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PS-14.02.08 MODIFIED CRITERION OF CHEMICAL BOND COVALENCY AND X-RAY DIFFRACTION CHARGE DENSITY

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According to the topological theory of molecular structure (R. Bader et al. Rep. Prog. Phys. 1981, **44**, 893) bond-type critical point (CP) of the electron density function $\rho(\vec{r})$ must exist between chemically bonded atoms. In order to distinguish a covalent bond from closed-shell interactions (ionic, van der Waals and hydrogen bonds) R. Bader proposed the criterion: $\nabla \rho(\vec{r}_{cp}) < 0$ for covalent bonds. However, some covalent bonds (e.g., F-F) do not obey this rule. D. Cremer & E. Kraka (Angew. Chem. 1984, **96**, 612) propose more general criterion: electronic energy density $H(\vec{r}) < 0$ in CP of a covalent bond.

When investigating chemical bonds by precision X-ray analysis one obtains a distribution of ρ , but not a wavefunction, and cannot calculate $H(\vec{r}_{cp})$. Herein we propose to apply approximate relationships of the density functional theory to determine $H(\vec{r}_{cp})$. Thomas-Fermi-Dirac formula provides the upper estimate of $H(\vec{r}_{cp})$, whereas Thomas-Fermi-Weizsäcker formula, its lower bound (since $\nabla \rho = 0$, Weizsäcker's correction vanishes in CP).

The verification of our supposition is undertaken in the present report. As an example, a series of diatomics with various bond types is considered. Hartree-Fock values of H in the bond CP are compared with their approximate estimates. The possibility to apply obtained results to bonds in crystals using the experimental ρ distribution is discussed.

PS-14.02.09

CHEMICAL BONDING AND TEMPERATURE EFFECTS IN THE CHARGE AND SPIN DENSITIES OF $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ AND $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$

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The charge densities of tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and orthorhombic $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ have been determined from X-ray and neutron data at RT and 25K; the spin density of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ has been determined from polarized-neutron data at 1.5K in a magnetic field of 4.6T.

The charge density based on the fitted deformation functions of all atoms in the structure is compared with the individual densities calculated from deformation functions of only Ni or the separate water molecules. In this way, the effect of simple superposition of the individual densities has been studied. Polarization of the lone-pair densities, reflecting the different coordination of the different water molecules, is clearly evident, effects normally considered too small to be detected experimentally (Fig.1).

There is a clear difference between the Ni^{2+} densities at RT and 25K (Fig.2a,b). We interpret this as due to a difference in the relative occupations of the electronic levels; indeed, an estimation from our observations of the change in occupation agrees with magnetisation measurements of the splitting of the two upper-most levels in the case of the hexahydrate. It is to our knowledge the first time such an effect has been observed by diffraction methods.

The charge and spin densities observed around Ni^{2+} are in good agreement with those expected from ligand field theory for a d^8 electron configuration of Ni^{2+} in a weak ligand field: two paired electrons in each t_{2g} , one unpaired electron in each e_g . Thus the deformation spin density is concentrated towards the ligands (= the directions of e_g) whereas there is a deficiency in the deformation charge density in these directions.

Fig.1. Charge densities of the three water molecules in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Water (1) is coordinated in the plane to Ni, water (2) is coordinated tetrahedrally to one Ni, water (3) is coordinated tetrahedrally to one Ni and one H-bond donor.

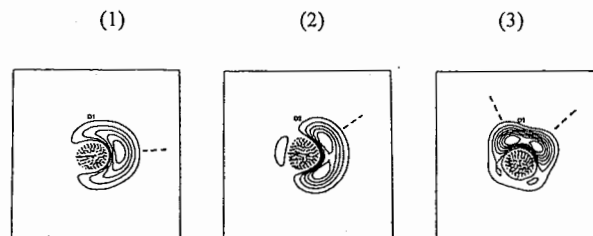
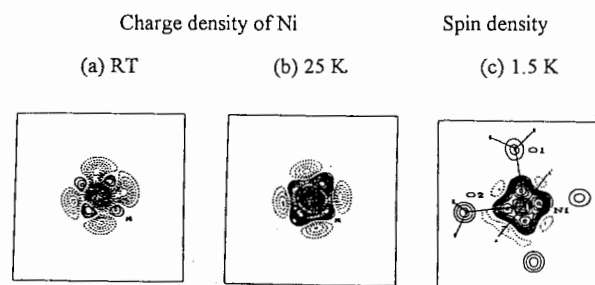


Fig. 2. Comparison of charge and spin densities around Ni^{2+} in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.



PS-14.02.10 AN X-RAY DIFFRACTION STUDY OF THE ELECTRON DENSITY DISTRIBUTION IN MOLECULAR CRYSTALS. By M.Yu. Antipin*, Yu.T. Struchkov. A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Acad. Sci., Moscow, Russia.

High-order low temperature X-ray diffraction data (Siemens P3/PC diffractometer, λMo , $\sin \theta/\lambda \leq 1.0\text{\AA}^{-1}$, $T=100-150\text{K}$) were collected for a long series of molecular crystals with different types of chemical bonds in order to elucidate some essential features of the electron density distribution (EDD) for these bonds. Among the organic compounds studied are highly strained spirocyclopropane derivatives (triangulanes) with an essential bond bending and new nitrogen-containing heterocycles (benzofuroxane, tetraazapentalene and tetrazine derivatives). An essential delocalization of the electron density in the π -regions was found in these aromatic heterocycles and the multipole analysis of EDD was performed. In the highly reactive phosphalkenes $(\text{Me}_2\text{N})_2\text{C}=\text{P}-\text{H}$, $\text{Cl}_2\text{C}=\text{P}-\text{N}(\text{SiMe}_3)_2$ and phosphalkyne $\text{Me}_3\text{C}-\text{C}\equiv\text{P}$ the position and orientation of the lone pairs at the P atoms was established. These compounds are low-melting liquids at ordinary conditions and suitable monocrystals were grown in situ from the melts directly on the diffractometer. Charge density analysis was also performed for carboranes (9-azido-*m*-carborane,

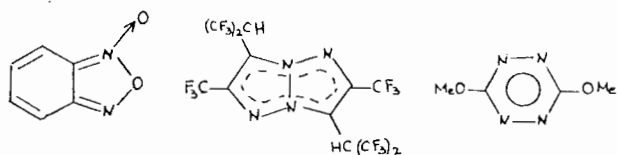
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8,9,10,12-tetrafluoro-*o*-carborane) and metallacarboranes CpFe(dicarb) and CpCo(dicarb) (Cp=C₅H₅, dicarb=dicarbollide) proving the absence of electron density accumulation inside the carborane cage and multicenter bonding at the triangular faces of the icosahedron. Among the organometallic compounds the metallocene derivatives Cp₂V, CpFeCp* (Cp*=C₅Me₅) and CpTi(η⁸-C₈H₈) were studied. On the contrary to the disordered ferrocene, the structures of Cp₂V and CpFeCp* are ordered at low temperature and the asymmetry of the 3*d*-electron distribution around metal atoms and the nature of metal-ligand bonds were analyzed. The observed EDD's in the molecules studied are essential for analysis of chemical bond features.

PS-14.02.11 ELECTRON DENSITY DISTRIBUTION IN THE NITROGEN-CONTAINING HETEROCYCLES. By E.A.Kuz'mina, M.Yu.Antipin* and Yu.T.Struchkov. A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russian Federation.

Using high-resolution ($\sin \theta/\lambda \leq 1.0 \text{ \AA}^{-1}$) 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.



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 tetraazapentalene (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.Urusov*, O.V.Yakubovich and N.N.Eremin, Moscow State University, Russia.

The precise X-ray investigation, including $\delta\rho$ maps calculation was carried out to study peculiarities of chemical bonds in crystals of cassiterite SnO₂ grown by oxidation of metallic tin: $a=4.739(1)$, $c=3.1877(9) \text{ \AA}$, sp.gr. P4₂/mnm, $Z=2$, $\rho_c=6.99 \text{ g/cm}^3$, $\mu_r=0.9$, $\lambda \text{ MoK}\alpha$, $2\theta-\theta$ scanning, $\sin \theta/\lambda \leq 1.08 \text{ \AA}^{-1}$, 141 independent reflections. Parameters of the high-angle ($\sin \theta/\lambda \geq 0.6 \text{ \AA}^{-1}$, 104 refl.) refinement are: $R=0.0062$, $wR=0.0072$, $s=1.1777$.

The deformation electron density ($\delta\rho$) maps for characteristic sections show main features common with $\delta\rho$ maps of isostructural rutile TiO₂ (R.Restory, D.Schwarzenbach and J.R.Schneider, Acta Cryst. (1987), B43, 251-257) and stishovite SiO₂ (M.A.Spackman, R.J.Hill and G.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⁺ ions.

PS-14.02.13 SECOND-NEAREST-NEIGHBOUR INTERACTIONS AND THE ELECTRON DENSITY DISTRIBUTION IN Y₂BaCuO₅

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Y₂BaCuO₅ has a tightly packed structure with all cations and the O3 anion coplanar in a mirror plane with $y/b = 0.25$. There are O1 and O2 atom pairs above and below that plane. Analysis of synchrotron data for a small Y₂BaCuO₅ 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 $\Delta\rho$ in the $y/b = 0.25$ plane displayed in the Figure shows that electron density is strongly depleted along the shorter links in that grid.