ESRF	**Experiment title:** Local magnetic properties of Photomagnetic Co/Fe nanocrystals organized as monolayer : XMCD at L_{23} edges	**Experiment number**: HE3863
Beamline: ID8	**Date of experiment**: from: 13Feb 2013 to: 19 feb 2013	**Date of report**: 28/02/2013
Shifts: 18	**Local contact(s)**: Erika Jimenez Romero	*Received at ESRF:*

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Report:

Scientific background

The goal of the experiment is to measure the magnetic properties of photomagnetic nano-sized crystals organized on HOPG (Highly Oriented Pyrolytic Graphite) substrate as a monolayer. The nanocrystals studied here are cobalt hexacyanoferrate $Cs^{I}Co^{III}Fe^{II}(CN)_6$ from the Prussian Blue Analogues family. [1] At low temperature, the system is diamagnetic (low spin S = 0 Co(III) and Fe(II)). Irradiation with red light (λ = 630 nm) at low temperature induces an electron transfer and leads to high spin Co(II) S=3/2 and low spin Fe(III) S=1/2. Exchange coupling between the paramagnetic ions yields an ordered magnetic phase. XMCD at Co and Fe $L_{2,3}$ edges is a unique tool to investigate the magnetic properties of our diluted systems and to follow the electronic and magnetic properties of the Co and Fe ions.

Experimental details

We measured three samples: (1) one monolayer of 10 nm particles on HOPG, (2) a layer of 20 nm obtained from the growth of the Fe/Co network on the previous monolayer, (3) one monolayer of 6 nm particles on HOPG. For each sample, me measured :

(i) at 4 K and 4 teslas, XMCD at Fe and Co $L_{2,3}$ edges before laser excitation,
(ii) at 4 K and 4 teslas, XMCD at Fe and Co $L_{2,3}$ edges after 30 mn, 1 hour and up to 6 hours of laser excitation;
(iii) at 300 K and 4 teslas, XMCD at Fe and Co $L_{2,3}$ edges (relaxation),
(iv) at 4 K and 4 teslas, XMCD at Fe and Co $L_{2,3}$ edges, after relaxation at 300K

At each step, we also measured the magnetization curves by measuring XMCD as a function of magnetic field. We measured angular dependance of the magnetization curves (at 0° and 60 °).

Results

Good quality data were obtained for sample 1 and 2. Sample 3 has noisier data due to the smaller size of the layer. We used very reduced x-ray flux to avoid any radiation damages and x-ray photoexcitation.

The nanoparticles are expected to contain Co(III) and Fe(II) in the initial state (before laser excitation) with small amount of Co(II) measured by infra-red spectroscopy. However it is difficult with conventionnal spectroscopies to determines the Co(II)/Co(III) composition. In all samples, the Co $L_{2,3}$ edges showed the presence of Co(II) and Co(III) in the initial state (before laser excitation). The large amount of Co(II) species might be due to surface effects that are probed at Co $L_{2,3}$ edges. The Fe $L_{2,3}$ edges show the presence of mostly Fe(II) species with very small amount of Fe(III).

After laser excitation, the Co $L_{2,3}$ edges show the transformation of Co(III) into Co(II) and the Fe $L_{2,3}$ edges show the transformation of Fe(II) into Fe(III) as shown in figure 1. After relaxation (the sample is warmed at 300 K) these effects are reversible. The amount of Fe-Co phototransformed seem small and has to be quantified through ligand field multiplets calculations. The calculations of the XMCD signals will also lead to the determination of the coupling between Fe and Co ions. The Fe ion forms a strongly covalent bond with CN. It's spectra will be calculated inculding π back bonding [2].

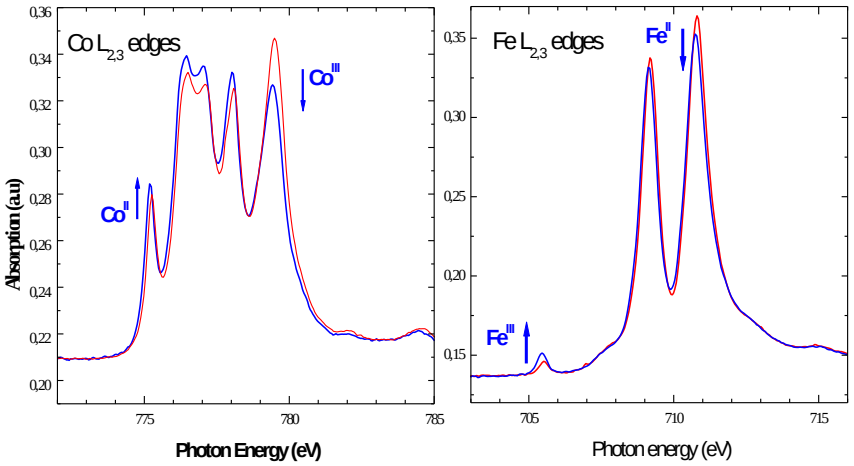

Figure 1 : (left) XAS at Co $L_{2,3}$ edges before (red) and after (blue) laser excitation; (right) same at Fe $L_{2,3}$ edges

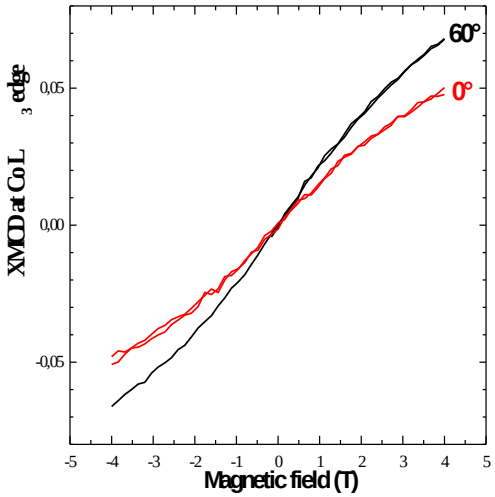

Figure 2 : Magnetization curves measured at the energy of the maximum of Co XMCD at 0° and 60 ° (angle between the surface normal and the x-ray propagation vector)

For each sample, we also observed an angular dependance of the magnetization curves (figure 2) that evidenced the presence of magnetic anisotropy in the plane. **It is an important information for these systems that are developped to be used in spintronic devices.** No opening of the hysteresis curves have been measured since lower temperature is needed.

From the report, it is clear that the monolayers of nanoparticles are too thick to be probed on its full depth with soft X-rays indicating that complementary XMCD measurements at K edges are necessary. For this study, we also asked for beamtime at ID12.

[1] Brinzei, D. et al. *J. Am. Chem. Soc.* **129**, 3778 (2007); Catala, L. et al. *Inorg. Chem.* **48**, 3360 (2009); Volatron, F. et al *Chem. Commun.* **47**, 1985 (2011).
[2] Hockin R. K. *et al*. J. Am. Chem. Soc., 128, 10442-10451 (2006)