



	<b>Experiment title:</b> Electronic and magnetic structure of colloidal Fe <sub>3</sub> O <sub>4</sub> nanoparticles as a function of size and shape probed by Fe 1s2p RIXS-MCD	<b>Experiment number:</b> HC-2896
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 01/10/2016 to: 05/10/2016	<b>Date of report:</b> 17-02-2017
<b>Shifts:</b> 11	<b>Local contact(s):</b> S. Lafuerza	<i>Received at ESRF:</i>
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## Report:

Among the different objectives of the proposal, namely the investigation of the electronic and magnetic structure of Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) as a function of size and shape by means of Fe 1s2p RIXS-MCD, in the HC-2896 experiment we focused on the electronic structure characterization and we only performed Fe *K* edge HERFD-XANES and *Kα* XES measurements. Determining the actual iron oxide phase in the NPs as well as establishing whether the synthesis of the different types of particles was reproducible were our priorities before moving to the more elaborate and time-consuming technique RIXS-MCD. Like this, the 11 shifts granted to this proposal were dedicated to perform a screening of a large number of samples including also references which would not have been possible to characterize if using the RIXS-MCD set-up.

The incident energy was selected by means of a pair of Si(311) crystals while 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 the resolution. The total experimental broadening 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 (7112 eV) were recorded at the maximum of the *Kα*<sub>1</sub> fluorescence emission line and the *Kα* XES spectra at an incident energy of 7200 eV. Regarding the sample environment, the liquid jet set-up used in the first experiment HC-1540 was discarded given the large number of samples to be characterized. Instead, the samples were measured as frozen solutions in a continuous He-flow cryostat at low temperature (25-30 K) in order to minimize any possible radiation damage. This allowed us to load several samples in the same holder which required a very small amount of liquid (< 1 ml). Besides solid samples of reference compounds were prepared in the form of pellets with different concentrations to deal with the self-absorption (SA) effect.

In the following a summary with the samples measured during the beamtime is provided (for simplicity, we do not include the different versions of each sample in terms of batch, modifications to the standard synthesis, storing conditions or ageing time):

- *Bulk references:*
  - o Commercial powders from Sigma-Aldrich:  $\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{FeO}$
  - o Thin film of  $\text{Fe}_3\text{O}_4$  epitaxially grown on  $\text{MgO}$  with thickness about 200 nm (SA-free) and the [110] direction as the surface normal
  - o  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in water solutions prepared from different salts ( $\text{FeCl}_2/\text{FeCl}_3$  and  $\text{FeSO}_4\cdot\text{H}_2\text{O}/\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ )
- *NPs from Inorganic Nanoparticles group of ICN2:*
  - o Spherical  $\text{Fe}_3\text{O}_4$  NPs of 7 nm in water solution (TMAOH 10 mM) made by coprecipitation
- *NPs from Magnetic Nanostructures group of ICN2:*
  - o Cubic  $\text{Fe}_3\text{O}_4$  NPs (130, 80, 60 and 30 nm) made by thermal decomposition and resuspended in hexane
  - o Spherical  $\text{Fe}_3\text{O}_4$  NPs (5 and 9 nm) made by thermal decomposition
  - o Spherical  $\gamma\text{-Fe}_2\text{O}_3$  NPs (4 and 6 nm) made by thermal decomposition
  - o Spherical  $\gamma\text{-Fe}_2\text{O}_3$  NPs of 10 nm made by coprecipitation
  - o Spherical  $\text{FeO}/\text{Fe}_3\text{O}_4$  NPs of 15-20 nm made by thermal decomposition
- *NPs from Sigma-Aldrich:*
  - o Spherical  $\text{Fe}_3\text{O}_4$  NPs of 5 and 20 nm in toluene made by thermal decomposition

A first remark is that, despite being at low temperature (25-30 K), we observed beam damage in the smallest NPs samples (< 15 nm). In all cases, the beam had a reducing effect and induced a tiny shift to low energy in the main rising edge which is however comparable to the shifts that we typically see among our samples. To overcome this problem we measured several spectra each on a different sample spot and limiting the time spent in each spot to 60 seconds.

One of our main objectives was to measure a good (that is, SA-free) HERFD-XANES spectrum in a perfectly stoichiometric bulk  $\text{Fe}_3\text{O}_4$  sample in order to appoint it as the reference spectrum of the nominal magnetite phase. As shown in Fig. 1(a), we found a very nice agreement between the spectra of the thin film and the cubic NPs of 130 nm in terms of edge position (we ascribe the small differences in the pre-peak and white line to the fact that the thin film is [110] oriented). Both samples were characterized by magnetization measurements and show the Verwey transition characteristic of magnetite, so their spectra can be used as the reference. On the other hand, the spectrum corresponding to the commercial powder (< 5  $\mu\text{m}$ ) from Sigma-Aldrich shows that this sample is oxidized. Interestingly, a clear evolution has been detected with decreasing size for the cubic NPs set: the two shoulders in the rising edge progressively disappear as it shifts to high energy when going from 130 to 30 nm revealing an oxidation effect (see Fig. 1(b)). In a similar way, all the HERFD-XANES in the large variety of NPs measured fall between the reference spectrum and those of the  $\gamma\text{-Fe}_2\text{O}_3$  NPs and bulk. Work is currently in progress to interpret the differences in the spectral features between samples and their likely correlation with the magnetic and other macroscopic properties. Still, we can already speculate that that the observed changes cannot be explained based on a simple oxidation of an outer shell of  $\text{Fe}_3\text{O}_4$  to maghemite as commonly proposed. The fact that the spectra are not a superposition of  $\text{Fe}_3\text{O}_4$  and maghemite suggests a slight modification in the stoichiometry of the entire particle ( $\text{Fe}_x\text{O}_y$  phase).

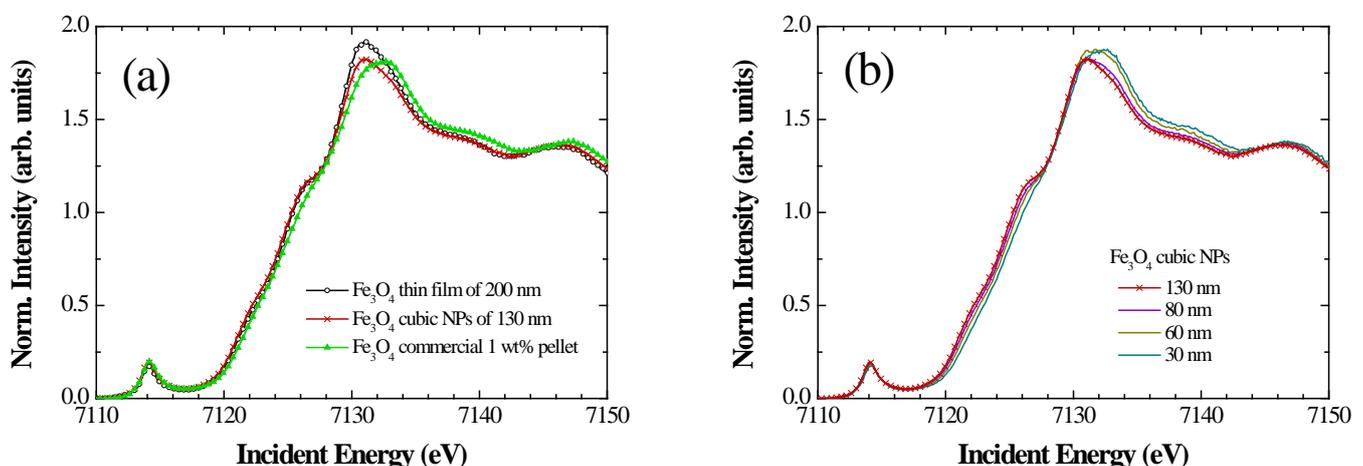


Figure 1. Normalized HERFD-XANES spectra measured at 25-30 K. (a) Comparison between spectra of samples candidates for the bulk stoichiometric  $\text{Fe}_3\text{O}_4$  reference and (b) Evolution as a function of size for various cubic  $\text{Fe}_3\text{O}_4$  NPs.