



	Experiment title: Magnetization evolution in colloidal Fe ₃ O ₄ nanoparticles as a function of size probed by Fe 1s2p RIXS-MCD	Experiment number: HC-1540
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Report:

The main goal of the experiment was to follow the changes in the Fe electronic and magnetic structure as a function of size in Fe₃O₄ colloidal nanoparticles (NPs) in the aqueous phase. Accordingly, we performed a thorough characterization by means of HERFD-XANES, K α XES and 1s2p RIXS-MCD in various Fe₃O₄ NPs samples. The incident energy was selected by means of a pair of Si(311) crystals seeking for good resolution. The inelastically scattered photons were analyzed using a set of four spherically bent Ge(440) crystals that were arranged with samples and photon detector (Avalanche Photo Diode) in a vertical Rowland geometry ($R \approx 1$ m). We used masks in the crystals to improve resolution which was about 0.5 eV as deduced from the full width half maximum of the elastic peaks. The HERFD-XANES across the Fe K-edge (7.112 eV) were recorded at the maximum of the K α_1 fluorescence emission line and the K α XES spectra at an incident energy of 7.200 eV. Circularly polarized incident x-rays for the MCD measurements were attained by using a 400 μ m diamond (111) quarter wave plate. Four different cuts were chosen in the 1s2p RIXS-MCD plane so that we measured for all the samples XANES-MCD at emitted energies 6.4023 and 6.4044 keV and XES-MCD at incident energies 7.1116 and 7.1136 keV. Full 1s2p RIXS-MCD planes were only collected in selected samples. Polycrystalline magnetite and maghemite (γ -Fe₂O₃) pellets were also measured as reference compounds. All the measurements were carried out at room temperature.

We note that the experiment was particularly challenging from the experimental set-up viewpoint. It was concluded from previous measurements that in order to obtain reliable spectra, the use of a liquid jet set-up and measuring in a free jet region is mandatory. In this way, the Fe₃O₄ NPs are permanently circulating giving a good intensity stability over time and at the same time radiation damage is avoided since the x-rays shine on fresh spots. In this experiment, a rotatory gear pump suitable for magnetic NPs was used to produce the continuous flow. Finally, a small electromagnet developed in the ESRF sample environment was adapted to apply the magnetic field on the liquid jet and achieve the magnetic saturation of the Fe₃O₄ NPs for the 1s2p RIXS-MCD measurements (see Fig. 1). The jet nozzle was motorized in order to centre the samples in

the magnetic field and the maximum field provided by this set-up was 0.5 Tesla. There was also the possibility to vary the field between 0.5 and -0.5 Tesla to perform field dependent measurements.

Different sets of Fe_3O_4 NPs were measured in order to probe the size dependence and also to check for the chemical environment and age effects in the electronic and magnetic properties of the samples. They are described in the following:

- **“Size” set:** NPs of **4, 12, 20 nm size** in TMAOH solvent (10 mM) synthesized 10 days before the experiment and stored in air. Besides, an equivalent 4 nm size sample but stored in Ar.
- **“Solvent” set:** NPs of 7 nm size in **H_2O only** and solvents: **TMAOH (50 mM) and tannic acid (50 mM)** synthesized 10 days before the experiment and stored in air. Besides, an equivalent TMAOH (50 mM) solvent sample but stored in Ar.
- **“Size-fresh” set:** NPs of **4, 12, 20 nm size** in TMAOH solvent (10 mM) synthesized during the beamtime.

While the $\text{K}\alpha$ XES spectra show very little changes between the different samples, the HERFD-XANES reveal interesting information. First of all, the HERFD-XANES spectra of the NPs is different with respect to those of bulk magnetite and maghemite and the position of the main edge suggests an Fe oxidation state in between those of the reference compounds. Also, we have clearly detected that the NPs synthesized 10 days before and stored in air are more oxidized than their fresh counterparts. However, if they are stored in Ar atmosphere the oxidation state is equivalent to the fresh sample case. Finally, the HERFD-XANES are very similar within the “solvent” and “size-fresh” sets.

We could successfully obtain MCD spectra in all the samples which demonstrates the feasibility of the experimental set-up for future RIXS-MCD experiments on magnetic NPs in a liquid jet. In Fig. 1 are shown as example the XES-MCD spectra across the $\text{K}\alpha_1$ line collected at 7.1136 keV, which corresponds to the strongest MCD signal that we recorded. Being consistent with macroscopic magnetometry measurements, the MCD signal of bulk magnetite is larger than those of the NPs samples. In decreasing order of magnitude, it follows the “solvent” set (7 nm size samples in TMAOH, tannic acid and H_2O_2) and then the “size” and “size-fresh” sets with no clear trend. Further measurements on new fresh samples and an improved control over the size distribution are needed in order to clarify this point.

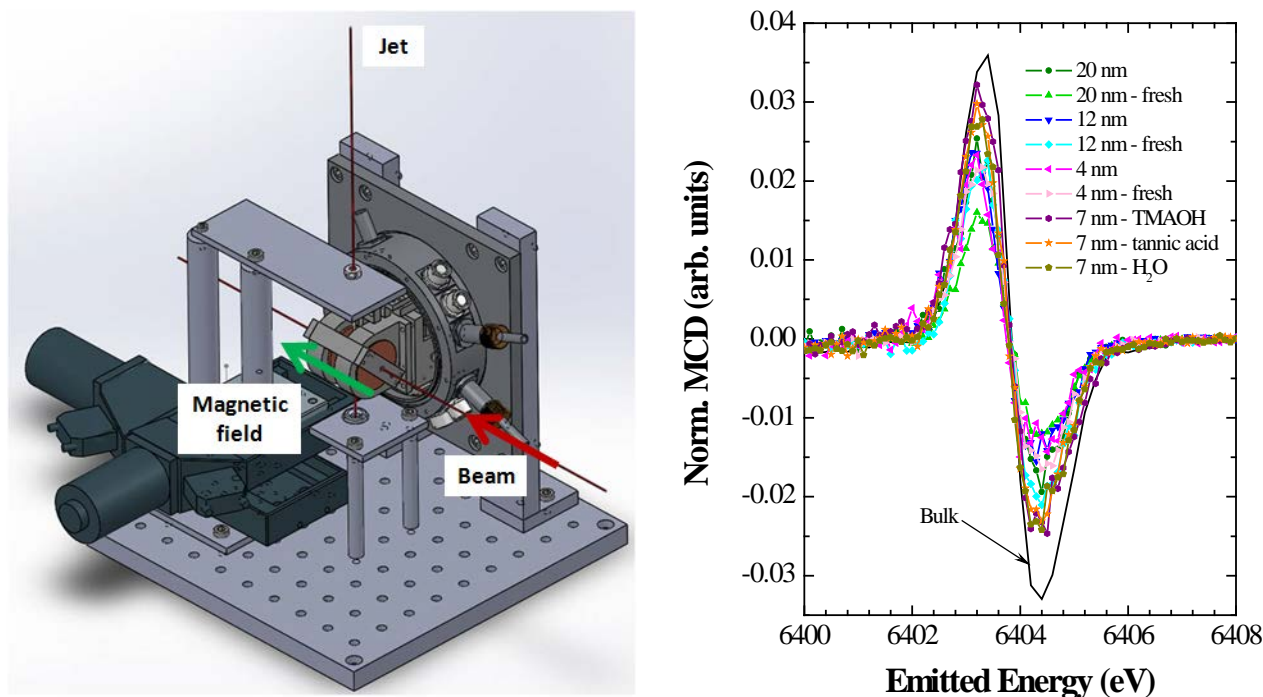


Figure 1. (Left) Design of the experimental set-up for MCD measurements on magnetic NPs in a liquid jet using a small electromagnet. (Right) XES-MCD spectra across the $\text{K}\alpha_1$ line detected at incident energy 7.1136 keV for bulk Fe_3O_4 and different NPs samples. The magnetic field applied was 0.5 Tesla. For the sake of comparison the spectra have been normalized to the spectral area of the average XES between the positive and negative circular polarizations spectra.