

**06.2-7** EXPERIMENTAL CHARGE DENSITY IN MOLECULES CONTAINING SULFUR. By F. Mo and G. Thorkildsen, Institutt for røntgenteknikk, Universitetet i Trondheim-NTH, N-7034 Trondheim-NTH, Norway.

The charge density in molecules containing S in various bonding environments is being studied at  $\sim 85\text{K}$  by X-ray diffraction. Examples will be taken from the analyses of ethane-1,2-bis(methyl)sulfone,  $\text{H}_3\text{C-SO}_2\text{-CH}_2\text{-CH}_2\text{-SO}_2\text{-CH}_3$ , in  $P2_1/c$  (A) and dithiooxamide,  $\text{S=C(NH}_2\text{)-(NH}_2\text{)C=S}$ , in  $P\bar{1}$  (B), both structures with  $Z=2$ . Intensities were collected to a limit in  $(\sin\theta)/\lambda \approx 1.27\text{\AA}^{-1}$ . Data processing includes corrections for coincidence loss, scan truncation, multiple diffraction, absorption, anomalous dispersion and extinction before averaging. Details on the analyses of errors due to scan truncation and multiple diffraction will be presented along with some results of the corrections. The quality of the data was adequate to allow meaningful refinements of H positions; thus, for structure A with  $s > 0.65\text{\AA}^{-1}$  the mean C-H = 1.07, range 1.04(3)-1.11(3)\AA, and for B with  $s > 0.75\text{\AA}^{-1}$  the mean N-H = 1.02, range 0.97(4)-1.06(5)\AA.

Deformation density maps have been calculated both with  $s < 0.75$  and  $s < 1.0\text{\AA}^{-1}$  for comparison. The polar character of the S-O bonds in A is clearly revealed in the maps. The density in these bonds is polarized towards O and extends into a single, broad lone-pair peak outside O. There is a negative trough on each bond near the O position. The S atom resides in negative density.

In B the density in the C-S bonds is displaced towards C. Elongated peaks in the C-N and C-S bonds indicate considerable  $\pi$  character. Above and below the C atoms are distinct minima similar to those observed in cyanuric acid (Dietrich & Scheringer, Acta Cryst. (1979). B35, 1191). There are well resolved lone-pair peaks near S, their positions relative to S differ in the two independent half-molecules, but in both, one of the peaks is directed along a short intermolecular  $\text{S}\cdots\text{H-N}$  contact.

**06.2-8** ELECTRON DENSITY STUDY OF CUPRITE,  $\text{Cu}_2\text{O}$ . By K. Eichhorn, J. Spilker and K. Fischer, Fachrichtung Kristallographie, Universität, D-6600 Saarbrücken, FRG.

Room-temperature X-ray measurements from D. Mullen (Z. Krist. (1981) 156, 85) were revised by an improved data reduction process, including profile analysis and a different background subtraction, corrections for anisotropic thermal diffuse scattering and secondary extinction. The weights  $1/(\sigma^2(F_o))$  were based on the actual agreement of symmetry-related reflections.

From statistical tests the Laue class of the X-ray data is  $m\bar{3}m$ , and space-group  $Pn\bar{3}m$  (No. 224) was chosen for the analysis. Cu, at position 4b (0,0,0), is linearly bonded to two oxygens at position 2a (1/4,1/4,1/4), each O-atom tetrahedrally coordinated to 4 Cu-atoms.

An L-shell refinement (Stewart, J. Chem. Phys. (1970) 53, 205) gives overall charges of +0.43(3) electrons on Cu and -0.86(5) on O. (X-X)-maps from high-order parameters indicate a charge-depletion at the Cu-site and in the plane through Cu perpendicular to the O-Cu-O axis, accompanied by a charge accumulation at the oxygen site. In addition, there is a 3-fold pattern of excess density close to Cu distributed around the Cu-O axis. Around the oxygen the maps display a tetrahedral deformation with peaks located on the Cu-O bond 0.62 \AA from the oxygen site. This indicates both ionic and covalent contributions to the bonding in cuprite.

Further work on the X-ray data is in progress, supplemented by neutron data collected by D. Mullen (loc. cit.) at 80, 120, 199, and 295 K.

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**06.2-9** ELECTRON-DENSITY DISTRIBUTION IN CRYSTALS OF MAGNETITE AT ROOM TEMPERATURE. By S. Sato and S. Todo, The Institute for Solid State Physics, The University of Tokyo, Roppongi 7-22-1, Minato-ku, Tokyo 106, Japan.

The electron-density distribution in magnetite was investigated by X-ray diffraction. Single crystals were prepared by the Bridgman method. A crystal shaped into a sphere of 0.286(4) mm in diameter was used for intensity measurement on an automated four-circle diffractometer with monochromated  $\text{Ag K}\alpha$  radiation up to a  $2\theta$  value of  $150^\circ$ . In total, 5253(382 unique) reflections in a hemisphere of the reciprocal space were collected. The structure was refined to  $R=0.020$  by the least-squares method. According to a simple crystal-field model, the d-electron distribution of an atom with the high-spin

$(3d)^5$  configuration in a tetrahedral environment is expected to be spherical. In the present case, however, the difference Fourier maps around the  $\text{Fe}^{3+}$  cation on the A site show a large deformation from the spherical distribution: four positive peaks of  $1.0 \text{ electron/\AA}^3$  are tetrahedrally located at 0.36 \AA from the Fe nucleus on the extension of the Fe-O bonds. This suggests excess charges in the  $t_2$  level, and is probably due to the formation of the Fe-O covalent bonds. The cation on the B site is octahedrally surrounded by six  $\text{O}^{2-}$  anions; the octahedron is trigonally elongated. Six peaks of  $0.6 \text{ electrons/\AA}^3$  appear on the D-maps; they are along the body-diagonal directions of the octahedron except the trigonal axis, 0.37 \AA away from the cation. This shows that the  $e_g$  level having the  $\sigma$  character is lower than the  $a_g$  level. The charge asphericity might be partly attributed to anharmonic vibrations of atoms. Further refinement is in progress.

**06.2-10** THE CHARGE DENSITY DISTRIBUTION IN  $[(\text{C}_5\text{H}_4\text{CH}_3) \text{M}(\text{CO})_3]_2$  FOR  $\text{M} = \text{Cr, Mo}$ . By D. Gregson and J.A.K. Howard, Department of Inorganic Chemistry, University of Bristol, Bristol, England.

The electron density distributions in the title complexes are being studied using the X-N technique. This pair of complexes has been selected because they have unsupported metal-metal bonds which require formal single bonds to satisfy their observed diamagnetism. Recent studies (e.g. M. Martin, B. Rees, A. Mitschler, Acta Cryst. B38 (1982) 6.) show that there is no significant accumulation of charge density between the metal centres in such systems, an interesting result in view of our conceptions of what constitutes a chemical bond. Further, the Cr-Cr bond is longer than that of the Mo analogue, in contrast to the expected pattern of increasing bond length down a group. A similar observation was made in the unsubstituted  $(\text{C}_5\text{H}_5)$  complexes (R.O. Adams and F.A. Cotton, Inorg. Chem. Acta, 7 (1973), 153; F.C. Wilson and D.P. Shoemaker, J. Chem. Phys., 27 (1957), 809.), and a detailed description of the electron density distribution should provide an interpretation of these observations. It is intended to present some results of this study at the conference.