



Experiment title: Burst of magnetism in transition metal oxide nanoparticles

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Report:

This is a preliminary report; the detailed data analysis is in progress.

The objective of the experiment was to trace the evolution of magnetism of iron and cobalt ferrite nanoparticles (NPs) during their synthesis from precursor ($\text{Fe}(\text{acac})_3$ and/or $\text{Co}(\text{acac})_2$) solved in benzyl alcohol. The measurements were performed using state-of-the-art reaction cell under magnetic field generated by electromagnet borrowed from ID24. During the reaction in high temperature we observed evolution of local atomic structure and projected magnetic moment of iron ions upon acetyloacetate decay and nucleation of nanoparticles with diameters ranging up to 10 nm. We have also probed the reference samples of iron oxides in the form of thin films, solutions of NPs and aliquotes of reactions performed in advance. The measurements were performed using 1s2p RIXS-MCD detection principle. Full RIXS planes were collected at selected reaction stages, i.e. from the solutions cooled after certain reaction time. Figure 1 shows the comparison of Fe 1s2p RIXS-MCD planes of the solution of magnetite and Co ferrite NPs formed during reactions performed at different temperature with and without application of external magnetic field.

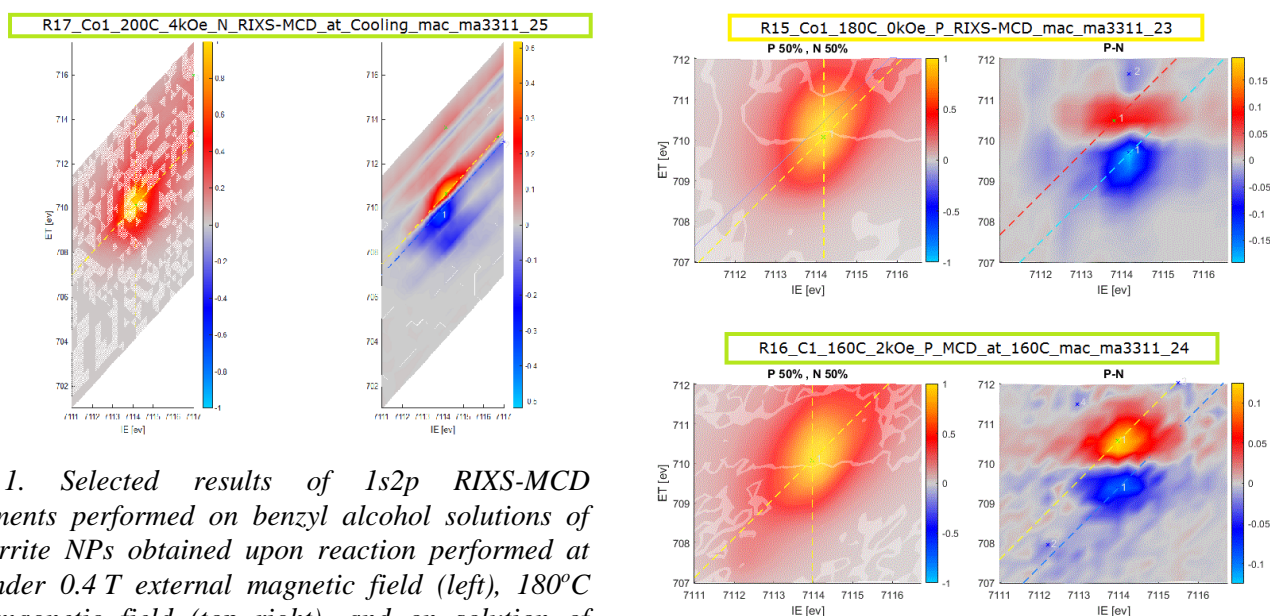
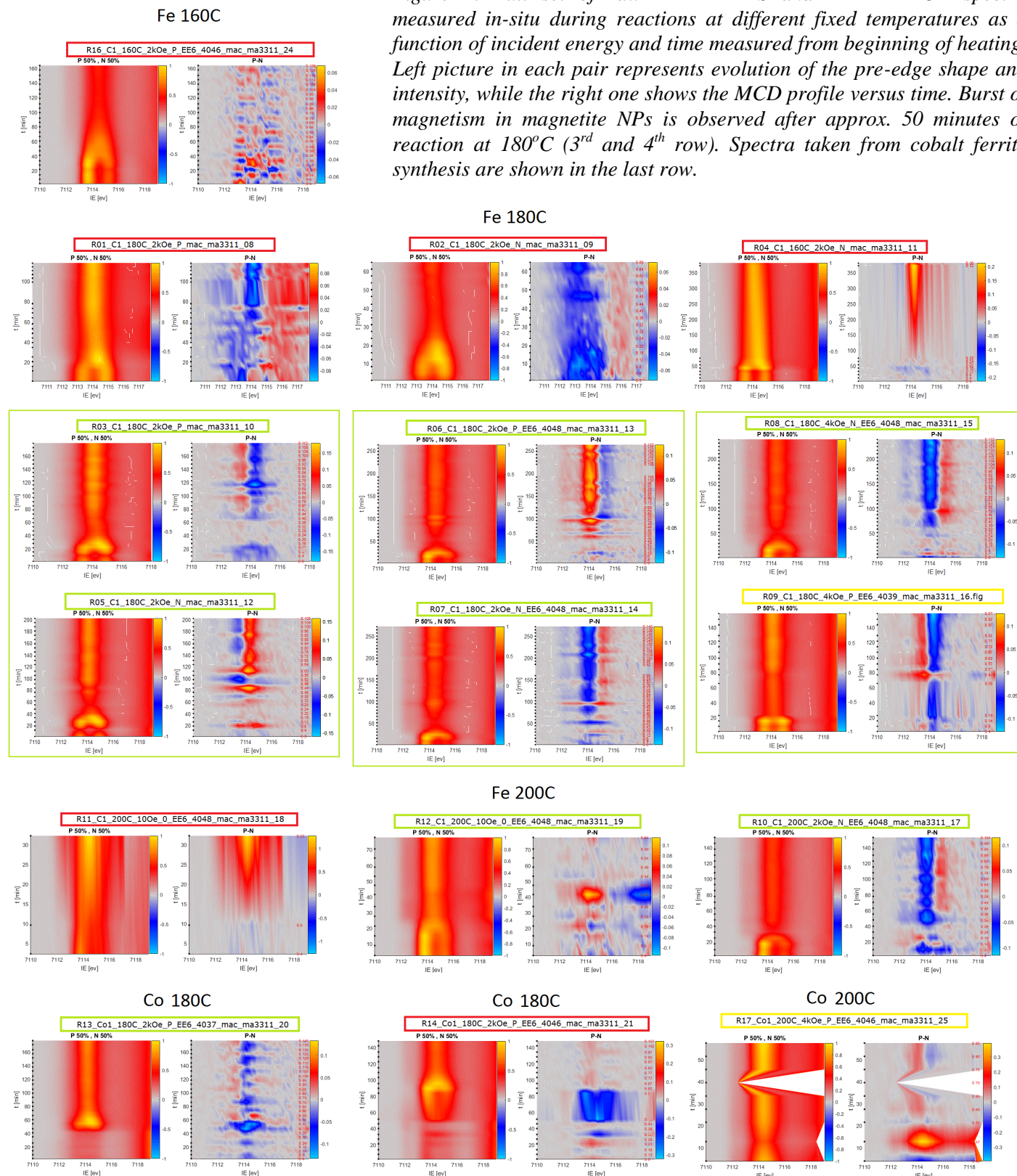


Figure 1. Selected results of 1s2p RIXS-MCD measurements performed on benzyl alcohol solutions of cobalt ferrite NPs obtained upon reaction performed at 200°C under 0.4 T external magnetic field (left), 180°C without magnetic field (top right), and on solution of magnetite NPs obtained upon reaction at 180°C under 0.2 T external magnetic field (bottom right).

Based on RIXS-MCD spectral shape, we have established the most suitable emission energy for high energy resolution fluorescence detected (HERFD) x-ray absorption (XAS) and magnetic circular dichroism (MCD) spectra at iron *K* edge, especially in pre-peak region. We probed *in-situ* time evolution of these spectra for reactions at 160°C, 180°C and 200°C, for concentration of 1:50 precursor to solvent, which gives strong signal-to-noise ratio and negligible self-absorption. HERFD-XAS was measured for both, photon and magnetic field polarizations, in pre-peak region, and without polarization in full XANES range, in order to determine changes in local chemical environment of iron ions. Figure 2. presents comparison of the raw results of all the reactions performed.

Figure 2. Full set of raw HERFD-XAS and HERFD-MCD spectra measured *in-situ* during reactions at different fixed temperatures as a function of incident energy and time measured from beginning of heating. Left picture in each pair represents evolution of the pre-edge shape and intensity, while the right one shows the MCD profile versus time. Burst of magnetism in magnetite NPs is observed after approx. 50 minutes of reaction at 180°C (3rd and 4th row). Spectra taken from cobalt ferrite synthesis are shown in the last row.



Preliminary tests showed that benzyl alcohol solution of $\text{Fe}(\text{acac})_3$ is stable in the beam (attenuated by reaction cell window made of PEEK) for at least 300 seconds of irradiation, i.e. 10 consecutive HERFD-XAS scans performed over Fe K pre-edge range (30 seconds each). Therefore, in order to avoid detection artifacts due to radiation sensitivity of the solution, after each or at most every two line scans (each performed at opposite helicity of circularly polarized incoming photons) the position of beam on the sample was changed using modified ‘radiation damage control’ procedure implemented in ID26 scanning macros. This procedure was applied to all the measurements performed on solutions. Nevertheless, the spectra shown in figure 2 need post-processing in order to screen all the artifacts, e.g. due to changes in local density of reactants in probed volume. Post-processing of all the *in-situ* data is currently on-going.

Figure 3 shows an example of post-processed data from magnetite NPs synthesis performed at 180°C and 0.2 T external magnetic field. A characteristic decay of double pre-edge peak of $\text{Fe}(\text{acac})_3$ is observed for approx. 20 minutes in HERFD-XAS. HERFD-MCD shows a weak feature that is tentatively assigned to time dependent changes in the intensity of pre-edge features (non-magnetic effect). Then, for another 30 minutes a low intensity, single pre-edge peak is observed to move towards lower incident photon energy along with a lack of significant MCD signal. Afterwards we can see development of strong, single pre-edge peak and, at the same time, appearance of strong MCD signal. From the first inspection of the results we see that at the

same time the tetrahedral position in ferrite spinel structure is being occupied (pre-edge peak increases), magnetism of iron develops, both in magnetite and cobalt ferrite NPs. Surprisingly, although the magnetic behavior of both NPs at the diameters of approx. 10 nm is different (superparamagnetic vs. single domain ferromagnetic), the kinetics and magnetic characteristics of both reactions tracked at iron tetrahedral sites looks similar.

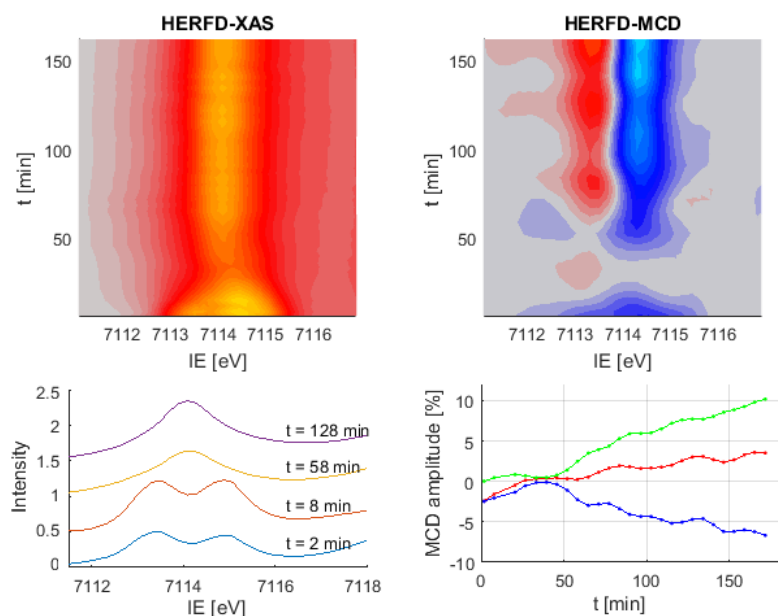
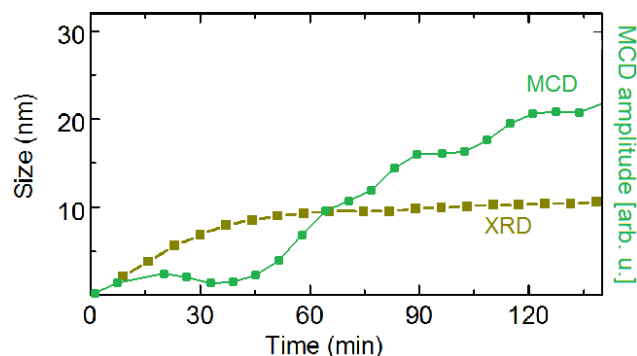


Figure 3. Time dependence of HERFD-XAS at the Fe K pre-edge (left), and respective MCD (right) during nucleation reaction of magnetite from $\text{Fe}(\text{acac})_3$ dissolved in benzyl alcohol. Reaction was performed at 180°C . Selected HERFD-XAS of pre-edge peak (horizontal cuts) at different stages of the reaction and MCD intensity (vertical cuts) as a function of time are presented in bottom row. MCD amplitude, a difference between positive (red) and negative (blue) features, is shown in green.

Figure 4. Comparison of Fe_3O_4 NPs size (determined from *in-situ* XRD experiment performed at BM01) and RIXS-MCD amplitude evolution versus time. MCD is derived from the data shown in figure 3. It is primarily dependent on ordering of Td iron sites.



Reactions performed *in-situ* in VSM magnetometer shows different behavior compared to RIXS-MCD. An increase in total magnetization of NPs solution is observed after shorter time of reaction, e.g. after about 30 minutes at 180°C . However, the shape of $M(t)$ curve shows a characteristic cusp at the NPs dimension equivalent to sudden MCD amplitude increase, that seems to appear at mean particle diameter of 7-8 nm as derived from linked results of *in-situ* XRD and MCD experiments shown in figure 4.