06.7-04   ELECTRON DENSITY & FIELD GRADIENTS IN α-Al$_2$O$_3$
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Electric field gradients ∇E and their signs at the nuclear positions of Al and O in corundum have been measured by E. Hundt(1) with dynamic NQR spectroscopy. With point symmetries 3 for Al and 2 for O, ∇E reduces to one term for Al and 3 for O. In this contribution we describe the calculation of the ∇E tensors from accurate x-ray data and the multipole refinement of the deformation density of α-Al$_2$O$_3$ using Hirshfeld's deformation functions(2). The observed gradients are also introduced as observations together with the structure factors to obtain an electron density with the correct electrostatic properties(3). Secondary extinction is refined with the algorithm of Becker and Coppens(4) together with all standard and deformation parameters. Two complete sets of intensities were measured from two spherical crystals with diameters 0.20 and 0.13mm, using MoK$_\alpha$ and AgK$_\alpha$ radiation, up to $\sin\vartheta/\lambda$ of 1.2 and 1.5Å^{-1} respectively, yielding 4402 and 8923 measurements or 397 and 804 averaged structure factors. Anisotropic secondary extinction effects were severe. The strongest intensity (300) suffered reductions of 43%(MoK$_\alpha$) and 26%(AgK$_\alpha$). Eight different refinements were carried out, four for each data set: extinction was assumed to be isotropic, or anisotropic; x-ray data was used alone in the refinement and ∇E was computed from the result, or ∇E was also used as an observation. Deformation maps were drawn for all refinements mentioned.

Best reliability indices were obtained assuming type I crystals and Lorentzian mosaic distributions. Extinction tensors were very similar for both Verneuil grown crystals , the mean mosaic spread being 8". Surprisingly, the isotropic correction also agrees well with the one obtained using the algorithm of Zachariasen(5).

Some generalizations about the results of the various refinements are: Standard parameters refine to virtually the same values in all refinements. Subsidiary parameters also agree within a few e.s.d's. R-values and goodness of fit (GOF) are lowered considerably with the introduction of the deformation functions; in particular, the (006) reflection cannot be computed adequately from the free-atom model. The magnitudes of the largest eigenvalues of the ∇E-tensors ∇E_{zz} and the asymmetry parameter $\eta = (\nabla E_{xx} - \nabla E_{yy})/\nabla E_{zz}$ for oxygen are computed with very large e.s.d's. The signs of ∇E_{zz}, the order of the eigenvalues and the orientational parameter of $\nabla E(O)$ with respect to a crystal fixed coordinate system are, however, correctly computed from the x-ray data if isotropic extinction is assumed. This information can no longer be retrieved in the case of anisotropic extinction.

The eight series of deformation maps agree well. Introducing ∇E as observation in the refinement modifies nearly exclusively the region within 0.4Å of the centers of the O-atoms where a deep hole is replaced by more shallow ripples. Refinement of anisotropic extinction served mainly to increase computing costs and programming time.

The maps show localized peaks of up to 0.25e/Å^3 on the short (1.86Å) Al-O bonds, and of up to 0.20e/Å^3 on the long (1.97Å) Al-O bonds. No metal-metal bonds analagous to those found in Ti$_2$O$_3$ and V$_2$O$_3$(6,7) are observed.

(1)Ph.D. Thesis, Univ. of Zürich, 1972   (2) Israel J.Chem. 16 (1972 226   (3) Acta Cryst. A35 (1979) 658   (4) Acta Cryst. A30 (1974) 129   (5) Acta Cryst. 23 (1967) 558 (6,7) Acta Cryst. A36 (1980) 803ff.

06.7-05   A MODEL STUDY IN MAPPING ELECTROSTATIC PROPERTIES FROM X-RAY STRUCTURE FACTORS. By A. Braam, A. Vos and R. F. Stewart, Dept. of Chemistry, 4400 Fifth Avenue, Carnegie-Mellon University, Pittsburgh, PA 15213 U.S.A.

X-ray structure factors for crystalline N$_2$ in the α-phase (assumed space group Pa3) were generated from the generalized x-ray scattering factor expansion of the molecular form factor for N$_2$($^1\Sigma_g^+$). The molecular form factor was derived from the Hartree-Fock wavefunction of N$_{2(g)}$ at the experimental Re-value. This wavefunction is spanned by Slater-type orbital bases. The model structure factors were derived to determine the resolution required to reconstruct several electrostatic properties and to study the influence of the thermally weighted vibrational average charge density on the electrostatic properties. The properties investigated include the electrostatic potential, the electrical field, the electron density and the electrical field gradients. Most studies were restricted to a deformation property, whereby the corresponding isolated atom property in the crystal was subtracted out. For a given sphere of diffraction data, the electrostatic potential is more accurately constructed than the electron density or electrical field gradient. The influence of increasingly larger amplitudes of vibration dramatically changes the electrical field gradients and electron density at the mean nuclear positions. Most features of chemical bonding in N$_2$ are cleanly revealed in the deformation electrostatic potential map.

06.7-06   MAPS OF ELECTROSTATIC PROPERTIES FROM X-RAY DATA FOR α-SiO$_{2(s)}$ AND Al$_2$O$_{3(s)}$. By M. Spackman, R. F. Stewart and Y. LePage. Department of Chemistry, 4400 Fifth Avenue, Carnegie-Mellon University, Pittsburgh, PA 15213, U.S.A.

X-ray diffraction intensities from MoK$\bar\alpha$ radiation were reduced by kinematic theory to structure factors; for corundum a secondary extinction model was included in the data reduction process. Both sets of reduced data are on a relative scale. Phases for the data sets were determined from a pseudoatom refinement model. Efforts to place the structure factors on an absolute scale were based on the generalized x-ray form factors extracted from self-consistent field wavefunctions of SiO and AlF. Deformation electrostatic potential maps, constructed by Fourier summation methods of the phased x-ray structure factors, were free from termination effects. The electrostatic potential difference maps reveal features of chemical bonding. The electropositive region on the exposed side of Si in the quartz structure somewhat resembles electropositive regions found in elemental Si. Electronegative regions are found around the oxygens and are polarized towards the near neighbor Si atoms. By contrast, the electronegative region about the O atoms in Al$_2$O$_3$ has little structure. The electropositive regions are around the Al sites and are polarized in a direction normal to the hexagonal stacking axis. Electric fields have also been mapped in projection upon several planes in the unit cells of α-SiO$_2$ and Al$_2$O$_3$.