MS23-O2 Charge Density Studies of Switchable Molecular Materials at Extreme Conditions: What; How & Why?

Helena J. Shepherd[1]

1. University of Kent

email: H.J.Shepherd@kent.ac.uk

Spin crossover (SCO) is the phenomenon of switching between high-spin (HS) and low-spin (LS) states shown by certain complexes of first row (d4 - d7) transition metals. It is accompanied by changes in colour, magnetism, optical and mechanical properties of the material, and may be induced by some perturbation such as a change in temperature, light irradiation, pressure, the presence of guest molecules etc. [1]. These characteristics present interesting opportunities for applications in sensing, display and actuating technologies [2]. The subtle electronic redistribution of electron density within these materials results in substantial structural reorganisation of the material, driven by changes in volume of the metal coordination sphere in excess of 25%.

In-situ high pressure and/or light-irradiation during structural studies of SCO materials have created new understanding of this fascinating class of switchable molecular materials, and although by no means routine, incorporation of such extreme conditions into the X-ray diffraction experiment is now reasonably common [3,4]. Charge density studies provide an opportunity to study the coupling between electronic and structural effects in these out-of-equilibrium processes, providing complimentary insights. Combining charge-density studies with extreme conditions, while experimentally very demanding, will allow development of the next generation of materials with improved switchable functionality. This presentation will evaluate the benefits, as well as the challenges, to be encountered in performing these kinds of cutting-edge experiments.

References:

[1] A. Bousseksou et al. Chem. Soc. Rev., 2011,40, 3313-3335

[2] G. Molnar et al. J. Mater. Chem. C, 2014,2, 1360-1366

[3] Helena J. Shepherd et al. Phys. Rev. B 84, 144107

[4] Sébastien Pillet, Helena J. Shepherd et al. Phys. Rev. B 86, 064106

Keywords: Extreme Conditions, Charge Density, Functional Molecular Materials

MS23-O3 Copper-pyrazine magnetic polymers under high pressure

Arianna Lanza[1,2], Rebecca Scatena[2], Leonardo H.R. Dos Santos[2], Mariusz Kubus[3], Karl W. Krämer[2], Lukas Keller[3], Tom Fennell[3], Björn Wehinger[3], Alun Biffin[3], Christian Rüegg[3], Nicola Casati[1], Piero Macchi[2]

1. Laboratory of Synchrotron Radiation, Paul Scherrer Institute, Switzerland
2. Department of Chemistry and Biochemistry, University of Bern, Switzerland
3. Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institute, Switzerland

email: arianna.lanza@dcb.unibe.ch

Coordination polymers based on copper ions linked by pyrazine (pyz) and halide bridges are easy to synthesize and crystallize. Depending on the stoichiometry, the counter ions and the reaction conditions, a wide variety of polymers has been obtained, showing different topologies and magnetic properties.[1]

Their characteristics and chemical simplicity make them suitable models for a systematic investigation of the variation of the material properties as a function of composition or pressure-induced structural modifications. Pressure may trigger phase transitions or even chemical reactions in these species. The most commonly observed phenomena are: a) orientational changes of the pyz spacers; b) orbital reordering and consequent re-orientation of the Jahn-Teller distortion; c) attachment/detachment of ancillary ligands. These phenomena (especially orbital reordering) have important consequences for the dimensionality of the magnetic exchange network.[1,2]

Recently, the magnetic properties of some Cu-pyz based materials have been examined and correlated with the topological and integrated properties of their electron and spin density distribution.[3]

In this talk, we will focus on $[(CuF_2(H_2O)_2)_x(pyz)]$ (x=1,2) and $[(Cu(pyz)_2X]Y$ (X=halide; $Y=BF_4^-$), investigated up to 15 GPa with single crystal and powder X-ray diffraction and theoretical charge and spin density calculations. The role of the ligands in the super exchange mechanisms and the experimental coupling constants will be rationalized by systematic electron density analysis on the room pressure and high pressure phases.

[1] Lanza, A.; Fiolka, C.; Fisch, M.; Casati, N.; Skoulatos, M.; Rüegg, C.; Krämer, K. W.; Macchi, P. *Chem. Comm.* **2014**, *50*, 14504.

[2] Halder, G. J.; Chapman, K. W.; Schlueter J. A.; Manson, J. L. *Angew. Chem.-Int. Ed.*, **2011**, *50*, 419.

[3] Dos Santos L.H.R.; Lanza A.; Barton A.M.; Brambleby J.; Blackmore W.J.A.; Goddard P.A.; Xiao F.; Williams R.C.; Lancaster T.; Pratt F.L.; Blundell S.J.; Singleton J.; Manson, J.L.; Macchi, P. *J. Am. Chem. Soc.*, **2015**, *187* (7), 2280.