



	<b>Experiment title:</b> Core/shell nanomagnets from the Prussian Blue family	<b>Experiment number:</b> HE3557
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<b>Shifts:</b> 18	<b>Local contact(s):</b> Andrei Rogalev	

**Names and affiliations of applicants (\* indicates experimentalists):**

Pr Talal Mallah ICMMO, Orsay

Dr. Marie-anne Arrio Dr. Philippe Sainctavit, IMPMC, Paris

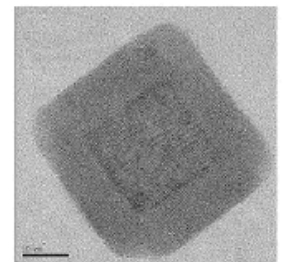
Dr. Christophe Cartier dit Moulin, IPCM, Paris

Dr Edwige Otero, SOLEIL, Saint Aubin

**Report:**

**Scientific background**

Prussian blue analogs are well known for the variety of their magnetic properties. Recently, spontaneous stabilization in water of almost all the Prussian Blue analog networks in the form of nanoparticles was achieved which opened the possibility to grow in a controlled manner multilayered coordination nanoparticles [1]. Chemical mapping using the EELS technique of a STEM as well as high resolution transmission electron microscopy clearly demonstrated the core-shell nature nanoparticles and the epitaxial growth of the shell network on the core one [1]. Such core-shell nanoparticles present complex magnetic properties due to the exchange interaction between the core and the shell and within each type of network. XMCD is the appropriate technique to study the synergy between the magnetic behaviors of the two different nanonetworks.



**Experimental details**

We focussed our experiments on  $\text{CsNi}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  nanoparticles, where Ni(II) and Cr(III) have a ferromagnetic interaction, surrounded by the ferromagnetic  $\text{Co}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  shell. The intrinsic magnetic anisotropy of Co(II) leads to particular behavior of the core/shell nanoparticles. We measured the following series of core/shell nanoparticles : (i) 6 nm  $\text{Ni}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  core, (ii) 6 nm  $\text{Ni}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  core surrounded by 2 nm  $\text{Co}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  shell, (iii) 6 nm  $\text{Ni}^{\text{II}}[\text{Co}^{\text{III}}(\text{CN})_6]$  core, (iv) 6 nm  $\text{Ni}^{\text{II}}[\text{Co}^{\text{III}}(\text{CN})_6]$  core surrounded by 2 nm  $\text{Co}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  shell. In (iv), replacing Cr(III) ( $S=3/2$ ) by a diamagnetic  $S = 0$  low spin Co(III) ion allows to have a paramagnetic core in interaction with the ferromagnetic shell and to separately study the role of the Cr(III) ion from the shell in the absence of Cr(III) in the core.

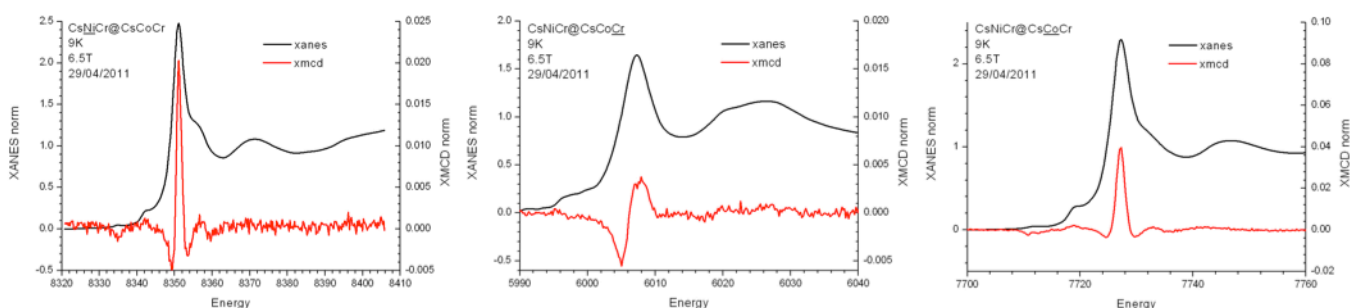


Figure 0 : XANES and XMCD measured at the Ni (left), Cr (center) and Co (right) K edge in the sample (ii) (6nm  $\text{Ni}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  core surrounded by 2 nm  $\text{Co}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  shell).

## Results

We measured XMCD with the HU38 Apple II undulator of ID12, at 9 K and +/- 6.5 T. For each sample, we recorded the XMCD signal at the Ni, Cr and Co ions for (ii) and (iv), Ni, Cr for (i) and Ni, Co for (iii) : for example, see figure 1 for sample (ii). Good quality data were obtained. For Ni(II) and Cr(III) K edge, the shape of the XANES and XMCD spectra are similar with the one we measured on bulk  $\text{CsNiCr}(\text{CN})_6$  bulk compound [2]. The sign of the XMCD signals indicate a ferromagnetic coupling between the Ni(II) and Cr(III) ions and between the Co(II) and Cr(III) ions [3]. For a same ion K edge, small differences in shape and amplitudes are observed in the different nanoparticles that shall be explained through calculations (see below).

Figure 2 shows the XANES and XMCD measurements at the Co K edge for compounds (ii), (iii) and (iv). For (iv), the edge is shifted at higher energy due to the presence of Co(III) (and the absence of Co(II)). In that case, no XMCD signal is observed as expected for a  $S=0$  low spin Co(III). For (iii), the presence of two major peaks in the edge is due to the Co(II) (peak at low energy : 7727.3 eV) in the shell and Co(III) (peak at high energy : 7730.8 eV) in the core. In that case, the XMCD signal is lower in the (ii) sample one that contains only  $S=3/2$  high spin Co(II). The XANES and XMCD spectra at K-edges need to be calculated to get quantitative informations. Our preceding calculation on the bulk systems were obtained using multiple scattering in the muffin-tin approximation [3]. These calculation need to be improved by the Spin polarized pseudo-potential approach developed at IMPMC in collaboration with D. Cabaret and M. Calandra [Ch. Gougoussis, PhD, University Paris VI, 2009]. The pre-edge region will be calculated in the Ligand Field Multiplet theory [4]. This work is in progress.

Moreover, we measured the element specific magnetization curves of Ni, Cr, Co for each sample. This was done by measuring the absorption at the energy of the maximum of the XMCD, by flipping the polarization and varying the magnetic field from -6 to + 6 teslas. For example, Figure 3 shows the magnetization curves obtained at the Co K edge in the samples (ii) and (iv). The magnetization curve of (iv) is less abrupt than the one of (ii) since Co(II) (in the shell) is less polarized by the paramagnetic Ni(II) core than in the (ii) sample where there are magnetic interaction between Co(II) from the shell and the Cr(III) from the core at the core/shell.

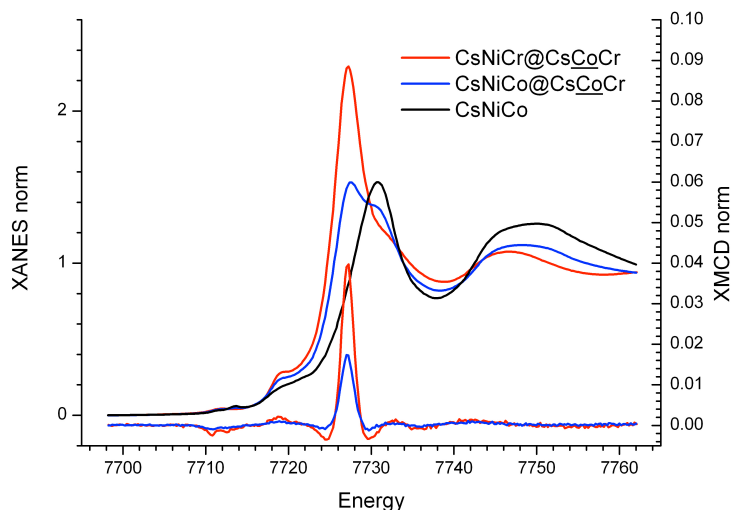


Figure 1 : XANES and XMCD at Co K edge of (ii), (iii) and (iv) samples

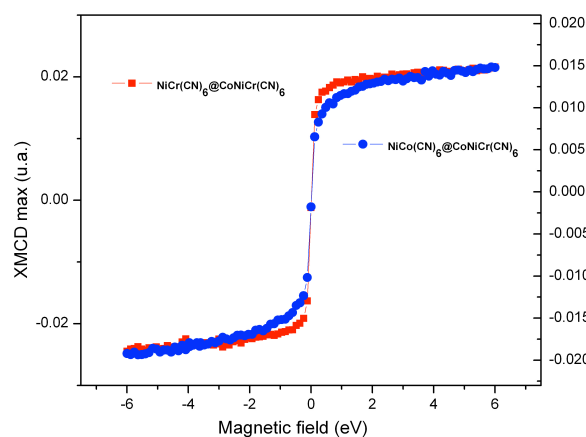


Figure 2 : Magnetization curves obtained at the Co K edge in (ii) and (iv)

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