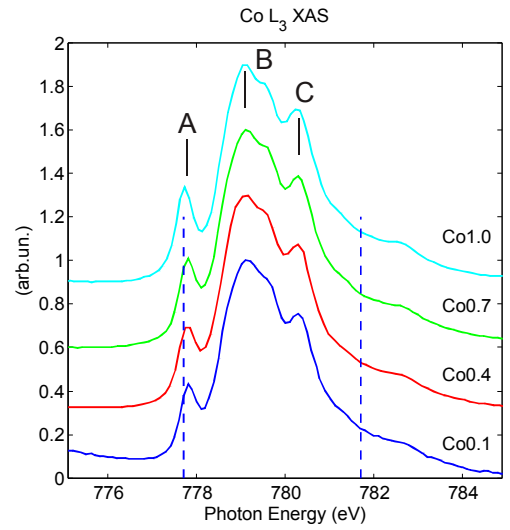
	<b>Experiment title:</b> Distribution of Co ions among octahedral and tetrahedral sites in cobalt ferrite nanoparticles studied with high resolution Co and Fe L3 RIXS	<b>Experiment number:</b> HE-3249
<b>Beamline:</b> ID08	<b>Date of experiment:</b> from: 21/07/2010 to: 28/07/2010	<b>Date of report:</b> 01/03/2011  <i>Received at ESRF:</i>
<b>Shifts:</b> 18	<b>Local contact(s):</b> N.B. Brookes	
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### Report:

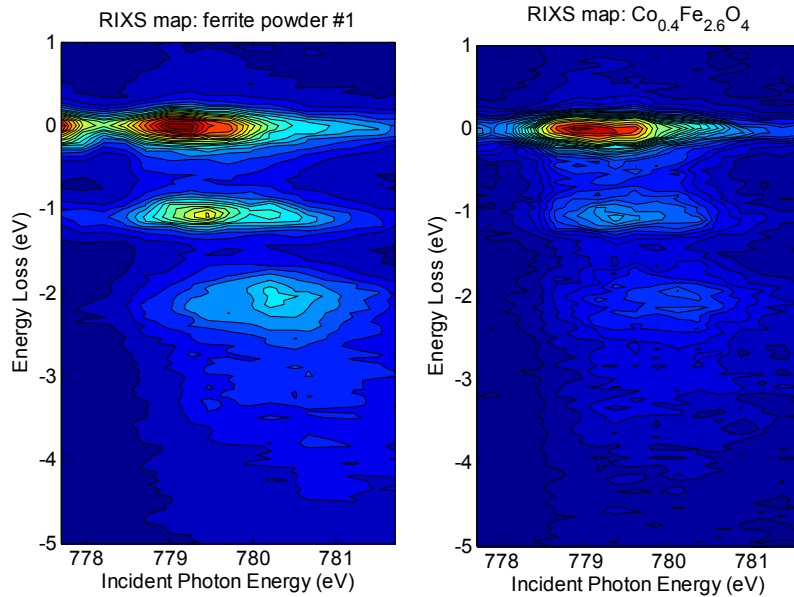
We have probed by RIXS the electronic structure of cobalt ferrite nanoparticles ( $\text{CoFe}_2\text{O}_4$  NPs) with average crystal size of 5 nm by Resonant Inelastic X-ray Scattering (RIXS) at the Co  $L_3$  absorption edge. The electronic and magnetic features of these NPs strongly depend on the chemical distribution of the  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  cations among the lattice sites of octahedral and tetrahedral symmetry. By this approach we explored, in an element and chemical selective way, the consequences of tailored progressive cobalt depletion of the ferrite yielding non-stoichiometric  $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$  NPs, and the changes related to the cation distribution between octahedral and tetrahedral lattice sites.

Co  $L_3$  XAS spectra of the NPs and the Co ferrite powder were measured to define the excitation energies for the RIXS measurements (see figure below). The materials are labelled by the nominal stoichiometry of the Cobalt, i.e.  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ . The Co1.0 sample indicates the cobalt ferrite powder used as reference compound. The dashed vertical lines define the energy excitation range covered for the RIXS maps (see below). The labels shown in the figure, indicate the excitation energies for the RIXS spectra as “A” (pre-peak), “B” ( $L_3$  max. intensity), “C” (high-energy peak). The XAS spectra looks very similar and in agreement with those of the literature [e.g. PRB 77, 064407 (2008); JMMM 231, 315 (2001); J. Phys.Chem. C 113, 7085 (2009)]. Looking closely at the  $L_3$  edge, there is only a minor difference between the spectra of the powder and the NPs in the peak around 777.7 eV, which is slightly shifted by -50 meV with respect to those of the NPs and sharper than in the other spectra. The positions of all the other spectral features are identical, as well as the relative intensities. In particular, the XAS spectra of the NPs do not exhibit any additional spectral feature – over their full energy range -- that could clearly indicate the occurrence of

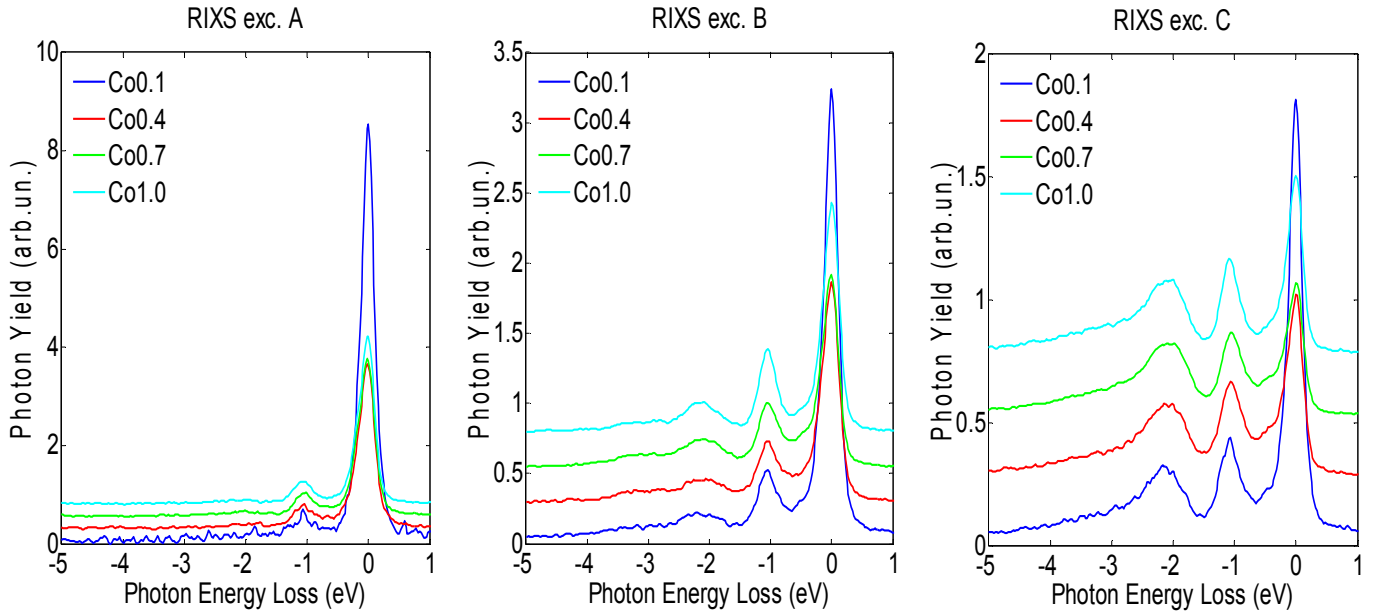
some kind of chemical interaction of the Co atoms with the surrounding organic ligands, e.g. via charge transfer. This situation is manifestly different from the case of the pure Co metallic NPs of the same nominal diameter (5 nm) investigated by de Groot [Nanoletters 2007], for which a strong peak appears at around 784.5 eV. Hence we could reasonably suppose that the electronic structure of the Co atoms at the NPs surface is not strongly altered by the surrounding organic shell.



We have recorded RIXS maps for with incident photon energy spanning the Co L<sub>3</sub> edge. The comparison of the ferrite powder and the Co<sub>0.4</sub> NPs are presented here below as coloured contour plots. The maps look very similar, apart for the weight of the elastic contribution, that is much stronger for the Co<sub>0.4</sub> than the reference powder. This is probably due to the larger contribution of the elastic scattering by the matrix (i.e. the Co atoms in Co<sub>0.4</sub> are more dilute than in Co<sub>1.0</sub> ferrite). They exhibit the same loss features at about  $E_{\text{loss}} = -1.1$  and  $-2.1$  eV. No large fluorescence contribution is present (on this energy scale it would appear to shift at 45° with the photon energy), hence indicating that the spectral features of the RIXS spectra are really due to inelastic scattering and correspond to dd excitations.

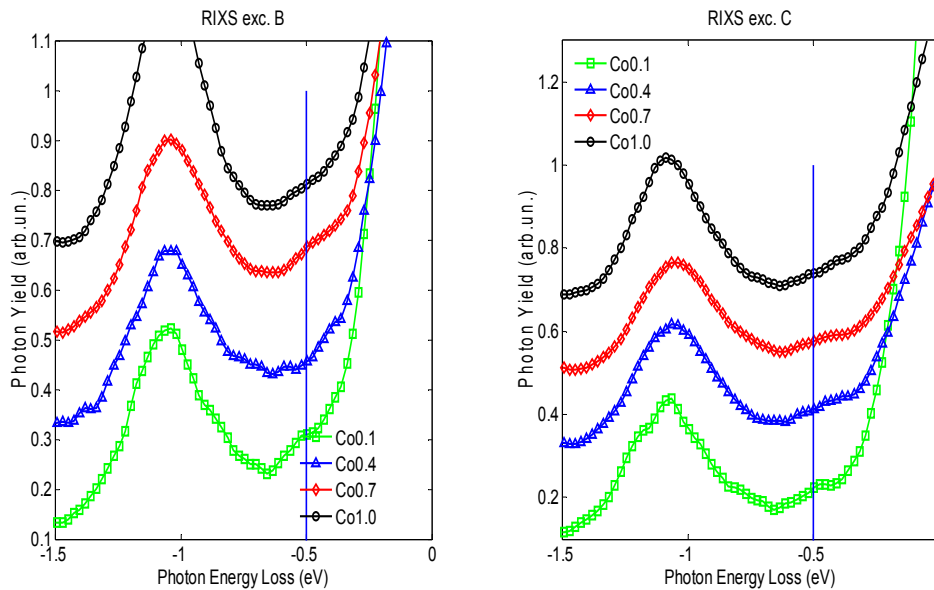


Detailed RIXS spectra have been measured for all the samples and the excitation energies of interest. Different emphasis has been addresses on excitations “B” and “C” with respect to “A”. This is reflected into the different statistics of the spectra and it is justified by to the limited information given at exc. “A”, in which the elastic contribution dominates over the inelastic features. The spectra have been scaled to the integral of the inelastic energy region (0.5 - 20 eV) after the subtraction of a constant background. Every group of spectra exhibit the same gross features, whose baricentrum is located at 1.1 eV and 2.1 eV.



These positions are very similar to those detected for CoO [PRB 2008], which is reasonably expected. In both materials the divalent Co atoms are nearly octahedrally surrounded by oxygen ligands, which justifies the close similarity between the RIXS spectral features.

However, a close inspection for the set of spectra reveals that tiny features appear in the intermediate region between the elastic peak and the first loss. They are typical of the Co NPs and do not appear in the ferrite powder. The spectral feature at about 0.5 eV (vertical line) is more visible for Co0.1 and Co0.7 samples at both excitation energies, while its appearance in Co0.4 may be limited by the poorer statistics. Moreover, the loss feature of the Co0.1 sample for exc. “C” looks more structured than for the other spectra, with a shoulder at 1.2 eV, i.e. splitted 0.1 eV from the main loss peak. A slightly asymmetry of this loss is visible even for exc. “B”.



The interpretation of these results and the assignment of the spectral features is currently on progress and will rely on multiplet splitting calculations for Co atoms in octahedral or tetrahedral symmetry. As a first attempt, we show the calculation of Tanabe-Sugano diagram

indicating qualitatively where the spectral features of tetrahedral Co are, with respect to the different strength of the crystal field in octahedral and tetrahedral environment. The diagram suggests that the tiny features at about 0.5 eV form the elastic peak are closely related to Co atoms experiencing a tetrahedral crystal field, while the main features are undoubtedly related to octahedral sites.

