14-Diffraction Physics and Optics


Using high-resolution (sin θ/λ ≤ 1.0 Å⁻¹) low temperature (120-140 K) X-ray diffraction data electron density distribution analysis in the new nitrogen-containing heterocycles (I-III) was performed in order to elucidate essential features of the chemical bonding.

![Chemical structure](image)

A conventional high-angle (R=3.0-4.0%) and multipole refinement (MOLLY program) procedures were used for constructing the dynamic and static deformation electron density (DED) maps, calculation of atomic charges and multipole parameters (final R values after multipole refinement were in the range of 1.9-2.4%). For the benzofuroxane molecule (I) atomic charges were found to be small, positive DED peaks were localized nearly at the mid-points of the chemical bonds except for dative N→O bond, where the corresponding maximum was shifted to the O atom. An essential delocalization of the electron density in the π-region was found in this heterocycle. In the fluorinated tetrazazepatetane (II) and tetrazine derivative (III) the strong π-component on the C=C, N=N and C=N bonds in the rings was established, testifying to the aromatic character of these heterocycles. Atomic charge distribution in (II) based on the multipole refinement data allowed to determine the contribution of the different resonance forms in the electronic structure. In the tetrazine derivative (III) high maxima on the DED maps corresponding to the lone pairs were found near N atoms in the molecular plane. The DED peaks on the C-N and N-N bonds were found to be shifted towards the centre of the heterocycle (bent bonds) probably due to the electrostatic repulsion between lone pairs and chemical bond electron density.

PS-14.02.12 ELECTRON DENSITY DISTRIBUTION IN CASSITERITE SnO₂. By V.S.Ursov*, O.V.Pakubovitch and N.N.Eremin, Moscow State University, Russia.

The precise X-ray investigation, including 6p maps calculation was carried out to study peculiarities of chemical bonds in crystals of cassiterite SnO₂ grown by oxidation of metallic Sn(1)=4.739(1), c=3.1877(9) Å, sp. gr. P₄₃mm, Z=2, p=6.99 g/cm³, μ=0.9, λ=MoKα, 2θ=9-80° scanning, sin θ/λ=0.08 Å⁻¹, 101 independent reflections. Parameters of the high-angle (sin θ/λ≥0.6 Å⁻¹, 104 reflections) refinement are: R=0.0062, WR=0.0072, 8=1.1777.

The deformation electron density (6p) maps for characteristic sections show main features common with 6p maps of isostructural rutile TiO₂ (R.Restory, D.Schwezenbach and J.R.Schneider, Acta Cryst., 1981, B31, 251-257) and stilboite SiO₂ (W.A.Spakman, R.J.Hill and E.V.Gibbs, Phys.Chem.Min. [1987], 14, 139-150). However, there are some peculiarities due to a more polarizable electron shell of Sn⁴⁺ compared to Ti⁴⁺ or Si⁴⁺.

PS-14.02.13 SECOND-NEAREST-NEIGHBOUR INTERACTIONS AND THE ELECTRON DENSITY DISTRIBUTION IN Y₃BaCuO₅. By J. Hester, R. Hau* and E. N. Maslen, Crystallography Centre, University of Western Australia, Nedlands, WA 6009, Australia.

Y₃BaCuO₅ has a tightly packed structure with all cations and the O₃ anion coplanar in a mirror plane with y/z = 0.25. There are O1 and O2 atom pairs above and below that plane. Analysis of synchronous data for a small Y₃BaCuO₅ crystal shows that second-nearest neighbour interactions dominate the redistribution of electron density. Within the mirror plane the cations are aligned in the sequence Ba—Y₂—Cu—Y₁—Ba over a total length of 13.10 Å. Atoms in those lines are cross-linked by zigzag connections along the a axis. The difference electron density map in the y/z = 0.25 plane displayed in the Figure shows that electron density is strongly depleted along the shorter links in that grid.