2 + f_y''^2 + 2f_y'' f_{a,y}') (T_{c,y}^2 + T_{a,y}^2) \pm 32\{ (f_{c,x}' f_{c,y}' + f_{a,x}' f_{a,y}' + f_x'' f_y'' + f_x'' f_{a,y}' + f_{a,x}' f_y'') (T_{c,x} T_{c,y} + T_{a,x} T_{a,y}) - [f_{c,x}' (f_{a,y}' + f_y'') - f_{c,y}' (f_{a,x}' + f_x'')] \times (T_{c,x} T_{a,y} - T_{c,y} T_{a,x}) \}; \quad (3a)$$

for reflections with $h + k + l = 4n \pm 1$,

$$F_{hkl} F_{hkl}^* = 16(f_{c,x}'^2 + f_{a,x}'^2 + f_x''^2 + 2f_x'' f_{a,x}') (T_{c,x}^2 + T_{a,x}^2) + 16(f_{c,y}'^2 + f_{a,y}'^2 + f_y''^2 + 2f_y'' f_{a,y}') (T_{c,y}^2 + T_{a,y}^2) \mp 32\{ (f_{c,x}' f_{c,y}' + f_{a,x}' f_{a,y}' + f_x'' f_y'' + f_x'' f_{a,y}' + f_{a,x}' f_y'') (T_{c,x} T_{a,y} - T_{c,y} T_{a,x}) + [f_{c,x}' (f_{a,y}' + f_y'') - f_{c,y}' (f_{a,x}' + f_x'')] \times (T_{c,x} T_{c,y} + T_{a,x} T_{a,y}) \}. \quad (3b)$$

By inspection, if terms higher than first order in $T_{a,j}$ are neglected, then (3) may be conveniently expressed in terms of an effective anharmonic factor $T_{a,YX}$, where

$$T_{a,YX} = T_{a,Y}/T_{c,Y} - T_{a,X}/T_{c,X}.$$

In contrast to the case with neutrons, with X-rays $T_{a,YX}$ is also present in the expression for all-even reflections (*cf.* Cooper, Rouse & Fuess, 1973). However, the coefficients of $T_{a,YX}$ always contain either $f_{a,j}'$ or f_j'' and their overall contribution to the square of the scattering amplitude is therefore generally small.

Equations (3) point to intensity differences between reflections having the same magnitudes of the scattering vector \mathbf{S} but different Miller indices; groups of these reflections are equivalent in the harmonic approximation (when bonding effects are also neglected) and their non-equivalence has now been predicted and demonstrated in a number of cubic crystals. Intensity differences due to the inclusion of anharmonic (and bonding) effects are also reflected in the Bijvoet differences and ratios discussed later in this section; no interpretation of these is complete without allowance for these effects.

Expressions for the temperature factor components in terms of the one-particle potential may be obtained in analogy with Dawson's treatment of the fluorite structure (Dawson, Hurley & Maslen, 1967). The zinc blende structure differs from fluorite in that both atomic species have the non-centrosymmetric site

symmetry $\bar{4}3m$ and hence both $T_{a,X}$ and $T_{a,Y}$ are non-zero.

Following Dawson, Hurley & Maslen (1967), we have

$$T_{c,j}(\mathbf{S}) = T_{c,j}(S) = \exp[-B_j(\sin \theta/\lambda)^2], \\ T_{a,j}(\mathbf{S}) = -(B_j/4\pi a_0^3) T_{c,j}(S) A_j hkl,$$

where B_j and A_j are experimentally obtained quadratic and cubic parameters and a_0 is the lattice parameter. B_j is the usual isotropic B factor of the atom j .

Neglecting fourth- and higher-order terms, the one-particle potential appropriate to a tetrahedral site symmetry is

$$V_j = V_{0j} + (\alpha_j/2)(x^2 + y^2 + z^2) + \beta_j xyz,$$

where x , y and z are the Cartesian coordinates of the atomic displacement \mathbf{u} . The Debye temperature of zinc selenide has been reported as 237 K (Sharma, 1972). At room temperature, therefore, the temperature factors may be evaluated from

$$T_j(\mathbf{S}) = \frac{\int \exp[-V_j(\mathbf{u})/k_B T] \exp(2\pi i \mathbf{S} \cdot \mathbf{u}) d\mathbf{u}}{\int \exp[-V_j(\mathbf{u})/k_B T] d\mathbf{u}},$$

where k_B is the Boltzmann constant and T is the absolute temperature (Willis & Pryor, 1975). This yields

$$B_j = 8\pi^2 k_B T/\alpha_j, \quad A_j = -\beta_j/k_B T.$$

Expressing $T_{a,YX}$ in terms of the coefficients α_j and β_j , we find

$$T_{a,YX} = hkl(k_B T)^2 (2\pi/a_0)^3 (\beta_Y/\alpha_Y^3 - \beta_X/\alpha_X^3) \\ = hkl(k_B T)^2 (2\pi/a_0)^3 \mathcal{B}_{YX},$$

where \mathcal{B}_{YX} is an effective cubic anharmonic parameter, our definition of which differs from that of Cooper, Rouse & Fuess (1973). Their parameter $\beta' = \mathcal{B}_{YX} \alpha_Y^3$.

As is well known (Nishikawa & Matukawa, 1928; Coster, Knol & Prins, 1930), in the non-centrosymmetric zinc blende structure anomalous dispersion effects give rise to unequal intensities of Bijvoet pairs of reflections which are equivalent in the absence of dispersion (Friedel, 1913). The derivation of the usual structure factor expressions for zinc blende with the inclusion of the real and imaginary parts of the dispersion corrections leads readily to the conclusion that dispersion-induced intensity differences between Bijvoet pairs exist only for reflections with odd indices and vanish for reflections with even indices.

The generalized structure factor formalism for zinc blende, requiring the introduction of antisymmetric components of the atomic scattering and temperature factors, leads to the more complicated expressions of (3).

We now form the Bijvoet ratios defined as

$$B = \frac{\Delta I}{I_{av}} = \frac{F_{hkl} F_{hkl}^* - F_{\bar{h}\bar{k}\bar{l}} F_{\bar{h}\bar{k}\bar{l}}^*}{\frac{1}{2}(F_{hkl} F_{hkl}^* + F_{\bar{h}\bar{k}\bar{l}} F_{\bar{h}\bar{k}\bar{l}}^*)}, \quad (4)$$

where I_{av} is the average kinematic intensity and ΔI is the intensity difference of a Friedel pair of reflections. Recalling that a change of the signs of the Miller indices corresponds to a change of sign of the odd functions f_a and T_a , we obtain from (3) the following expressions: for reflections with $h + k + l = 4n$ (upper sign) and reflections with $h + k + l = 4n + 2$ (lower sign),

$$\begin{aligned} \Delta I = & 64[f_{a,x} f_X''(T_{c,x}^2 + T_{a,x}^2) + f_{a,y} f_Y''(T_{c,y}^2 + T_{a,y}^2) \\ & \pm (f_{a,x} f_Y'' + f_{a,y} f_X'')(T_{c,x} T_{c,y} + T_{a,x} T_{a,y}) \\ & \mp (f'_{c,x} f_Y' - f'_{c,y} f_X'')(T_{c,x} T_{a,y} - T_{c,y} T_{a,x})] \end{aligned} \quad (5a)$$

$$\begin{aligned} I_{av} = & 16[(f'_{c,x}{}^2 + f_{a,x}^2 + f_X''^2)(T_{c,x}^2 + T_{a,x}^2) \\ & + (f'_{c,y}{}^2 + f_{a,y}^2 + f_Y''^2)(T_{c,y}^2 + T_{a,y}^2)] \\ & \pm 32[(f'_{c,x} f'_{c,y} + f_{a,x} f_{a,y} + f_X'' f_Y'') \\ & \times (T_{c,x} T_{c,y} + T_{a,x} T_{a,y}) - (f'_{c,x} f_{a,y} \\ & - f'_{c,y} f_{a,x})(T_{c,x} T_{a,y} - T_{c,y} T_{a,x})]; \end{aligned} \quad (5b)$$

for $h + k + l = 4n \pm 1$,

$$\begin{aligned} \Delta I = & 64[f_{a,x} f_X''(T_{c,x}^2 + T_{a,x}^2) \\ & + f_{a,y} f_Y''(T_{c,y}^2 + T_{a,y}^2) \\ & \mp (f_{a,x} f_Y'' + f_{a,y} f_X'')(T_{c,x} T_{a,y} - T_{c,y} T_{a,x}) \\ & \mp (f'_{c,x} f_Y' - f'_{c,y} f_X'')(T_{c,x} T_{c,y} + T_{a,x} T_{a,y})], \end{aligned} \quad (5c)$$

$$\begin{aligned} I_{av} = & 16[(f'_{c,x}{}^2 + f_{a,x}^2 + f_X''^2)(T_{c,x}^2 + T_{a,x}^2) \\ & + (f'_{c,y}{}^2 + f_{a,y}^2 + f_Y''^2)(T_{c,y}^2 + T_{a,y}^2)] \\ & \mp 32[(f'_{c,x} f'_{c,y} + f_{a,x} f_{a,y} + f_X'' f_Y'') \\ & (T_{c,x} T_{a,y} - T_{c,y} T_{a,x}) + (f'_{c,x} f_{a,y} - f'_{c,y} f_{a,x}) \\ & (T_{c,x} T_{c,y} + T_{a,x} T_{a,y})]. \end{aligned} \quad (5d)$$

Equation (5a) predicts that when either anharmonicity or bonding cannot be neglected ($f_a, T_a \neq 0$) and dispersion effects are present, reflections with even indices will also exhibit Bijvoet intensity differences. In the case of low-angle reflections affected by bonding electron density redistribution such Bijvoet differences have been observed by Colella (1971), Barnea, McIntyre & Moss (1974) and Bilderback & Colella (1976). For high-angle reflections, where anharmonic effects are largest, the observation of Bijvoet differences of even reflections was first reported by McIntyre, Moss, Boehm & Barnea (1975). The latter effect has also been observed quite markedly in CuCl by Valvoda & Ječný (1978). Both these effects will only appear when at least

one f'' is non-zero. They will, therefore, in general, not be observable with neutrons.

Neglecting terms higher than first order in $T_{a,j}$, setting $f_{a,j} = 0$, and introducing $T_{a,yx}$ results in considerable simplification of (5). For reflections with $h + k + l = 4n$ (upper sign) and reflections with $h + k + l = 4n + 2$ (lower sign),

$$\begin{aligned} \Delta I = & \mp 64(f'_{c,x} f_Y'' - f'_{c,y} f_X'') T_{c,x} T_{c,y} T_{a,yx} \quad (6a) \\ I_{av} = & 16[(f'_{c,x}{}^2 + f_X''^2) T_{c,x}^2 + (f'_{c,y}{}^2 + f_Y''^2) T_{c,y}^2] \\ & \pm 32(f'_{c,x} f'_{c,y} + f_X'' f_Y'') T_{c,x} T_{c,y}; \end{aligned} \quad (6b)$$

for $h + k + l = 4n \pm 1$,

$$\begin{aligned} \Delta I = & \mp 64(f'_{c,x} f_Y'' - f'_{c,y} f_X'') T_{c,x} T_{c,y} \quad (6c) \\ I_{av} = & 16[(f'_{c,x}{}^2 + f_X''^2) T_{c,x}^2 + (f'_{c,y}{}^2 + f_Y''^2) T_{c,y}^2] \\ & \mp 32(f'_{c,x} f'_{c,y} + f_X'' f_Y'') T_{c,x} T_{c,y} T_{a,yx}. \end{aligned} \quad (6d)$$

It is seen that while for all-even reflections it is solely the value of ΔI which depends on $T_{a,yx}$, in the all-odd reflections only the denominator I_{av} depends on this factor. This leads to a possible internal consistency test of experimental measurements: in all-even reflections I_{av} should to first order be the same for reflections having the same value of $\sin \theta/\lambda$ and different sets of Miller indices; in all-odd reflections it is ΔI which provides such a consistency test.

We note that Valvoda & Ječný (1978) have presented X-ray structure factor expressions for the zinc blende structure where anomalous dispersion and the antisymmetric components of the temperature factor are included, but not the antisymmetric components of the scattering factor. Their expressions follow from (2) with $f_{a,j}$ set to zero.

Measurement procedure

All measurements were carried out with a large as-grown single crystal of zinc selenide kindly loaned to us by Sidney G. Parker of Texas Instruments. Parker (1971) describes the method of growth and the physical properties of this crystal. Integrated intensities were measured by the extended-face crystal technique (Mair, Prager & Barnea, 1971a,b; Barnea, 1975) using a very smooth (100) growth face in the shape of a truncated 11×13 mm rectangle. The (100) face was mounted perpendicular to the goniometer head axis on a Picker four-circle manual diffractometer with a full-circle Eulerian cradle. The Philips fine-focus molybdenum X-ray tube was powered by a stabilized Philips PW 1130 generator. The incident beam was collimated to give a divergence of 0.33° for all but the lowest-angle reflections. All measurements were carried out with the direct beam completely intercepted by the crystal.

Photographs of the diffracted beam for several reflections gave clear images of the form expected from a homogeneous single crystal – one straight line inclined to the diffraction plane for each of the $K\alpha_1$ and $K\alpha_2$ components (McIntyre & Barnea, 1980). Balanced zirconium and yttrium oxide filters were placed before the scintillation counter. The measurements were carried out at 296 ± 4 K.

Integrated intensities were measured by the following procedure. Reflections were located with the aid of computed values of the 2θ , φ , and χ angles (ω was set to zero to correspond to symmetric reflection). The reflections were maximized and the diffracted beam was centred in χ with the aid of half-slits. A θ - 2θ scan was used to measure the integrated intensity. A scanning range of $3\frac{1}{2}^\circ$ 2θ was found to be satisfactory for all but the highest-angle reflections. Three low-angle reflections for which the diffracted beams were not completely accepted by the receiving aperture were remeasured with a direct-beam divergence of 0.25° . The error due to counting statistics was reduced to less than one percent by using multiple scans. In order to eliminate absorption effects due to alignment error of reflections, to improve statistics and to check consistency, each reflection was remeasured with $\varphi' = \varphi + 180$ and $\chi' = 180 - \chi$ (we refer to the position in which the normal to the crystal face is in the plane of incidence as the $\chi = 90^\circ$ position).

At least two equivalent reflections were measured for each set of hkl and $\bar{h}\bar{k}\bar{l}$. The internal consistency of measurements was judged by the extent to which the intensities of the two symmetric measurements of each reflection and those of equivalent reflections agreed. 139 independent reflections were measured. The average deviation of the intensity of a reflection from the mean value of the entire set of measurements of that reflection and its equivalents was 1.7%.

Analysis of data

The data were corrected for first-order anisotropic thermal diffuse scattering (TDS) whose contribution was calculated with the *XTDS2* program of Walker & Chipman (1971). The elastic constants of ZnSe required for this calculation were due to Lee (1970). The lattice parameter was taken to be 5.6670 \AA . The two intensity measurements of each reflection and the intensities of equivalent reflections were averaged after application of the TDS correction. The anisotropic TDS correction depends on the vector about which the crystal is rotated and is in general somewhat different for each equivalent reflection and mode of measurement.

The observed integrated intensities were analysed

using the *LSEFC5* least-squares program developed specifically for the analysis of anharmonic thermal vibrations in zinc blende structures. The program included provisions for the refinement of extinction parameters. The quantity minimized was

$$\mathcal{S} = \sum_i [w_i(I_{oi} - I_{ci})]^2,$$

where I_{oi} is the observed intensity of the i th reflection (corrected for TDS), I_{ci} is the corresponding calculated intensity and w_i is the weight given to the difference $I_{oi} - I_{ci}$. Apart from the subtraction of TDS, corrections for all systematic effects were applied to the calculated intensities. These were calculated using the free atomic scattering factors of Doyle & Turner (1968) and the dispersion corrections of Cromer & Liberman (1970). The extinction factor was that defined by Zachariasen's (1967) theory. A more detailed discussion of extinction in ZnSe will be published elsewhere. In this paper we shall confine ourselves to a comparison of refinements which include the entire data set with refinements in which reflections exhibiting appreciable extinction were omitted.

The weights were given by the reciprocal estimated variances of $I_{oi} - I_{ci}$. The variance of $I_{oi} - I_{ci}$ was estimated by an adaptation of the procedure proposed by Abrahams (1969) and Abrahams, Bernstein & Keve (1971). The law of propagation of errors was used to calculate the variance in the observed intensity after each correction. A nominal error of 10% was assigned to the calculation of TDS contributions and one of 20% to the extinction correction $1 - y$ where y is the extinction factor. This resulted in the relative downgrading of the importance of reflections affected by extinction. Since the weights are given by the reciprocal of the variance of $I_{oi} - I_{ci}$, the possible uncertainty in the extinction model is also reflected in the total variance. The contribution of the population statistics σ_{pop}^2 was smoothed to compensate for the spread due to the small populations by averaging the coefficient of variation $\sigma_{\text{pop}}/I_{oi}$ over sets of reflections of almost equal intensity.

Discussion

The experimental data and results are summarized in Tables 1, 2 and 3. Table 1 lists the observed and calculated reflection data. The observed and calculated Bijvoet ratios, B_o and B_c , are formed by the difference in the intensities of the Bijvoet pair divided by the average intensity.

Table 2 lists the final parameters for ZnSe and their estimated standard deviations. The table includes also

Table 1. Reflection data for the ZnSe extended-face crystal and Mo K α X-radiation

h	k	l	I_{oi}^*	I_{cl}	σ'/I_{oi}	y	$B_o(\times 100)$	$B_c(\times 100)$
7	-5		53481	52982	0.016	0.986	-9.8	-9.3
7	7	1	50883	51371	0.016	0.986		
7	7	-1	45797	46661	0.016	0.988	10.5	9.6
9	3	3	51806	51141	0.016	0.986		
9	3	-3	46982	46430	0.016	0.988	9.8	9.6
8	6	2	(81156)	81986	0.017	0.978		
8	6	-2	(80986)	81922	0.017	0.978	0.2	0.1
10	0	2	(81243)	81954	0.016	0.978		
7	7	3	37434	38512	0.016	0.989		
7	7	-3	41478	42589	0.016	0.988	-10.2	-10.1
9	5	1	41453	41479	0.016	0.989		
9	5	-1	37227	37400	0.016	0.990	10.7	10.3
9	5	3	32564	31370	0.016	0.991		
9	5	-3	35887	34950	0.016	0.990	-9.7	-10.8
10	4	2	52624	55261	0.017	0.984		
10	4	-2	52665	55219	0.017	0.984	-0.1	0.1
7	7	5	27627	27754	0.016	0.992		
7	7	-5	24734	24567	0.016	0.993	11.1	12.2
11	1	1	25791	25576	0.016	0.993		
11	1	-1	29406	28762	0.016	0.992	-13.1	-11.7
9	5	5	22867	23710	0.023	0.993		
9	5	-5	20109	20841	0.023	0.994	12.8	12.9
9	7	1	21705	21803	0.022	0.994		
9	7	-1	24437	24670	0.017	0.993	-11.8	-12.3
11	3	1	24165	24350	0.023	0.993		
11	3	-1	21411	21482	0.023	0.994	12.1	12.5
9	7	3	20611	20644	0.023	0.994		
9	7	-3	18162	18032	0.024	0.995	12.6	13.5
11	3	3	18857	18860	0.023	0.995		
11	3	-3	21619	21471	0.023	0.994	-13.6	-13.0
8	8	4	34500	34839	0.017	0.990		
8	8	-4	34706	34739	0.017	0.990	-0.6	0.3
7	7	7	17132	17109	0.024	0.995		
7	7	-7	19680	19513	0.024	0.995	-13.8	-13.1
11	5	1	16658	16385	0.023	0.995		
11	5	-1	18980	18790	0.023	0.995	-13.0	-13.7
9	7	5	15101	15142	0.023	0.996		
9	7	-5	17864	17380	0.023	0.995	-16.8	-13.8
11	5	3	17182	16309	0.024	0.996		
11	5	-3	15084	14069	0.024	0.996	13.0	14.7
9	9	1	14756	14972	0.023	0.996		
9	9	-1	12592	12866	0.023	0.997	15.8	15.1
9	9	3	12608	12382	0.024	0.997		
9	9	-3	14892	14382	0.024	0.997	-16.6	-15.0
11	5	5	12980	12440	0.024	0.997		
11	5	-5	15054	14441	0.024	0.997	-14.8	-14.9
11	7	1	14622	13793	0.024	0.997		
11	7	-1	12300	11792	0.024	0.997	17.2	15.6
13	1	1	13632	13911	0.023	0.997		
13	1	-1	11619	11910	0.023	0.997	15.9	15.5
9	7	7	12785	12259	0.024	0.997		
9	7	-7	11077	10338	0.024	0.998	14.3	17.0
11	7	3	11228	11485	0.023	0.997		
11	7	-3	13144	13405	0.023	0.997	-15.7	-15.4
13	3	1	11629	11157	0.024	0.998		
13	3	-1	13699	13077	0.024	0.997	-16.3	-15.9
12	6	2	22874	21904	0.023	0.995		
12	6	-2	22699	21861	0.023	0.995	0.8	0.2
9	9	5	12391	11670	0.024	0.998		
9	9	-5	10251	9807	0.025	0.998	18.9	17.3
13	3	3	11842	12131	0.023	0.998		
13	3	-3	10053	10269	0.023	0.998	16.3	16.6
8	8	8	20221	20884	0.023	0.996		
8	8	-8	20154	20735	0.023	0.996	0.3	0.7
11	7	5	10815	11243	0.024	0.998		
11	7	-5	8956	9417	0.024	0.998	18.8	17.7
13	5	1	12274	11732	0.024	0.998		
13	5	-1	10237	9906	0.025	0.998	18.1	16.9
10	10	0	19345	20085	0.026	0.996		
10	10	6	19119	20154	0.023	0.996		
10	10	-6	19114	20016	0.023	0.996	0.0	0.7
14	0	2	19783	20085	0.023	0.996		
1	1	1	(8979884)	5881686	0.164	0.458		
1	1	-1	(8715469)	5724962	0.160	0.466	3.0	2.7
2	0	0	(64598)	53682	0.056	0.992		
2	2	0	(7365934)	5156487	0.152	0.497		
3	1	1	(2610770)	2499646	0.109	0.697		
3	1	-1	(2710633)	2602637	0.112	0.687	-3.6	-4.0
2	2	2	(27574)	28166	0.058	0.996		
2	2	-2	(25497)	28398	0.058	0.996	7.8	-0.8
4	0	0	(3225753)	2990063	0.112	0.649		
3	3	1	(1510830)	1498458	0.066	0.800		
3	3	-1	(1416589)	1429901	0.064	0.808	7.0	4.7
4	2	0	26774	26713	0.016	0.996		
4	2	2	(1856639)	1898303	0.099	0.751		
4	2	-2	(1845555)	1898194	0.099	0.751	0.6	0.0
3	3	3	(915284)	892054	0.058	0.872		
3	3	-3	(954510)	937970	0.058	0.866	-4.2	-5.0
5	1	1	(951534)	934019	0.035	0.866		
5	1	-1	(887003)	888050	0.034	0.872	7.0	5.0
4	4	0	(1174704)	1253992	0.087	0.821		
5	3	1	(584580)	579229	0.025	0.911		
5	3	-1	(615703)	610854	0.026	0.907	-5.2	-5.3
4	4	2	20890	20284	0.022	0.997		
4	4	-2	21133	20467	0.022	0.997	-1.2	-0.9
6	2	0	(840865)	851426	0.035	0.869		
5	3	3	(416268)	408902	0.021	0.933		
5	3	-3	(389407)	386360	0.021	0.937	6.7	5.7
6	2	2	17056	16515	0.022	0.997		
6	2	-2	17500	16609	0.022	0.997	-2.6	-0.6
4	4	4	(593593)	591794	0.055	0.902		
4	4	-4	(587805)	591622	0.055	0.902	1.0	0.0
5	5	1	(282904)	284773	0.019	0.950		
5	5	-1	(265603)	268161	0.019	0.953	6.3	6.0
7	1	1	(275863)	269448	0.019	0.953		
7	1	-1	(290090)	286053	0.019	0.950	-5.0	-6.0
6	4	2	(413086)	420236	0.023	0.925		
6	4	-2	(411937)	420137	0.023	0.925	0.3	0.0
5	5	3	(188718)	193053	0.017	0.964		
5	5	-3	(202179)	205696	0.018	0.961	-6.9	-6.3
7	3	1	(206190)	202952	0.017	0.962		
7	3	-1	(192189)	190295	0.017	0.964	7.0	6.4
7	3	3	(141065)	139786	0.017	0.972		
7	3	-3	(151661)	149711	0.017	0.970	-7.2	-6.9
6	4	4	7628	8125	0.023	0.998		
6	4	-4	7983	8281	0.023	0.998	-4.6	-1.9
6	0	6	(219207)	225367	0.019	0.953		
8	2	2	(221887)	225388	0.019	0.953		
8	2	-2	(221522)	225346	0.019	0.953	0.2	0.0
5	5	5	(106002)	108638	0.016	0.976		
5	5	-5	(98804)	100637	0.016	0.978	7.0	7.6
7	5	1	(104035)	103131	0.016	0.978		
7	5	-1	(111910)	111123	0.016	0.976	-7.3	-7.5
6	6	2	5908	6460	0.066	0.999		
6	6	-2	6112	6553	0.066	0.999	-3.4	-1.4
7	5	3	(83871)	82903	0.016	0.981		
7	5	-3	(77374)	76320	0.016	0.982	8.1	8.3
9	1	1	(85333)	84035	0.016	0.980		
9	1	-1	(78571)	77455	0.016	0.982	8.3	8.1
8	4	2	4805	5177	0.066	0.999		
8	4	-2	4968	5245	0.066	0.999	-3.3	-1.3
6	6	4	(128062)	130891	0.017	0.968		
6	6	-4	(127807)	130761	0.017	0.968	0.2	0.1
9	3	1	63004	60055	0.016	0.985		
9	3	-1	68273	65574	0.016	0.984	-8.0	-8.8
8	4	4	(99917)	102632	0.017	0.974		
8	4	-4	(100503)	102533	0.017	0.974	-0.6	0.1
7	5	5	48461	48276	0.016	0.987		

* I_{oi} in parentheses were excluded from refinement 2.

Table 2. *Final values of parameters for ZnSe*

	Refinement 1	Refinement 2
α_{Zn}	3.160 (0.013)	3.163 (0.017) $\times 10^{-19} \text{ J } \text{Å}^{-2}$
α_{Se}	4.344 (0.033)	4.364 (0.035) $\times 10^{-19} \text{ J } \text{Å}^{-2}$
\mathcal{B}_{ZnSe}	-7.0 (0.9)	-6.8 (1.1) $\times 10^{36} \text{ J}^{-2} \text{Å}^3$
B_{Zn}	1.021 (0.004)	1.020 (0.005) Å^2
B_{Se}	0.743 (0.006)	0.739 (0.008) Å^2
r^*	5.12 (0.68)	— $\times 10^{-7} \text{ m}$
K	118.2 (1.2)	116.9 (1.7)
R''	0.0281	0.0314
σ_1	1.322	1.559

Table 3. *Thermal parameters obtained for ZnS, ZnSe and ZnTe*

	ZnS	ZnSe	ZnTe
a_0	5.4093	5.6670	6.1026 Å
α_x	3.633 (0.019)	3.163 (0.017)	2.463 (0.065) $\times 10^{-19} \text{ J } \text{Å}^{-2}$
α_y	4.408 (0.024)	4.364 (0.035)	4.213 (0.062) $\times 10^{-19} \text{ J } \text{Å}^{-2}$
\mathcal{B}_{Yx}	-4.9 (1.3)	-6.8 (1.1)	-5.1 (1.3) $\times 10^{36} \text{ J}^{-2} \text{Å}^3$
β'	-4.2 (1.1)	-5.6 (0.9)	-3.8 (1.0) $\times 10^{-19} \text{ J } \text{Å}^{-3}$
α_x/α_y	0.824 (0.006)	0.725 (0.007)	0.585 (0.018)
B_x	0.879 (0.005)	1.020 (0.005)	1.296 (0.034) Å^2
B_y	0.724 (0.004)	0.739 (0.008)	0.758 (0.011) Å^2
B_x/a_0^2	3.00 (0.02)	3.18 (0.02)	3.48 (0.09) $\times 10^{-2}$
B_y/a_0^2	2.47 (0.01)	2.30 (0.02)	2.04 (0.03) $\times 10^{-2}$
B_x/a_0^4	10.27 (0.06)	9.89 (0.05)	9.34 (0.25) $\times 10^{-4} \text{ Å}^{-2}$
B_y/a_0^4	8.46 (0.05)	7.17 (0.08)	5.47 (0.08) $\times 10^{-4} \text{ Å}^{-2}$
$(B_x + B_y)/a_0^2$	5.47 (0.03)	5.48 (0.04)	5.52 (0.12) $\times 10^{-2}$

the scale factor K , the effective domain radius r^* , the reliability index

$$R'' = \left[\frac{\sum_l w_l (I_{oi} - I_{ci})^2 / \sum_l w_l I_{oi}^2}{\sum_l w_l I_{oi}^2} \right]^{1/2}$$

and the goodness of fit

$$\sigma_1 = \left[\frac{\sum_l w_l (I_{oi} - I_{ci})^2 / (m - n)}{\sum_l w_l I_{oi}^2} \right]^{1/2},$$

where m is the number of independent observations and n is the number of variables. Refinement 1 refers to a refinement in which all reflections were included and an extinction parameter refined. It is evident from Table 1 (which lists the results of refinement 1) that those reflections most affected by extinction are in systematic disagreement with the calculated intensities, in spite of the extinction correction. Since anharmonic effects are most dominant in the region of high Bragg angles, we carried out a further refinement from which we excluded all reflections for which y in refinement 1 was less than 0.98 (two other weak reflections, the 200 and 222, most affected by bonding, were also excluded). Refinement 2 included no correction for extinction. Comparison of the results of the two refinements shows excellent agreement between the thermal parameters. We therefore believe that extinction did not affect our final results.

Comparison of intensities of symmetrically non-equivalent reflections occurring at the same Bragg angle (*e.g.* 775, 775̄, 11,1,1 and 11,1,1̄ reflections)

manifests clearly the differing anharmonic contribution to these sets. The significance of the anharmonic parameter was evaluated by comparing the reliability indices of least-squares refinements including and neglecting anharmonicity. The significance level was then estimated from the significance tables of Hamilton (1965). The ratio of the indices was found to be 1.22 and this corresponds to a significance level of less than 0.005. Attempts to refine individual values of β_j by using (3) were unsuccessful. This is in agreement with a similar experience reported by Cooper, Rouse & Fuess (1973) for ZnS and ZnTe. Effects due to quartic terms were not expected to be significant at room temperature.

Our final thermal parameters should be compared with those reported by Raccach, Euwema, Stukel & Collins (1970) who found $B_{Zn} = 0.97 \pm 0.07$ and $B_{Se} = 0.74 \pm 0.01$, in good agreement with our values listed in Table 2. It should be noted that the two sets of results may not be strictly comparable since our data were corrected for thermal diffuse scattering, and Raccach, Euwema, Stukel & Collins do not mention any such correction. Another comparison is afforded by the results of a neutron diffraction study by Cooper, Rouse & Fuess (1973) of ZnS and ZnTe. Their results and the results of our study are summarized in Table 3. The quantities in parentheses are the estimated standard deviations. Table 3 also lists various ratios of the B factors and of their sum to various powers of the lattice parameter a_0 .

Several systematic trends are noted: The value of the harmonic thermal parameter α of both atoms decreases with increasing atomic number and as the unit cell becomes larger. The decrease of α_x is more rapid than that of α_y . This is very similar to the trends observed for the fluorites CaF_2 , SrF_2 and BaF_2 (Cooper & Rouse, 1971). A further trend can be recognized in the B factors of the two atoms divided by the square of the lattice parameter. The values of B_{Zn}/a_0^2 increase and the values of B_Y/a_0^2 decrease with increasing atomic number of atom Y .

It is interesting to note that the sum of the B factors divided by the square of the lattice parameter is constant for all three crystals. This is, of course, very reasonable, implying a not-unexpected linear relationship between the sum of the squares of the amplitudes of the thermal vibrations and the lattice parameters squared. An almost constant value of this ratio (10.5 ± 0.5) is similarly obtained for the alkali halides (NaF, NaCl, KCl, KBr and RbCl) using the values listed by Linkoaho (1969); LiF and LiCl have somewhat different values of this ratio — 11.2 and 13.3 respectively.

In Table 4 we compare the experimental B factors of Table 3 with theoretical calculations due to Vetelino, Gaur & Mitra (1972) and Hewat (1970). It is seen that neither of the sets of calculated B factors is in

agreement with the experimental values, those of Hewat being in somewhat better agreement.

The Debye temperature calculated from our harmonic B factors by the formula of Barron, Leadbetter, Morrison & Salter (1966) was 235 ± 1 K in good agreement with the value of 237 ± 6 K of Sharma (1972).

The errors in the anharmonic parameters of the three crystals preclude any statement about trends.

Table 1 compares the observed Bijvoet ratios B_o

$$B_o = (I_{hkl} - I_{\bar{h}\bar{k}\bar{l}}) / \frac{1}{2}(I_{hkl} + I_{\bar{h}\bar{k}\bar{l}}),$$

where I_{hkl} is the observed intensity of a reflection with Miller indices h , k and l , with the calculated (extinction corrected) values B_c . It is seen that the agreement between the calculated and observed Bijvoet ratios is excellent; the experimental error of the listed ratios estimated from differences between equivalent reflections was about ± 1.5 units of $100B_o$. This magnitude of the error tends to obscure the differences between Bijvoet ratios of reflections having different Miller indices but occurring at the same value of $\sin \theta/\lambda$. That such differences are to be expected when anharmonicity is allowed for can be seen from (6a) and (6d).

The reported value of B_o for the 222–22 $\bar{2}$ pair of reflections, as well as the intensity of the 200 reflection, will be discussed in the context of bonding in a separate note (Moss, McIntyre, Boehm & Barnea, 1980).

We were precluded from reliably observing the intensity difference of the 666–66 $\bar{6}$ pair of reflections by their very low intensities; a reliable measurement of this difference is of considerable interest, since it reflects directly the magnitude of the anharmonic parameter.

Conclusions

The generalized structure factor expressions for the non-centrosymmetric zinc blende structure predict, when dispersion effects are included, the breakdown of Friedel's law for reflections with all-even, non-zero

Table 4. Comparison of experimental and calculated B factors (\AA^2)

		Experimental	Theoretical ¹	Theoretical ²
ZnS	B_{Zn}	0.879 (0.005)	0.566	0.81
	B_S	0.724 (0.004)	0.584	0.78
ZnSe	B_{Zn}	1.020 (0.005)	0.624	0.94
	B_{Se}	0.739 (0.008)	0.621	0.92
ZnTe	B_{Zn}	1.296 (0.034)	0.732	1.24
	B_{Te}	0.758 (0.011)	0.724	1.40

(1) Vetelino, Gaur & Mitra (1972).

(2) Hewat (1970).

indices. This breakdown can be due either to bonding effects or to anharmonicity and will, in general, be due to both simultaneously. It should be noted that since the anharmonic term favours motion in the anti-bonding direction, the effects of bonding and anharmonicity on the Bijvoet ratios are opposite in sign.

Bijvoet ratios of reflections at the same $\sin \theta/\lambda$ are generally different. This difference may be sufficiently large to be measurable and must hence be allowed for in the accurate interpretation of Bijvoet ratios.

Intensity measurements of high internal consistency, such as are obtained with extended-face crystals, will often exhibit anharmonic effects, the customary neglect of which may no longer be justified.

Our experimental results give us no reason to doubt the theoretically calculated dispersion corrections (and f'' in particular) on which our interpretation is based.

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Calculation of the Lattice Energies and the Energies of Complexation of Some Paraquinones and Parahydroquinones

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Abstract

The lattice energies and the solid-state energies of complexation of a number of benzo- and naphthoquinones and -hydroquinones are calculated by methods making use of atom-atom potentials. For the lattice energies, quantitative agreement with experimental data is satisfying. For the much smaller energies of complexation, qualitative agreement, with the right sign and of the right order of magnitude, is obtained.

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Introduction

The quinones form molecular complexes with a number of chemical species, e.g. hydroquinones. The crystal structures of three of these molecular complexes, 1,4-naphthoquinone-1,4-naphthohydroquinone (2/1), 1,4-naphthoquinone-1,4-hydroquinone (1/1) and 1,4-benzoquinone-1,4-hydroquinone (1/1) are known, as well as the crystal structures of the four individual compounds (Table 1). The various enthalpies of com-

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