



	Experiment title: Origin of ferromagnetism in cobalt ferrite nanoparticles	Experiment number: MA-3850
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Shifts: 18	Local contact(s): Sara Lafuerza Bielsa	<i>Received at ESRF:</i>
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Report:

Aim of the experiment was to trace and study the evolution of magnetism in cobalt ferrite nanoparticles (NPs) in-situ, during synthesis, and its extension of investigation started during MA-3311 experiment. Reaction takes place in cell designed specially for synchrotron radiation experiments. CoFe_2O_4 NPs synthesize by nucleation and growth from products of $\text{Co}(\text{acac})_2$ and $\text{Fe}(\text{acac})_3$ thermal decomposition. Precursor is dissolved in benzyl alcohol (BnOH) and whole solution is sealed in heated container possessing one thin wall for the incoming polarized beam. Molar concentration ratio of 2:1:200 $\text{Fe}(\text{acac})_3$: $\text{Co}(\text{acac})_2$:BnOH was used to obtain good signal-to-noise ratio with small self-absorption effects. To analyze effect of cobalt oxidation number also $\text{Co}(\text{acac})_3$ was used as a cobalt donor. Products of reaction with the same concentration and under the same conditions were studied in laboratory using transmission electron microscopy to determine NPs size and using vibrational sample magnetometry to study magnetic properties.

Synchrotron measurements exploited Magnetic Circular Dichroism (MCD) on iron and cobalt *K*-edges, mainly in pre-edge region. Parallel magnetic field up to 0.4 T was produced by electromagnet lent by courtesy of ID24 beamline. High energy resolution fluorescence detected (HERFD) x-ray absorption (XAS) was measured continuously during reaction for parallel and anti-parallel field to polarization orientations (HERFD-MCD). Polarization was also altered for pairs of scans to check if sign of MCD effect is reversing with opposite circular polarization or magnetic field direction. Overall two or four scans combination was used to obtain one HERFD-MCD profile.

High resolution Rowland type spectrometer with proper analyzer crystals resolves only one energy of secondary emission during HERFD scan. In the experiment two kinds of analyzer's crystals were mounted simultaneously to measure on iron and cobalt elements during one reaction. HERFD-MCD was measured alternately for iron and cobalt. Crystal corresponding to intended element was focused on the sample,

while second crystal was set aside. This methodology limits amount of counts, but ensure matching of collected spectra in time.

Compared to magnetite, cobalt ferrite NPs are much less agglomerating and thus there is no problem with changes in bulk concentration throughout reaction, but still NPs are exposed to strong radiation. To avoid artifacts caused by radiation sensitivity of the solution, after two scans (for two polarizations, in pre-peak region) beam spot was shifted to another place on thin walled reaction cell window using 'radiation damage control' procedure implemented in ID26 scanning macros. Scans in pre-peak energy range were usually performed with emission energy maximizing MCD signal. They were interspersed with faster scan in wider energy range near *K*-edge (XANES scans). The latter was carried out to control edge position and counts. It can also be used to normalize pre-peak scan intensity. XANES scans were performed with emission energy maximizing edge intensity to shorten the time needed. Nevertheless reactions finishing in less than an hour are too short to measure both edge and pre-peak MCD signal with good statistics.

Emission energy was chosen based on 1s2p RIXS and RIXS-MCD planes measured for reference samples of iron and cobalt oxides in the form of thin films, solutions of NPs and aliquotes of reactions gathered in advance (fig. 1). Choice was made to optimize MCD signal for both early and late stages of reaction, or to study interesting features of the RIXS plane and possibly multiplet interactions. This experiment was supported on experience gained after MA-3311, where mostly magnetite synthesis reaction was studied. To verify if the experiment conditions are maintained between experiments, magnetite synthesis was carried out and compared with previously acquired data. There was no visible change in measured profiles or kinetic of reaction. RIXS-MCD plane for cobalt after 50 min of reaction presents possible issues perturbing the measurement and later on analysis. Although scans seems to be altered periodically, there is no proper period or pattern and no correlation to machine parameters. In spite of raising experience and quality of scans it is still too erroneous to measure element specific hysteresis loops of reacting solutions.

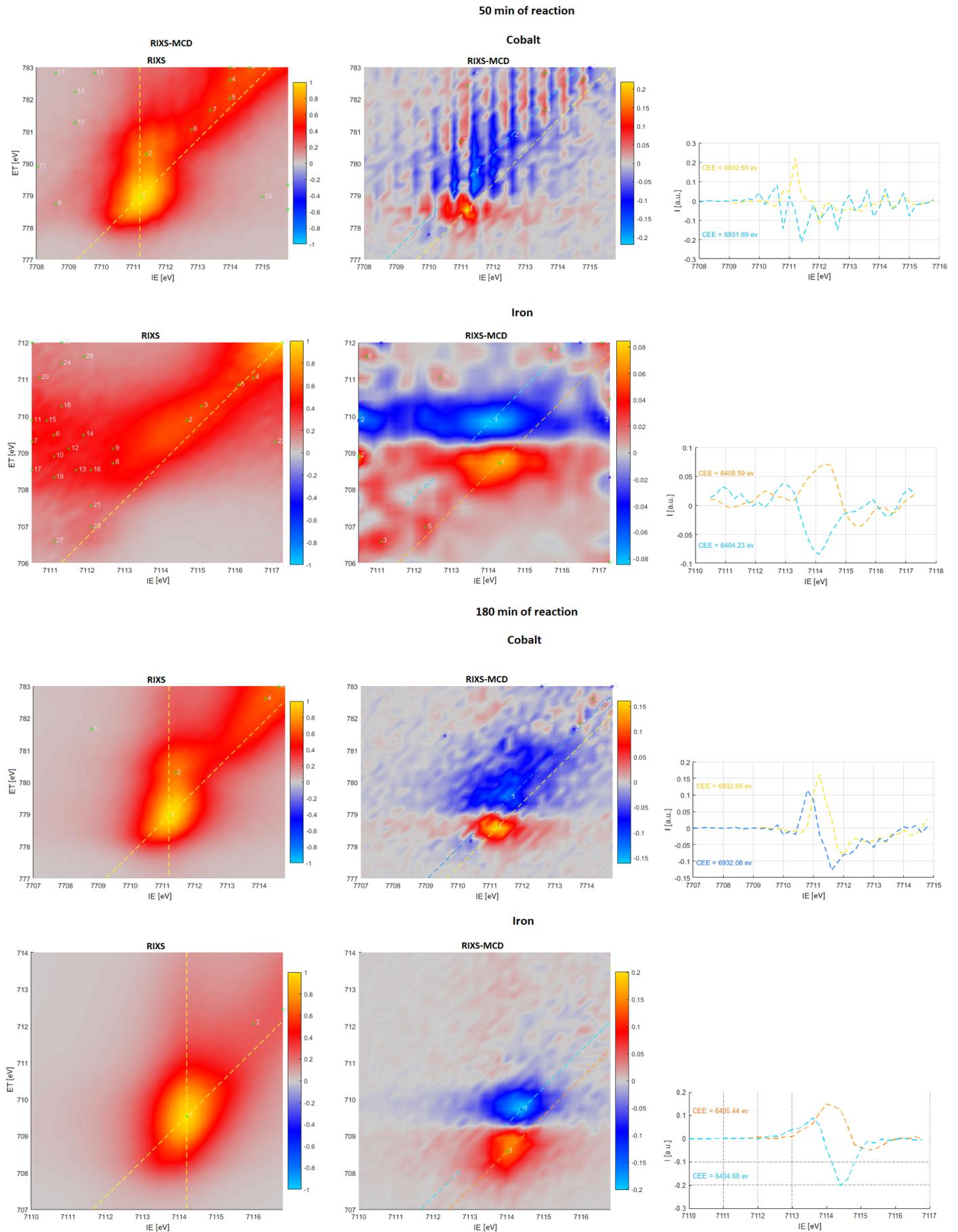


Figure 1. RIXS (left) and RIXS-MCD (middle) planes for synthesized NPs for cobalt and iron K-edge pre-peaks. On the right there are constant emission energy slices across intensity extrema (marked with crosses). Emission energy for HERFD-MCD scans was usually chosen to maximize MCD signal amplitude and thus not always gives strong positive and negative features.

HERFD and HERFD-MCD scans in pre-peak region and XANES scans for exemplary reaction in 160°C and 0.4 T are presented in fig. 2. All scans are presented as 2D colorful maps of intensity versus time and incident energy. Double acetyloacetate pre-peak at the beginning decays fast, what results in significant changes in spectra over measurement time and thus artificial MCD signal. Due to relatively small signal on cobalt edge, especially MCD signal, tests to improve visibility of features prevented to test various concentrations of Co(acac) precursor. To obtain stronger signal it was necessary to use 0.4 T magnetic field instead of 0.2 T. According to MA-3311 results, stronger external magnetic field for magnetite changes intensity negligibly, so hysteresis loop of cobalt probably would be much less steep than loop of iron.

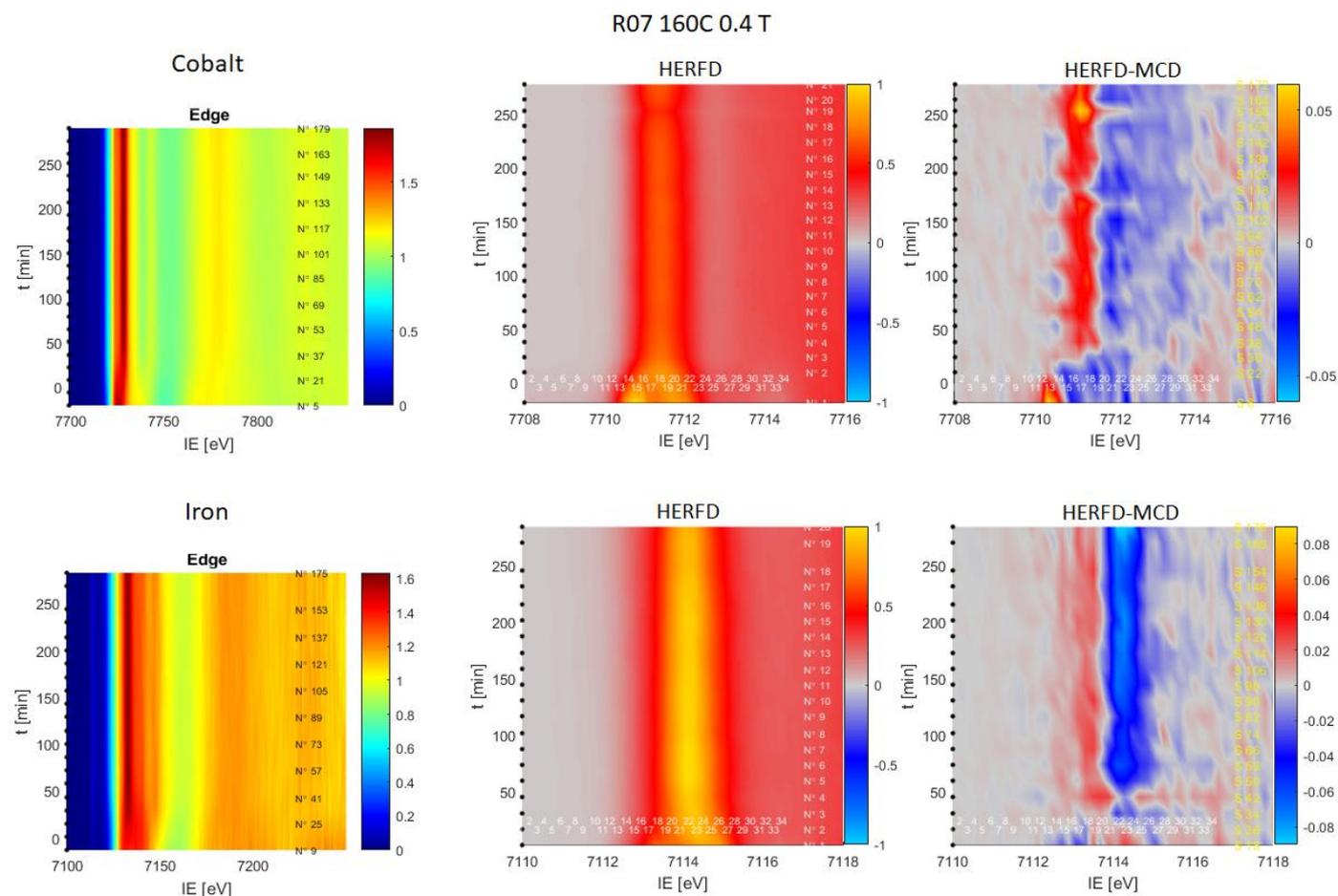


Figure 2. Figure is divided into cobalt (up) and iron (down) halves. From the left there are: edge, HERFD and HERFD-MCD profiles versus time. Edge scans are normalized in respect to edge jump and pre-peaks are recalculated to have equal values at the end of range, so MCD signal is guaranteed to be zero. This condition is established by RIXS planes. Then whole map is normalized to maximum measured value.

MCD amplitude rises rapidly near the fiftieth minute of reaction and behaves very similarly for both measured elements. At 180°C fast rise occurs after only 20 minutes of reaction, which is much faster than for magnetite synthesis, where at 180°C strong signal appeared after 50 minutes. Such fast changes do not allow to get satisfying counts statistics for both iron and cobalt during one reaction at 180°C. Distinctive peaks in iron edge jump are slightly moving and changes in intensity. Edge position is moving to the left at the beginning of reaction. Changes in cobalt edge are more complicated: edge is not moving, but some features disappear and some new emerge: for example white line reduces at the beginning and instead new peak emerge at around 5 eV higher energy. Approximately, first two main peaks after edge jump behaves in opposite way for iron and cobalt, what may be caused by exchanging tetrahedral and octahedral geometries during transition from acetyloacetate molecule to ferrite structure.

Experiment proves that it is possible to trace two elements during reactions in-situ, but gathered spectra need a lot of optimization. Preliminary analysis indicate that changes in iron pre-peak and magnetism development follow the same path as measured in previous experiment. Presence of cobalt alter spectra of

iron only slightly in quantitative way. This means that tetrahedral sites, mostly manifesting component in pre-peak intensity, are interacting with surrounding in similar way in cobalt ferrite and iron oxide ferrite. Synthesized cobalt ferrite NPs show very wide hysteresis loops and therefore big difference in magnetic anisotropy is probably result of interactions of octahedral sites. Here changes are also much faster, so cobalt is probably embedding more naturally into sites normally occupied by iron in iron oxide ferrites. Results presented in this preliminary report and rest of gathered data are analyzed in detail and compared with previous results for further publication.