

06.7-6 ELECTROSTATIC PROPERTIES FROM ACCURATE X-RAY DIFFRACTION DATA. By K. Eichhorn, Fachrichtung Kristallographie, Universität des Saarlandes, D-6600 Saarbrücken, Federal Republic of Germany.

Since X-ray structure factors are the Fourier components of the (thermally smeared) electron density in the unit cell, they can be used, at least in principle, to evaluate electrostatic quantities like inner and outer moments, potential and field strength, and also the electrostatic part of (molecular) interaction energies. The results are limited by both the accuracy and the resolution of the X-ray experiment and it is best to restrict oneself to quantities which depend mainly on low-order reflections.

Outer moments may be obtained by either Fourier methods (Coppens & Hansen, *Isr. J. Chem.* (1977) 16, 163) or by least-squares fits ranging from simple L-shell refinement (Stewart, *J. Chem. Phys.* (1970) 53, 205) to the more involved multipole models (Stewart, *Acta Cryst.* (1976) A32, 565; Hirshfeld, *Isr. J. Chem.* (1977) 16, 226). Following Buckingham (*Quart. Rev.* (1959) 13, 183), these may then serve to expand the electric potential as a series of multipole moments. These potentials can also be obtained by Fourier summation with modified coefficients  $F/\pi S^2$ , downgrading the effect of high-order data. The electrostatic potential may be interpreted as interaction energy of a charge distribution with a unit point charge, leading to an expression of the long-range electrostatic interaction component in terms of multipole-multipole interactions (Moss & Feil, *Acta Cryst.* (1981) A37, 414).

This approach has been successfully used to study the influence of the short H-bridge ( $O...O = 2.43 \text{ \AA}$ ) in 1-hydroxypyridinium trichloroacetate on the electron density of both donor- and acceptor-atom, and to derive heights of barriers to internal rotation from multipole-multipole interactions in accord with experimental values.

06.7-7 CLUSTER CALCULATION OF ELECTRONIC STRUCTURE AND HYPERFINE INTERACTIONS FOR GARNETS. By S. Nagel and S.S. Hafner, Institute of Mineralogy, University of Marburg, Lahnberge, 3550 Marburg, Germany (F.R.G.).

Because of their large spread in chemical composition, crystal structures of the garnet type  $C_3A_2d_3O_{12}$  are excellent examples to test models of chemical bonding at atomic sites. We have applied the multiple scattering  $X_\alpha$  method for studying the relationship between chemical bonding and nuclear hyperfine coupling measured with resonance techniques. Precise NMR data of  $^{27}\text{Al}$ ,  $^{69,71}\text{Ga}$ , and Mössbauer data of  $^{57}\text{Fe}$  are well known for a large number of garnets. Calculations have been performed for  $aO_6$  and  $dO_4$  clusters with geometries as found in the garnets  $c = \text{Lu, Y, Gd}$ ,  $a + d = \text{Al, Ga}$  and  $c = \text{Ca, Fe}$ ,  $a = \text{Al}$ ,  $d = \text{Si}$ . For stabilization we used the respective crystal potentials obtained for a point charge lattice. The second derivatives of the potential ( $V_{zz}$ ) at the a and d positions were calculated from the cluster wavefunctions including those for the core electrons. Distant contributions from ions not included in the cluster were obtained via lattice sums using the lowest multipole moments obtained for the cluster ions.

$V_{zz}$  was found to be negative for both a and d positions except for a in  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ . For  $^{27}\text{Al}$  and  $^{67,71}\text{Ga}$  the sign of the quadrupole coupling constant has not been determined experimentally. Our results are, however, consistent with the signs found from Mössbauer mea-

surements for  $^{57}\text{Fe}$ . The magnitudes of the calculated  $V_{zz}$  for both a and d positions in the series  $c \text{ } ^{ZZ}\text{Lu, Y, Gd}$  show quantitatively the same decrease as the experimental results. The theoretical values are, however, too large by a factor of 1.5 - 2 for a and too small by about 0.7 for d yielding a ratio  $V_{zz}(d)/V_{zz}(a)$  of about 1.5 - 3 instead of the experimental result of about 3 - 9. Whereas in  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  the  $^{27}\text{Al}$  quadrupole coupling constant was found to have the largest value among all Al-garnets, the calculations for an  $\text{AlO}_6$  cluster yield the smallest value for  $V_{zz}$  corresponding to the smallest deviation of the octahedron from ideal symmetry.

In all cases the major contributions to  $V_{zz}$  are due to a transfer of charge from the ligands into Al or Ga orbitals which are empty in the ideal ionic state. For the Ga garnets there are also important contributions from the d shell which is distorted because of a small covalent participation of ligand orbitals. Effective charges found for the Al and Ga ions at the octahedral site are +2.80 and +2.50, whereas at the tetrahedral site these charges are +2.82 and +2.76.

It is concluded that charge transfer covalency is the main source for a non vanishing  $V_{zz}$  at the a and d positions of garnets, rather than antishielding effects of ideal ions. This is consistent with a recent study of Beri et al. (*Phys. Rev.* (1983) B28, 2335) about antishielding effects in  $\text{Fe}_2\text{O}_3$ . The systematic deviations between the present theoretical and the experimental results may be attributed to the influence of other oxygen neighbours.

06.7-8 FORMAL ATOMIC CHARGES IN CUBIC BORON-NITRIDE BN. By A. Kirfel, B. Josten and G. Will, Mineralogisches Institut der Universität Bonn, Lehrstuhl für Mineralogie und Kristallographie, Poppelsdorfer Schloß, D-5300 Bonn, FRG

Accurate measurements of X-ray structure amplitudes (up to  $s = 1.38 \text{ \AA}^{-1}$ ) and ensuing structure refinements have been used to calculate structure factors for spherical charge integrations around the atomic sites (Sasaki et al., *Acta Cryst.* (1980) A36, 904). Charge values  $Z(R)$  were corrected for Fourier series termination effects and investigated in terms of radial charge distributions  $dZ/dR$  and their derivatives  $d^2Z/dR^2$  indicating effective atomic radii of  $0.83 \text{ \AA}$  for N, and consequently  $0.73 \text{ \AA}$  for B. The corresponding electron counts yield 5.99 el (N) and 3.04 el (B). Thus, the spheres describing 34.1 % of the unit cell volume contain 75.25 % of the electrons in the unit cell. Distributing the remaining more delocalized electrons equally on B and N renders a significant charge transfer  $T = 0.47 \text{ el}$  from B to N emphasizing the ionic contribution to the B-N bond. Results are compared to corresponding calcula-