above information. We used nano beam diffraction to obtain particle structure and orientation at low irradiation dose and spatially resolved valence electron energy loss spectroscopy to measure the optical properties of the same nanoparticles. The use of spatially resolved EELS together with approximately 0.35 eV energy resolution of our instrument allows us study spatial origin of the spectral features. Component deconvolution can be used on spatially resolved EELS spectra to separate the Au particle contribution to EEL spectra from the substrate contribution [2].

To optimize our Hitachi HF 3300 microscope and evaluate its suitability we used a sample of gold nanoparticles deposited onto an amorphous germanium substrate. We used 100 kV incident energy and collected 50 spatially resolved spectra with 5 s acquisition time. We then acquired nano beam diffraction patterns and energy filtered series to measure local sample thickness.

It appears that the even very small Au particles are composed of several crystallites. The spatially resolved EELS reveals strong peaks at about 2.25 eV and at about 5.5 eV corresponding to surface and bulk plasmon for a particle of approximately spherical shape [3]. We also find that although the overall shape of the Au particles appear to be largely intact after about 50 C/cm^2 at 100 kV, the 3 nm to 5 nm thick amorphous germanium is entirely removed at the same dose. The electron sputtering threshold for Ge is about 115 keV, taking Ge atom desorption energy E_D to be equal to sublimation energy E_S, or 181 keV if $E_D=(5/3)E_S$ [4]. The microscope vacuum is 3×10^{-8} torr during our experiments excluding chemically enhanced etch by gaseous species from microscope vacuum. Therefore sputtering is unlikely to explain the fast damage of the amorphous Ge film. The amorphous Ge film appears to be protected in the areas where Au particles are located.

[1] P.E. Batson, *Microsc. Microanal* **2008**, *14*, 89. [2] F. Wang et al, *Ultramicroscopy* **2009**, *109*, 1245. [3] B.R. Cooper, H. Ehrenreich, *Phys. Rev.* **1965**, *138*, A494. [4] R. Egerton et al. *Ultramicroscopy* **2010**, *110*, 991.

Keywords: EELS, deconvolution, damage.

MS66.P01

Molecular Spin Crossover – What can pressure reveal?

Helena J. Shepherd,[a,b] Gábor Molnár,[a] Philippe Guionneau,[b] Patrick Rosa,[b] Azzedine Bousseksou,[a] [a]*LCC-CNRS, Toulouse (France).* [b]*University of Bordeaux, ICMCB-CNRS, Bordeaux (France).* E-mail: helena.shepherd@lcc-toulouse.fr

The spin crossover (SCO) phenomenon is the switching of a transition metal complex between its high spin (HS) and low spin (LS) electronic configurations as a result of some perturbation to the species (e.g. changes in temperature or pressure, or after light irradiation). Molecular species in the HS and LS states are distinguished by differences in their structure, color and magnetic moment [1].

In this class of materials the local and long-range structure directly impacts the magnetic behavior of the sample in a dramatic way. Understanding this relationship is crucial to the development of applications that exploit these switchable properties in the fields of molecular electronics, data storage and sensing.

High pressure studies may permit the decoupling of structural and spin-state transitions and thus allow access to unique phases that cannot be investigated using more conventional diffraction methods alone.

Single crystal X-ray diffraction techniques at elevated pressure and variable temperatures, complimented by high pressure Raman spectroscopic and magnetic studies, have been used to probe the structure-properties relationship of the molecular materials [Fe(bapbpy)(NCS)$_2$] [2] and [{Fe(bpp)(NCS)$_2$}$_2$4,4'-bipy]MeOH [3]. The former undergoes an unprecedented pressure-induced two-step

SCO; it is characterized by an ordered intermediate phase with long range order of [HS-LS-LS] sites within the lattice in the pressure range 4-11 kbar (see image). The latter material undergoes a gradual spin conversion under pressure, which is in stark contrast to its rather abrupt thermal SCO behavior.

These examples serve to illustrate the wealth of information, obtained through high pressure studies of functional molecular materials, which is often vital to understanding complex ambient pressure behavior.
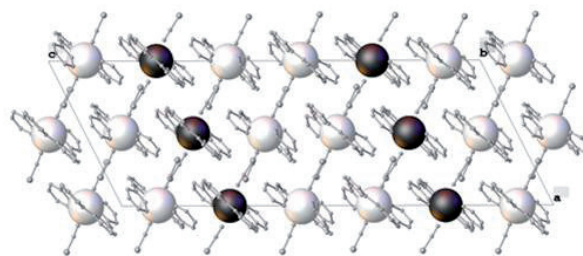
[1] P. Gütlich, H.A. Goodwin *Top. Curr. Chem.* **2004**, *233*, 1. [2] S. Bonnet, G. Molnár, J. Sánchez Costa, M.A. Siegler, A.L. Spek, A. Bousseksou, W.-T. Fu, P. Gamez, J. Reedijk, *Chem. Mater.* **2009**, *21*, 1123. [3] A. Kaiba, H.J. Shepherd, D. Fedaoui, P. Rosa, A.E. Goeta, N. Rebbani, J.-F. Létard, P. Guionneau. *Dalton Trans.,* **2010**, *39*, 2910.

Keywords: magnetism, molecular, pressure

MS66.P02

Reversible structural modulation and magnetic properties in a Co-based SMM

Larry R. Falvello,[a,b] Javier Campo,[b] Elena Forcén-Vázquez,[b] Isabel Mayoral,[b] Fernando Palacio,[b] Cristina Sáenz de Pipaón,[b] Milagros Tomás.[c] [a]*University of Zaragoza, Department of Inorganic Chemistry,* [b]*University of Zaragoza – C.S.I.C., Aragón Materials Science Institute, and* [c]*University of Zaragoza – C.S.I.C., IQSCH, Pedro Cerbuna 12, 50009 Zaragoza, (Spain).* E-mail: falvello@unizar.es

The topological properties of transition metal citrate cubanes lead to a variety of structure types and topotactic reactivity in the crystalline state. The citrate cubane, with general formula [M(II)$_4$(citr)$_4$]$^{(8-)}$ [M = transition metal, citr = quadruply deprotonated citrate, $C_6H_4O_7^{(4-)}$], has been prepared with two distinct topologies in Co(II) and Mn(II) complexes.

Within this context, a cubane-based Co(II) complex is described -- Co$_4$(citr)$_4$[Co(H$_2$O)$_4$]$_4$, **2**, which was prepared in a two-stage process beginning with isolation of a sub-periodic crystalline material, **1**, whose modulated structure and chemical composition have been analyzed using single-crystal x-ray diffraction.

A reversible solid-state reaction can be provoked in **1** to yield **2**, whose three-dimensional structure is not modulated. The modulated structure of **1** is explained in terms of concerted hopping of peripheral Co(II) between neighboring molecules in **2**, producing a distinct chemical species.

Magnetic measurements conducted on the **1/2** single molecule magnet (SMM) system required special precautions to avoid interchange of the two species under experimental conditions. The distinct magnetic properties of the two interchangeable solids establish both as being based on SMM.

For **1** the average structure has a = 23.2064(14), b = 9.6655(4), c = 23.5066(11) Å, β = 111.037(6)°, V = 4921.2(2) Å^3, space group *C2/c*. The refined modulation vector parameters are of the form *(0β0)*, with β near 3/8. For the unmodulated structure of **2**, a = 22.7842(10),

P.MS.66