06.2–2 SPATIAL PARTITIONING OF THE CHARGE DENSITY IN COMPLEX CRYSTALS: $Na_2S_2O_3$ AND $MgS_2O_3 \cdot 6H_2O$. By J.W.Bats and H.Fuess, Institut für Kristallographie und Mineralogie der Universität Frankfurt am Main, West Germany

The electron density distribution in $Na_2S_2O_3$ and $MgS_2O_3 \cdot 6H_2O$, which was previously determined by X-N methods, was further refined by multipole expansion (program MOLLY, Hansen & Coppens, Acta Cryst. (1978) A34, 909). Averaging over chemically equivalent atoms greatly improved the appearance of the deformation density (Fig. 1).

Net atomic charges were calculated by direct space integration separating the atoms by the fuzzy boundary method (Hirshfeld, Isr. J. Chem. (1977) 16, 198). Results for $Na_2S_2O_3$: Na +.23, S(1) -.24, S(2) +.40, O -.21 e; for $MgS_2O_3 \cdot 6H_2O$: Mg +.32, S(1) -.39, S(2) +.19, O(s) -.24, O(w) -.19, H(w) +.15 e. Net atomic charges from MOLLY and a κ formalism (Coppens et al., Acta Cryst. (1979) A35, 63) generally are larger by a factor 2 to 3. This results from an expansion or contraction of the atomic valence shells in the latter methods. The much less than ionic charges on Na and Mg result from the nature of the 3s valence shells of these atoms, which are very diffuse. The majority of the 3s electrons is located considerably closer to O and S than to the metals. Thus the ionic nature of the metal atoms appears ambiguous and is realistic only within a radius of 1 Å from the atomic nuclei.

The total net charge on the $Mg(H_2O)_6$ group is +0.9e for the fuzzy boundary method but increases to +1.9e for MOLLY and +2.2e for a κ-refinement. Thus in complex crystals spatial partitioning of cation and anion is not unambiguous. In the present case about 1 electron cannot be uniquely assigned.

A similar result is found for the dipole moment of the water molecules. Both the multipole and κ-refinement give μ = 2.7D. Direct space integration using a discrete boundary gives values from 1.1 to 1.7D and depends considerably on the boundary conditions.

Conclusion: spatial partitioning which appears successful for molecular crystals is ambiguous for ionic crystals with complex ions.

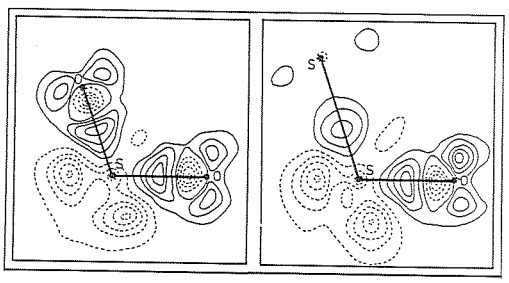

Fig. 1 : Static deformation density of $Na_2S_2O_3$

resolution : $\sin\theta/\lambda = 1.0$ Å^{-1}

contour inverval: 0.1 e/Å^3

zero contour omitted.

06.2–3 ELECTRON DENSITY DISTRIBUTION OF RUTILE, TiO_2. By R. Restori and D. Schwarzenbach, Institut de Cristallographie, Université de Lausanne, CH - 1015 Lausanne, Switzerland.

The accuracy of the measured structure amplitudes required for a meaningful electron density study increases with the atomic numbers of the elements forming the compound. At the same time, the importance of absorption and dispersion corrections increases. The effects of anharmonic motions of the heavy atoms may not be negligible, and secondary extinction may be more severe since the reflecting power increases also. These latter effects are generally corrected for by additional adjustable parameters, the physical reality of which are difficult to assess. In connection with our program on electron distributions and physical properties of simple inorganic structures, we became interested in identifying those features of the density maps which may be reliably determined in a compact heavy atom structure like rutile, TiO_2. In a previous paper (Collected Abstracts 7th Europ. Crystallogr. Meet., Jerusalem 1982, p. 79) we reported full-sphere X-ray data (I) measured at room temperature with Pd-filtered AgKα radiation to $(\sin\theta/\lambda)_{max}$ = 1.57 Å^{-1} using a fragment of a chemically pure Verneuil grown crystal of TiO_2 which we were unable to grind into a sphere. A second full-sphere data set (II) has since been measured at 100K with LiF-monochromated AgKα radiation to $(\sin\theta/\lambda)$ = 1.73 Å^{-1} using a natural spherical crystal of diameter 0.18 mm containing about 1% of Fe_2O_3. These data were corrected for TDS. Judging from the fit of equivalent reflections, extinction is isotropic in (II), but not in (I). In addition, the isotropic extinction corrections of the symmetry averaged structure amplitudes are less severe in (II) than in (I), $y(\min,|F|)$ = 0.86 and 0.76 respectively. Results from data set (II) are therefore considered to be more reliable. Charge density refinements of (II) were carried out using a full matrix least-squares program including, besides the standard parameters, isotropic extinction, 3rd and 4th order cumulants, up to 35 spherical harmonic charge density functions up to hexadecapolar order, and the κ-formalism (P. Coppens et al., Acta Cryst. A35 1979, 63). Parameters representing monopolar properties were strongly correlated. The scale factor was very unstable and changed by 3% from the procrystal value, despite the presence of extremely high order data. Some cumulant parameters were significant at the 10σ level. An R-value of .007 was reached (procrystal .10), but the fit of the data above $\sin\theta/\lambda$ = 1.6 Å^{-1} was less satisfactory than below that value. The main features of the resulting density maps are quite independent of the data set and the refined model, and are in agreement with a d^2sp^3 hybridization of Ti: bonding maxima of 0.3 e.Å^{-3} on both Ti-O bonds and an electron deficiency between nearest Ti-atoms along c. Model dependent features appear, however, in the vicinity of the atoms. The charge densities of rutile and corundum (J. Lewis, D. Schwarzenbach & H.D. Flack, Acta Cryst. A38, 1982, 733) do not seem to be sufficiently different to explain the very different physical properties of these materials.