58. Anharmonic Potential of Atomic Thermal Motion in ZnX ($\text{X}=\text{S}, \text{Se}, \text{Te}$)

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Cowley initiated in 1969 the lattice dynamical theory of anharmonic thermal vibrations in crystals. Several experimental derivations of the probability function of anharmonicity were proposed on the basis of neutron and X-ray diffraction intensities (Johnson, 1969; Willis, 1969; Kurki-Sunio *et al.*, 1979), and comparative studies of these multimodule distribution functions have been published (Moss *et al.*, 1980; Zucker *et al.*, 1982; Kuhs, 1982).

In order to obtain a deeper understanding of the nature of thermal motions of atoms in crystals, however, we must carry out comprehensive studies of the effects of temperature, crystal symmetry, and chemical bond character on the anharmonicity. In our earlier paper we dealt with the anharmonic vibrations in MgAl_2O_4 up to 1660° .

In the present work, X-ray diffraction experiments were made with ZnX 's ($\text{X}=\text{S}, \text{Se}, \text{Te}$), all of sphalerite structure-type ($\bar{F}43m$, $z=4$, Zn and X respectively at 0,0,0 and $1/4, 1/4, 1/4$, both with $\bar{4}3m$) but of bond character different from one another, and the results will be described in this paper, together with discussion of one-particle potentials, effective charges and force constants in these compounds (on neutron diffraction study, see Cooper *et al.* (1973)).

Harmonic refinement: X-ray intensity data were collected with a four-circle diffractometer. Corrections were allowed for L_p and absorption effects. Refinement including temperature factors $T(h)$ based on harmonic oscillation and an isotropic extinction parameter was conducted by the ordinary least squares method (Table I).

The effect of thermal diffuse scatterings (TDS) was also taken into account prior to the refinement, and the first-order scattering by one-phonon acoustic lattice vibration was assumed for the TDS correction. The program SXTDS1 (Merisalo and Kuritts, 1970) was employed for the evaluation of α in $I_0 = I_{\text{Bragg}}(1 + \alpha)$. Three independent elastic constants, c_{11} , c_{44} and c_{12} were used, but the correction was carried out in terms, not only of these elastic constants, but also of the scanning mode and the scanning vector defined by the UB matrix.

Table I. Harmonic and anharmonic thermal parameters

		ZnS			ZnSe			ZnTe		
a (Å)		5.4053			5.6609			6.0862		
$\sin\theta/\lambda$		1.32			1.32			1.32		
No. ref.		107			93			142		
		Harm.		Anharm.	Harm.		Anharm.	Harm.		Anharm.
		-	TDS	TDS	-	TDS	TDS	-	TDS	TDS
R (%)		1.74	1.66	1.29	1.68	1.68	1.60	1.63	1.58	1.54
R wt (%)		1.78	1.72	1.32	1.62	1.62	1.61	1.56	1.51	1.50
Zn	β_{11} $\times 10^5$	749(7)	758(6)	746(6)	877(12)	882(12)	870(9)	897(9)	899(8)	938(6)
	γ_{123} $\times 10^7$			320(9)			932(10)			1289(17)
	δ_{1111} $\times 10^8$			90(9)			487(10)			270(15)
	δ_{1122} $\times 10^8$			-85(6)			307(6)			200(6)
X	β_{11} $\times 10^5$	600(10)	613(10)	610(8)	593(7)	597(7)	567(4)	619(4)	622(4)	651(5)
	γ_{123} $\times 10^7$			258(11)			836(15)			528(20)
	δ_{1111} $\times 10^8$			-437(10)			-435(12)			-150(17)
	δ_{1122} $\times 10^8$			-87(9)			-124(10)			-166(13)
G ext. $\times 10^6$		6.88	6.88	7.13	8.72	8.72	8.78	3.00	3.00	3.10

Fig. 1. Difference Fourier syntheses from the harmonic refinement with the TDS correction. The chart of A, B and C represent that of ZnS, ZnSe and ZnTe, respectively, each showing a section passing through the Zn and X atoms and parallel to (110). Contours are drawn at intervals of $0.2 \text{ e}/\text{\AA}^3$, starting from the $0.2 \text{ e}/\text{\AA}^3$ contour. Solid and broken lines present positive and negative contours, respectively.

Residual electron density: Difference Fourier syntheses after the harmonic refinements of ZnS ($R=0.0174$), ZnSe ($R=0.0168$) and ZnTe ($R=0.0163$) exhibit residual electron densities around Zn and X atoms (Fig. 1), the former assuming a tetrapod-like shape. Because none of lone-pair electrons, split atoms, and aspherical electron distribution based on Zn ($3d^{10}4s^2$) is conceivable in the structures of the present compounds, the residual densities around Zn must be due to anharmonic vibrations. In spite that the point symmetry at the site of the X atom is the same as that of the Zn atom, the configuration of the residual densities around X differs from that around Zn. This situation is no doubt due to a combination of thermal motions with aspherical electron distributions of X atoms, atomic thermal displacements of almost the same extent having been reported for Zn and X from a neutron diffraction study (Moss *et al.*, 1980). This conclusion is in harmony with the calculation of the valence charge density distributions in Ge, GaAs, and ZnSe (Cohen, 1973), which revealed that the valence charge density in ZnSe is localized only around Se atoms.

Lattice dynamical consideration: Analyses of lattice vibrations in ZnX were undertaken in terms of transverse optical wave number (ν_{TO}) and longitudinal wave number (ν_{LO}) measured by means of the Raman spectroscopy. The evaluated force constants $K(\text{Zn}\dots\text{X})$ and effective charge $Ze(\text{Zn})$ are presented in Table II. In comparison

Table II. Effective charge and force constant

	ZnS	ZnSe	ZnTe
$d(\text{Zn-X})$	2.342	2.454	2.637 ($\text{\AA}$)
V	158.3	182.1	225.8 ($\text{\AA}^3$)
μ	21.51	35.76	43.23 (g)
ν_{TO}	282	207	117 (cm^{-1})
ν_{LO}	352	246	206 (cm^{-1})
<u>Rigid ion model</u>			
$Ze(\text{Zn})$	0.88	0.76	0.74
$K(\text{Zn}\dots\text{X})$	0.597	0.513	0.446 ($\text{mdyn/\AA}$)
R	0.157	0.121	0.106
<u>Shell model</u>			
e	8.00	8.33	9.86
e_∞	5.14	5.90	7.28
$Ze(\text{Zn})$	0.84	0.71	0.65
$K(\text{Zn}\dots\text{X})$	0.709	0.590	0.509 ($\text{mdyn/\AA}$)
R	0.291	0.236	0.216

with ZnS and ZnSe, ZnTe is smaller in force constant and less in ionic bond character, which tendency is consistent with its large electron conductivity and low Debye temperature. The bond characters of ZnTe indicate that among the three compounds under examination, this one possesses the largest Grüneisen parameter γ_G in $\Delta\nu/\nu$

$= -\gamma_o \chi T$ where χ is the volume expansion coefficient. According to Cochran (1973),

$$T(Q)_{\text{anh}} = T(Q)_h (1 + \gamma_o \chi T)$$

holds; the anharmonicity in the temperature factor is intensified with the increase of the Grüneisen parameter.

Anharmonic potential: Among various approaches to the anharmonic refinement, we chose in this study the way to deal with the structure factor with anharmonic temperature parameters expressed in the form of Edgeworth expansion (Johnson, 1969); the temperature factor $T(h)$ is then given by

$$T(h) = \exp \left(\frac{i^2}{2!} \sum \sum B h_j h_k + \frac{i^3}{3!} \sum \sum \sum C h_j h_k h_l + \frac{i^4}{4!} \sum \sum \sum \sum D h_j h_k h_l h_m \right) \quad (1)$$

where B , C and D are the second, third and fourth order Edgeworth expansion coefficients respectively, coefficients higher than the fourth being neglected. For the cubic site symmetry $\bar{4}3m$, $\beta_{11}(=\beta_{22}=\beta_{33})$ of six β_{ij} 's belonging to B , γ_{123} of ten γ_{ijk} 's to C and $\delta_{1111}(=\delta_{2222}=\delta_{3333})$ and $\delta_{1122}(\delta_{1133}=\delta_{2233})$ of fifteen δ_{ijkl} 's to D , are independent variables.

The temperature factor $T(h)$ is the Fourier transform of the probability density function $P(u)$:

$$T(h) = \int P(u) \exp \{2\pi i(H \cdot u)\} du$$

and this probability density function $P(u)$ is related with the effective one-particle potential (OPP), $V(u)$, by a cubic site symmetry (Willis, 1969) as

$$P(u) = \exp \{ -V(u)/kT \} / \iiint \exp \{ -V(u_1 u_2 u_3)/kT \} du_1 du_2 du_3,$$

where k is Boltzmann's constant. With the assumption that each atom independently vibrates within the range of an average potential defined by its neighbours, the anharmonic potential $V(u)$ is given by

$$V(u) = V_0 + \frac{1}{2} \alpha \mathbf{u}^2 + \beta u_1 u_2 u_3 + \gamma \mathbf{u}^4 + \delta \left(u_1^4 + u_2^4 + u_3^4 - \frac{3}{5} \mathbf{u}^4 \right) \quad (2)$$

where $\mathbf{u}^2 = u_1^2 + u_2^2 + u_3^2$ and $\mathbf{u}^4 = (u_1^2 + u_2^2 + u_3^2)^2$.

The use of the OPP as a function of anharmonic thermal parameters has been studied by many workers (Willis, 1969; Mair and Wilkins, 1976; Zucker *et al.*, 1982; Kuhs, 1982; Kontio and Stevens, 1982). In the present calculation, α , β , γ and δ in the OPP equation (2) were determined from the coefficients B , C and D in the Edgeworth expansion (1) and potential parameters were evaluated from these β_{11} , γ_{123} , δ_{1111} and δ_{1122} (Table I).

The one-particle potential along the Zn-X bond to $\langle 111 \rangle$ directions are plotted against the atomic displacement u from the Zn

Fig. 2. One-particle potentials along the $\langle 111 \rangle$ direction of ZnX ($\text{X}=\text{S}, \text{Se}, \text{Te}$). The axis of abscissa represents the bond distance Zn-X from the position of Zn atom.

position, (0 0 0), for each of the three compounds (Fig. 2). It is obvious in this figure that the potential curve of ZnTe is located lower and deviates from the parabolic harmonic potential curve to much larger an extent than those of the other two compounds. This fact, together with the difference Fourier maps, indicates that ZnTe having the smallest effective charge and force constant shows the most salient anharmonicity of atomic thermal vibration among the three materials examined in this study.

References

- Cochran, W. (1973): The dynamics of atoms in crystals. Edward Arnold Ltd.
 Cohen, M. L. (1973): Science, **179**, 1189.
 Cooper, M. J., and Rouse, K. (1973): Acta Cryst., **A29**, 49–56.
 Cowley, R. A. (1969): The lattice dynamics of an anharmonic crystal. Adv. Phys., **12**, 421–480.
 Johnson, C. K. (1969): Acta Cryst. **A25**, 187–194.
 Kontio, A., and Stevens, E. D. (1982): ibid., **A38**, 623–629.
 Kurki-Suonio, K., Merisalo, M., and Peltonen, H. (1979): Physica Script., **19**, 57–63.
 Kuhs, W. F. (1983): Acta Cryst., **A39**, 148–158.
 Mair, S. L., and Kurittu, J. (1978): J. Appl. Cryst., **11**, 179–182.
 Moss, B., McMullan, R. K., and Koetzle, T. F. (1980): J. Chem. Phys., **73**, 495–508.
 Willis, B. T. M. (1969): Acta Cryst., **A25**, 277–300.
 Zucker, U. H., and Schulz, H. (1982): ibid., **A38**, 563–568.