

## 14-Diffraction Physics and Optics

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

by Artem E. Masunov & Sergei F. Vyboishchikov\*  
 Chemical Department, Moscow State University,  
 Moscow, 119899, Russia.

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  $\rho$ , 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  $\rho$  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  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$

I. Olovsson <sup>(1)</sup>, G.J. McIntyre <sup>(2)</sup>, H. Ptasiewicz-Bak <sup>(3)</sup>

<sup>(1)</sup>Institute of Chemistry, University of Uppsala, Sweden

<sup>(2)</sup>Institut Laue-Langevin, Grenoble, France

<sup>(3)</sup>Institute of Nuclear Chemistry and Technology, Warsaw, Poland.

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  $\text{Ni}^{2+}$  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  $\text{Ni}^{2+}$  are in good agreement with those expected from ligand field theory for a  $d^8$  electron configuration of  $\text{Ni}^{2+}$  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.

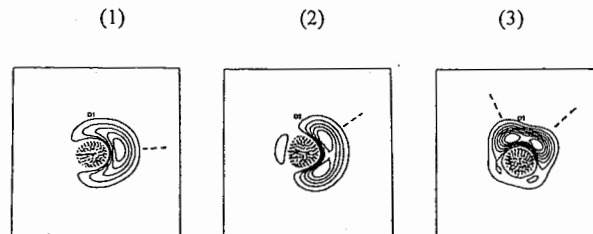
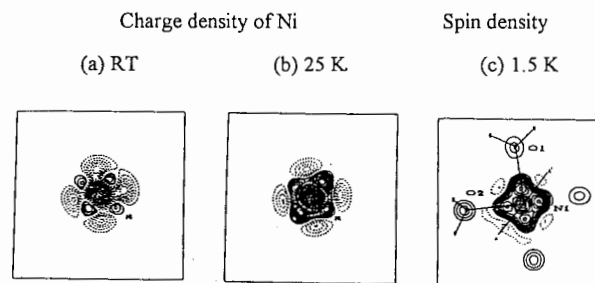


Fig. 2. Comparison of charge and spin densities around  $\text{Ni}^{2+}$  in  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ .



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,  $\lambda \text{Mo}$ ,  $\sin \theta/\lambda \leq 1.0 \text{\AA}^{-1}$ ,  $T=100-150\text{K}$ ) 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  $\pi$ -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,