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 $\lesssim 0.0012$ A, for nicotinic acid $\lesssim 0.0060$ A. 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 $0.1 eA^{-3}$. For heavier atoms the effect may well be larger.

06.5–2 X-RAY DIFFRACTION STUDY ON THE ANHARMONIC THERMAL VIBRATIONS OF ATOMS IN ZnX(X=S,Se,Te)

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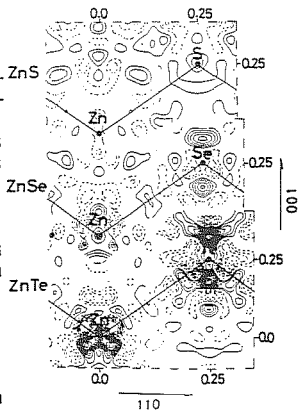
In relation to our previous study on the temperature dependence of the anharmonic thermal vibration of atoms by high temperature refinements of $MgAl_2O_4$ up to 1933 K (Yamanaka et al. Acta Cryst. (1984) B40) an interaction between valence charge density and the anharmonicity has been elucidated by X-ray structure refinements of ZnX (X=S,Se,Te) having a zincblend structure ($F\bar{4}3m$, z=4, Zn on $\bar{4}3m$ at 0,0,0 and X on $\bar{4}3m$ at 1/4,1/4,1/4).

Spherical samples of ZnS, ZnSe, ZnTe were prepared from griding 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 MoKα 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



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 α 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 $T(Q)=\exp[\Sigma(i^n/n!)\,\psi_{pqr\ldots}\,q_p q_q q_r\ldots]$ (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 form 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).

After the anharmonic refinements, the residual electron densities previously mentioned disappeared in the difference Fourier maps of ZnX.

		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
Rwt (%)		1.78	1.32	1.62	1.61	1.56	1.50
β_{11} (Zn)	10^6	749	746	877	870	897	938
β_{11} (X)	10^6	600	610	593	567	619	651
γ_{123}(Zn)	10^7		320		932		1289
γ_{123}(X)	10^7		258		836		528
δ_{1111} (Zn)	10^8		90		487		270
δ_{1111} (X)	10^8		-437		-435		-150
δ_{1122} (Zn)	10^8		-85		307		200
δ_{1122} (X)	10^8		-87		-124		-166
Gext.	10^6	6.88	7.13	8.72	8.78	3.00	3.10

06.5–3 ANHARMONICITY OF CUBIC $CsPbCl_3$ NEAR THE PHASE TRASITION

By M. Sakata, H. Miyatake and J. Harada, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.

$CsPbCl_3$ exhibits a cubic to tetragonal phase transition at 320K due to the condensation of M_3 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 $B_{33}(Cl)<<B_{11}(Cl)$. 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 anharmonisities. 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 squars refinements were then carried out for the folliwing three potential models to Cl ion :

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

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

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

with $U_{//}^2 = U_x^2 + U_y^2$ where α,γ,δ 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

employed to calculate temperature factor <exp (iKU)> in order to avoid the inclusions of possible ambiguities arising from further approximations.
The results show that i) any models cannot satisfy the observed data sets unless potential parameters are regarded as temperature dependent(Mair's proposal for model A is preserved) and ii) model A is not good enough. Model B shows a great improvement of R-factor (from 2 to 1.2%) and the result of model C does not show any difference from model B at high temperature (higher than 423K), but in the temperature range from 325 to 373K near the transition temperature, model C is much better than model B since a remarkable improvement of R-factor is noticed (e.g. from 1.92 to 0.88% at 326K). Judging from the sufficiently low value of R-factors for the data at all the nine temperatures observed (R : between 0.88 and 1.46%), we believe model C would be the best for this substance.

06.5–4 ON THE STUDY OF FORBIDDEN REFLECTIONS IN V_3Si. By A.I.Kolosovsky, Yu.A.Rosenberg L.I.Kleshchinsky, V.M.Kiselev, Inst.of Transp. Engineers, 664074 Irkutsk and N.V.Shokhirev, Inst.of Chem.Kinetics, Sib.Branch of Academy of Sciences, 630090 Novosibirsk, USSR.

The integrated reflecting powers of forbidden Bragg reflections 410 and 430 in the crystals V_3Si have been measured in a symmetric Bragg géometry on a single-crystal spectrometer at the CuK_α radiation. The vertical divergence of the primary beam made 10' and the horizontal one 3'.The calculated umweganregung patterns were in accordance with the experiment and the forbidden reflection intensities were measured in the umweg-free regions by means of the ω-scan method. The 410 reflection maximum intensity was 20 c/s and the background 17 c/s; for the reflection 430 the values are 9.5 and 8, where 3 c/s is the fluorescent background of V and 5 the "diffraction" one. The primary beam intensity estimated by the forbidden 222 reflection in a perfect Si crystal was $2 \cdot 10^7$ c/s.
The obtained integrated reflecting power values are $1.71 \cdot 10^{-10}$ and $1.37 \cdot 10^{-10}$ for 410 and 430 respectively. The values of structure factors F(410)=0.30±0.03 and F(430)=0.145± 0.015 computed upon these determinations are in good agreement with the results of B.Borie (Acta Crystallogr.A 37,238,1981) obtained by a somewhat other technique.
The paper considers also the low temperature behaviour of these reflections.

06.5–5 A NEUTRON DIFFRACTION STUDY OF THERMAL EXPANSION AND ANHARMONIC THERMAL VIBRATIONS IN SODALITE, $Na_4Si_3Al_3O_{12}Cl$. By Richard K. McMullan, Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973; and Subrata Ghose, Department of Geological Sciences, University of Washington, Seattle, Washington 98195.

Sodalite, $Na_4Si_3Al_3O_{12}Cl$ is cubic, space group $P\bar{4}3n$, with a = 8.882 (1) Å at 295K, Z=2. The crystal structure consists of a cubo-octahedral framework of alternating AlO_4 and SiO_4 tetrahedra, with four- and six-membered rings; Cl occurs at the center of the cubo-octahedral cage and Na below the six-membered rings, both in tetrahedral coordination.

The unit cell dimensions and crystal structures of sodalite from Litchfield, Maine were determined from neutron diffraction data at 295, 500, 600, and 700K with $R(F^2)$ factors 1.5, 2.0, 1.9 and 1.8 respectively. The Al-Si order within the framework has been confirmed, the Al-O and Si-O bond distances being 1.7407(4) and 1.6200(4) Å at 295K. The thermal expansion of the tetrahedral framework, which is nonlinear, is principally effected through the increase of the Al-O-Si angles from 138.24(2)° at 295K to 140.25(3)° at 700K; concurrently, the Na-O distance increases from 2.356(1) to 2.400(1)Å. The anharmonic thermal vibrations of the framework atoms are negligible, whereas those of Na and Cl increase considerably with temperature.

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06.6–1 LESSONS FROM THE I.U.Cr. X RAY ATTENUATION PROJECT. D.C. Creagh, Department of Physics, Royal Military College, Duntroon, A.C.T. 2600, AUSTRALIA, and J.H. Hubbell, Radiation Physics Division, Centre for Radiation Research, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

The I.U.Cr. X ray Attenuation Project which was inaugurated in 1978 under the auspices of the Commission for Crystallographic Apparatus is now almost finished. Some laboratories have yet to report their results and we are still receiving enquiries by laboratories wishing to join the project. It is our intention to provide specimen materials to these laboratories and to produce, at a later stage, addenda to the project reports which are now in the final stages of preparation.

This paper will discuss such important questions as:

* the need for complete sample characterization to ensure that the correct experimental configuration is chosen for the measurement;
* the strengths and weaknesses of different experimental configurations; and,
* the deficiencies of existing published data sets.

We are deeply saddened that the Chairman of the Commission for Crystallographic Apparatus, Sixten Abrahamsson, died before the presentation of the report on our project, in which he had taken a great interest.