

s2.m1.o3 Charge density analysis in semiconducting charge transfer complexes: a comparison between experiment and DFT calculations. C. Katan, P. Rabiller, L. Toupet, *GMCM univ. Rennes 1 France*, M. Souhassou, N. Hansen and C. Lecomte, *LCM3B univ. Nancy 1 France*.
Keywords: charge spin densities.

Mixed-stack charge transfer crystals are built from donor (D) and acceptor (A) planar aromatic molecules such as tetrathiafulvalene (D) and benzoquinone (A) derivatives. An essential feature of these compounds is the charge transfer from D to A. Charge transfer occurs mainly along the stack, which confers a strong one-dimensional character to properties like conductivity. Some of these small gap semiconductors exhibit under temperature and/or pressure a "neutral to ionic" phase transition, which involves both structural and electronic changes: loss of inversion symmetry and uncommonly large charge transfer variation. Even with similar stacking, small changes in A and D chemical formulae lead to very different critical parameters of the phase transition, which one-dimensional models cannot reproduce.

Understanding three-dimensional interactions becomes a crucial point for these materials. The topological analysis of the charge density, as developed in the theory of "Atoms in Molecules" by R.F.W. Bader, constitutes an appropriate tool for this purpose. It is particularly useful since it can equally well be applied to electron densities obtained from either theoretical calculations as from high-resolution X-ray diffraction experiments. It provides a clear definition of atomic basins allowing the determination of the net charge transfer. Moreover information about intermolecular interactions such as hydrogen bonds can be deduced from the analysis of the critical points of the charge density.

A first study of a mixed-stack charge transfer crystal is presented. The selected compound, tetrathiafulvalene-p-tetrachlorobenzoquinone, is the prototype for the neutral to ionic phase transition, which occurs at about 80K at atmospheric pressure. Comparison is made between density functional theory (DFT) calculations and experimental data obtained at 100K using a CCD detector.

s2.m1.o4 Spin densities in new molecular magnetic compounds. B. Gillon, J.A. Stride, *Laboratoire Léon Brillouin (CEA-CNRS), C.E. Saclay, 91191 Gif-sur-Yvette, France*.

Keywords: spin density, molecular magnetism, polarised neutron diffraction

Spin density determination brings unique insights onto the magnetic interaction mechanisms leading to ferromagnetic interactions in molecular compounds, by providing direct information about the spin delocalisation and spin polarisation effects, which are known to play important roles in such interactions.

We report on such investigations in recently synthesized hetero-bimetallic compounds, in which metallic ions of two different types, with different local spin values, interact through a bridging organic group.

The compound $\text{Mn}^{\text{II}}\text{Ni}^{\text{II}}(\text{NO}_2)_4(\text{en})_2$ (with en = ethylenediamine) is one of the rare bimetallic compound forming ferromagnetic chains, which has been synthesized to date¹. The mechanism responsible for the ferromagnetic interaction between the Mn^{2+} ($3d^5$, $S = 5/2$) and Ni^{2+} ($3d^8$, $S=2$) ions, which are bridged by one NO_2^- group to form ... $\text{Mn}(\text{NO}_2)\text{Ni}$... chains, will be discussed in the light of the spin density determination from polarised neutron data at 2.5 K under 7 Teslas and of DFT theoretical calculations on a molecular model.

Ferromagnetic ordering temperatures up to 50K have been recently obtained for a new family of cyano-bridged compounds² combining a 3d Mn^{2+} ion and a 4d Mo^{3+} ion ($3d^3$, $S = 1/2$). A peculiar feature of these compounds is the Mo^{3+} coordination number of seven, which is not usual in coordination chemistry. The induced spin density at 4K under 3 Teslas, in the $\text{K}_2\text{Mn}_3(\text{H}_2\text{O})_6[\text{Mo}(\text{CN})_7]_2 \cdot 6\text{H}_2\text{O}$ compound, actually shows a ferrimagnetic arrangement of the magnetic moments on the Mn^{2+} and Mo^{3+} sites.

[1] Kahn O. et al. "Metamagnetic behaviour of the novel bimetallic ferromagnetic chain compound $\text{Mn}^{\text{II}}\text{Ni}^{\text{II}}(\text{NO}_2)_4(\text{en})_2$ (en = ethylenediamine).", *Inorg. Chem.*, (1997), 36: 1530 - 1531.

[2] Larionova J. et al. "Structure, ferromagnetic ordering, anisotropy and spin reorientation for the two-dimensional cyano-bridged bimetallic compound $\text{K}_2\text{Mn}_3(\text{H}_2\text{O})_6[\text{Mo}(\text{CN})_7]_2 \cdot 6\text{H}_2\text{O}$.", *J. Am. Chem. Soc.*, (1999), 121: 3349 - 3356.