

is concluded that better estimates are obtained with anharmonic temperature factors if a significant improvement in fitting the experimental data with the anharmonic model is obtained.

Anharmonic temperature factors were programmed for structures where the anharmonicity is due to librations of (rigid) molecules. Here only three anharmonic parameters are needed (three parameters of the (supposed) principal librations about a supposed origin). The anharmonic third order vibration tensors of the individual atoms concerned are all calculated from these three librational parameters. In refinements with the structures of thiopyridone and nicotinic acid (room temperature X-ray data) the weighted R values were significantly lowered (significance level  $\alpha < 0.005$ ) with these three extra parameters. The values of the librational components obtained do not always agree with those obtained from a TLS analysis of the harmonic vibration tensors. For the anharmonic model the distances between the mean positions were always shorter than those for the harmonic model. For thiopyridone the decreases were  $\leq 0.0012$  Å, for nicotinic acid  $\leq 0.0060$  Å. For urea, thiourea and p-dicyanobenzene at low temperature, deformation densities were calculated with only harmonic and with the three additional anharmonic parameters. Comparison of the maps shows that the effect of the anharmonic motions on the density distribution is small and rarely exceeds  $0.1eA^{-3}$ . For heavier atoms the effect may well be larger.

densities around X(S,Se,Te) ascribe to both effects of the anharmonicity and valence electron density given by the pseudopotential calculation (Cohen, Science (1973) 179, 1189). These features are more remarkable in ZnTe having a covalent bonding character stronger than those of ZnSe or ZnS.

Before the anharmonic refinement, the effect of thermal diffuse scattering (TDS) was taken into account for the diffraction intensity correction. A theoretical approach for the TDS correction derived from Merrisalo and Kurrits (J. Appl. Cryst. (1978) 11, 179) was employed. The evaluation of the TDS correction factor  $\alpha$  in the equation of  $I_{obs} = I_{Bragg}(1 + \alpha)$  was conducted in terms of not only elastic constants of ZnX but also scanning modes and scattering vector defined by the UB matrix. The TDS correction resulted in the improvement of the reliability (R-factor) of the refinement.

For the anharmonic refinement, a cumulant expansion of  $T(Q)$  in the form  $T(Q) = \exp[\sum (i^n/n!) \psi_{pqr...} q_p q_q q_r \dots]$  (Johnson, Acta Cryst. (1969) A25, 187) was adopted. The coefficients of the higher order anharmonic tensors of atoms in ZnTe are exceedingly larger than those in ZnS (Table 1), probably resulting from the difference in the nature of chemical bonds unlike the results of a neutron diffraction study by Cooper et al. (Acta Cryst. (1973) A29, 49).

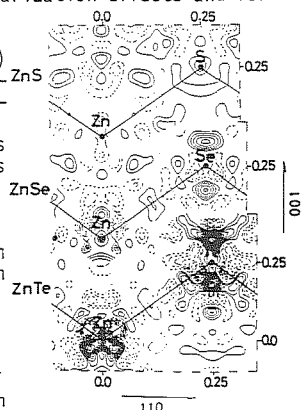
	ZnS		ZnSe		ZnTe	
a (Å)	5.4053		5.6609		6.0862	
sinθ/λ	1.32		1.32		1.32	
No. ref.	107		93		142	
	Harm.	Anharm.	Harm.	Anharm.	Harm.	Anharm.
R (%)	1.74	1.29	1.68	1.60	1.63	1.54
R <sub>w</sub> (%)	1.78	1.32	1.62	1.61	1.56	1.50
B <sub>11</sub> (Zn) 10 <sup>6</sup>	749	746	877	870	897	938
B <sub>11</sub> (X) 10 <sup>6</sup>	600	610	593	567	619	651
γ <sub>122</sub> (Zn) 10 <sup>7</sup>		320		932		1289
γ <sub>122</sub> (X) 10 <sup>7</sup>		258		836		528
δ <sub>1111</sub> (Zn) 10 <sup>8</sup>		90		487		270
δ <sub>1111</sub> (X) 10 <sup>8</sup>		-437		-435		-150
δ <sub>1122</sub> (Zn) 10 <sup>8</sup>		-85		307		200
δ <sub>1122</sub> (X) 10 <sup>8</sup>		-87		-124		-166
G ext. 10 <sup>6</sup>	6.88	7.13	8.72	8.78	3.00	3.10

06.5-2 X-RAY DIFFRACTION STUDY ON THE ANHARMONIC THERMAL VIBRATIONS OF ATOMS IN ZnX(X=S,Se,Te) T. Yamanaka, Y. Takéuchi and M. Tokonami, Faculty of Science, University of Tokyo, Tokyo, Japan

In relation to our previous study on the temperature dependence of the anharmonic thermal vibration of atoms by high temperature refinements of MgAl<sub>2</sub>O<sub>4</sub> up to 1933 K (Yamanaka et al. Acta Cryst. (1984) B40) an interaction between valence charge density and the anharmonicity has been elucidated by X-ray structure refinements of ZnX (X=S,Se,Te) having a zincblend structure (F $\bar{4}3m$ , z=4, Zn on 43m at 0,0,0 and X on 43m at 1/4,1/4,1/4).

Spherical samples of ZnS, ZnSe, ZnTe were prepared from grinding the crystals grown by the chemical transport method. X-ray diffraction intensity measurement at 20°C were carried out with a four-circle diffractometer using MoK $\alpha$  radiation monochromated by pyrolytic graphite. Intensities measured in the range  $0.12 < \sin\theta/\lambda < 1.32$  were corrected for Lorentz and polarization effects and for absorption. This study was initiated by the refinement of the temperature factor  $T(Q)$  based on the harmonic oscillation model besides the isotropic extinction parameter.

Difference Fourier syntheses based on the structure factors obtained from the harmonic refinements of ZnS(R=1.74%), ZnSe(1.68%) and ZnTe(1.63%) revealed the residual electron density around atoms, as shown in Fig. 1. A tetrapod shape electron density around Zn is found to be from the anharmonic thermal vibration in consideration of  $3d^{10}4s^2$  of Zn giving spherical electron



06.5-3 ANHARMONICITY OF CUBIC CsPbCl<sub>3</sub> NEAR THE PHASE TRANSITION By M. Sakata, H. Miyatake and J. Harada, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.

CsPbCl<sub>3</sub> exhibits a cubic to tetragonal phase transition at 320K due to the condensation of M<sub>3</sub> phonon mode in perovskite structure. In connection with this phase transition an anomalous temperature dependence of the temperature parameters of Cl ion has been known to exist in the cubic phase, besides a very big anisotropy  $B_{33}(Cl) \ll B_{11}(Cl)$ . An analysis of this behavior has been made by the present authors and others (Sakata et al. (Acta Cryst. (1980) A36, 55) in terms of one particle potential approximation including higher order anharmonicities. Harmonic potential model is, however, shown to be sufficient if potential parameter is regarded as temperature dependent by Mair (Acta Cryst. (1982) A38, 790). Further least squares refinements were then carried out for the following three potential models to Cl ion:

$$\text{Model A: } V_{ii} = V_0 + (1/2)\alpha U_{ii}^2$$

$$\text{Model B: } V_{ii} = V_0 + (1/2)\alpha U_{ii}^2 + \delta U_x^2 U_y^2$$

$$\text{Model C: } V_{ii} = V_0 + (1/2)\alpha U_{ii}^2 + \delta U_x^2 U_y^2 + \gamma U_{ii}^4$$

with  $U_{ii}^2 = U_x^2 + U_y^2$  where  $\alpha, \gamma, \delta$  are potential parameters and  $U_x, U_y$  etc are the displacements of the ion on the plane. In the analysis a direct numerical integration method was