

06.4-3 ELECTRON MOMENTUM DISTRIBUTION IN AMORPHOUS AND CRYSTALLINE TiCu AND TiCuH_x VIA γ -RAY COMPTON SCATTERING.* BY G. Bambakidis, Physics Department, Wright State University, Dayton, Ohio U.S.A., and I. Theodoridou and N. G. Alexandropoulos, Physics Department, University of Ioannina, Ioannina, Greece.

The one-dimensional electron momentum distribution for amorphous and crystalline samples of TiCu and TiCuH_x was deduced from the Compton line profile $J(q)$. The profile was obtained using a Compton spectrometer and a 500 mCi ²⁴¹Am annular source, following the same procedure utilized previously in a study of the NbH_{1.2} system (Theodoridou and Alexandropoulos, Zeit. Phys. B, to be published). The experimental results are compared to the momentum distribution obtained from a cluster calculation of the electronic structure of TiCu and TiCuH_x, based on the Johnson-Slater X α -scattered wave method.

The TiCu-H system has been better characterized than most crystalline/amorphous hydrides, which together with the availability of appropriate samples make this system an attractive one for isotropic Compton scattering studies.

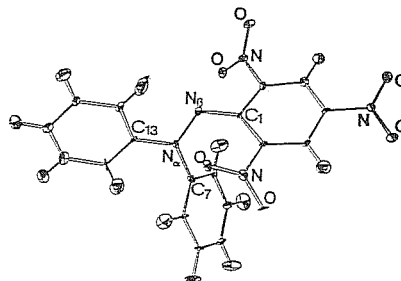
*partially supported by a NATO Research Collaboration Grant.

06.4-4 ON THE STRUCTURAL FACTORS OF BRAGG REFLECTIONS IN DIAMOND AND SILICON CALCULATED BY THE METHOD OF BONDING FUNCTIONS. By N.V. Shokhirev, Inst. of Chem. Kinetics, Sib. Branch of the Academy of Sciences, 630090 Novosibirsk and Yu.A. Rosenberg, L.I. Kleshchinsky, L.G. Andrievskaya, Inst. of Transp. Engineers, 664074 Irkutsk, USSR.

The wave function for the ground state of crystals with a diamond structure consists of bonding functions and atomic orbitals of the core, the overlap of the inner orbitals of a given atom and the valence orbitals of neighbours is neglected. These wave functions are used to calculate X-ray structural factors. The calculations take into account the overlap density of neighbouring $(2N+1)^{2-1}$ diatomic cells. The overlap integral matrix is inverted by the three-dimensional Fourier transformation. The calculations are carried out for $N=2$; a further increase in N does practically not affect the data obtained. The calculated results demonstrate a weak dependence of the ratio between S- and P-orbit populations upon the hybridization degree. The calculated structural factors of the Bragg reflections differ from those in experiment by no more than 1% in silicon and by 3% in diamond. The structure factors of the forbidden 222 reflection are systematically twice as low as those in experiment which results from the quality of the atomic orbitals employed (B. Roos, P. Seigbahn, Theor. Chim. Acta 17, 209, 1970) and from the neglect of anti-bonding orbits at deriving the wave function.

06.4-5 DETERMINATION BY POLARIZED NEUTRON DIFFRACTION OF THE SPIN DENSITY DISTRIBUTION IN A NON-CENTROSYMMETRICAL CRYSTAL OF DPPH: C₆H₆. By J.-X. Boucherle, B. Gillon, J. Maruani and J. Schweizer, CMOA du CNRS, DRF/DN du CENG and ILL, BP 156X, 38042 Grenoble Cedex, France.

The spin density distribution of the stable free radical diphenylpicrylhydrazyl has been studied in the crystalline form DPPH: C₆H₆ (Acta Cryst., to be published) at low temperature, with the magnetic moments oriented by an external field. It has been represented by a multipolar expansion on the different atoms, the coefficients of which have been determined by comparison with the flipping ratios measured by polarized neutron diffraction (Boucherle, Gillon and Schweizer, Proc. Int. Symp. Neut. Scat., Amer. Inst. Phys. (1982), 333). The spin density distribution thus obtained confirms and specifies the results from magnetic resonance, particularly the wide delocalization of the unpaired electron, including π - π and π - σ spin polarization effects, and the theoretical models used to relate hyperfine couplings to spin populations and conformational angles (Mol. Phys., to be published).



The structure of DPPH in DPPH: C₆H₆

06.5-1 THE EFFECT OF ANHARMONIC MOTIONS ON ATOMIC POSITIONS, BOND LENGTHS AND DEFORMATION DENSITIES. By C. Scheringer, Institut für Mineralogie der Universität Marburg, D 3550 Marburg, Federal Republic of Germany.

The positions of the atoms, i.e. the positions of the origins of the probability density functions (pdf's), depend on the definition of the pdf and the temperature factor which is actually used in the refinement. If there are no first order terms in the reciprocal lattice vector h , the mean positions (means of the pdf) are determined. If there are first order terms in h , other positions are defined. It is shown how the mean positions can be calculated from the temperature factors. When the temperature factor is formulated in the isolated - atom - potential approach, the maximum of the pdf is determined in the refinement. For temperature factors which contain the bond-length correction of molecular librations, correspondingly altered positions are determined.

Defining the temperature factor so that the mean positions are obtained, is advantageous in several respects. No first order terms of h need be considered in programming. The harmonic temperature factor is a simple Gaussian function. Anharmonic expansions need not be corrected for terms which are merely due to the choice of the origin of the pdf other than its mean.

In least-squares refinements, with the same set of data, harmonic and anharmonic temperature factors usually do not give the same estimates of the mean positions and, hence, not the same estimates of the bond lengths. The problem of parameter bias that arises here, is analyzed. It

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 ≤ 0.0012 Å, for nicotinic acid ≤ 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 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 $T(Q) = \exp[\sum (z^n/n!) \psi_{pqr} \dots q_p q_r \dots]$ (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).

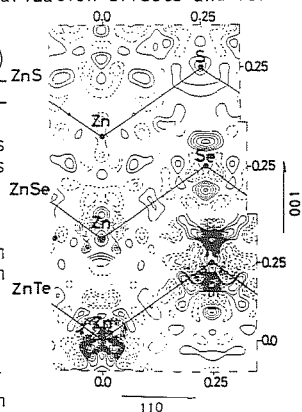
	ZnS		ZnSe		ZnTe	
a (Å)	5.4053		5.6609		6.0862	
sinθ/λ	1.32		1.32		1.32	
No. ref.	107		93		142	
	Harm.	Anharm.	Harm.	Anharm.	Harm.	Anharm.
R (Z)	1.74	1.29	1.68	1.60	1.63	1.54
R _w (Z)	1.78	1.32	1.62	1.61	1.56	1.50
B ₁₁ (Zn) 10 ⁶	749	746	877	870	897	938
B ₁₁ (X) 10 ⁶	600	610	593	567	619	651
γ ₁₂₂ (Zn) 10 ⁷		320		932		1289
γ ₁₂₂ (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
G ext. 10 ⁶	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)
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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 MgAl₂O₄ 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 α 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 3d¹⁰4s² of Zn giving spherical electron



06.5-3 ANHARMONICITY OF CUBIC CsPbCl₃ NEAR THE PHASE TRANSITION By M. Sakata, H. Miyatake and J. Harada, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.

CsPbCl₃ exhibits a cubic to tetragonal phase transition at 320K due to the condensation of M₃ 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 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