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# Selective magnetometry of superparamagnetic iron oxide nanoparticles in liquids

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## 1. Details of the synthesis procedure

Zn doped magnetite nanoparticles were precipitated in NaOH aqueous solution from metal chlorides, namely  $FeCl_3$ ,  $FeCl_2$  and  $ZnCl_2$ . This was followed by purification using magnetic chromatography. The chemical composition of the precipitated materials was analysed with inductively coupled plasma optical emission spectroscopy (ICP-OES) in order to estimate the relative amount of zinc and iron in particles. Based on ICP-OES the actual composition of these particles was  $Zn_{0.35}Fe_{2.65}O_4$  and  $Zn_{0.53}Fe_{2.47}O_4$ .

Iron oxide  $(\gamma - Fe_2O_3)$  and cobalt ferrite  $(CoFe_2O_4)$  nanoparticles were obtained from thermal decomposition reaction of  $Fe(acac)_3$  and  $Co(acac)_2$  dissolved in benzyl alcohol (BnOH). Stoichiometric solutions were poured into reaction cells preheated to  $180^{\circ}C$  and maintained for approx. 140 minutes. Reaction was ended by quick cooling of the solution after draining the cell using a glass pipette.

In all cases the initial concentration of the sum of metal precursor with respect to solvent was in the proportion 0.2 mmol / 1 mL.

## 2. Reference samples

Synthetic single crystal of magnetite was grown at Purdue University by the skull melter crucibleless technique [1].

Commercially available powder of Iron(III) oxide Sigma-Aldrich (310050) was used as a reference of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

## 3. Experimental set-up

1s2p RIXS-MCD measurements were performed on ID26 beamline at the European Synchrotron Radiation Facility (Grenoble, France), using incoming radiation from the undulator fundamental

monochromatized with a pair of Si(311) crystals. The horizontally polarized X-rays were transformed to circularly polarized using a 500  $\mu$ m thick diamond (111) quarter wave plate (QWP) [2]. The constant rate of circular polarization, Pc ~ 80 %, was kept by tuning the angular position of QWP at each incident energy position.

Inelastically scattered photons were detected using Johann type multianalyser emission spectrometer equipped with four spherically bent Ge(440) Bragg crystal analysers diffracting in vertical Rowland geometry (R ~ 1 m) into a single-photon-counting detector (APD). The combined resolution of the setup, determined as full width at half maximum of elastic peak, was  $\Delta E = 0.8 \pm 0.1$  eV. The spot of the incident beam on the sample was approx. 0.3 x 0.1 mm<sup>2</sup> (HxV).

## 4. Data acquisition

RIXS and RIXS-MCD planes were collected at a constant magnetic field flux of B = 0.4 T as a series of emission energy scans at gradually increasing incident energy. At each incident energy, two scans with opposite helicity of circularly polarised incident beam were measured. In this way two RIXS planes were collected, each using opposite helicity of circularly polarised X-rays. RIXS shown in Figure 1(d) is an average, while RIXS-MCD shown in Figure 1(e) is a difference between these two planes.

HERFD-XAS and XMCD spectra were collected at magnetic field flux of B = 0.2 Tesla as a series of four constant emission energy scans collected with opposite helicity (L: left- and R: right-handed) and opposite magnetic field direction (denoted P and N), namely LP, LN, RN, RP. HERFD-XAS spectra were obtained as (LP+LN+RN+RP)/4, while XMCD as (LP-LN)/2 + (RN-RP)/2.

At first, several consecutive HERFD-XAS scans using horizontally polarized beam were collected, each at a different vertical position of the sample. Reproducibility of the spectral shape and the intensity of the consecutive scans was an indicator of the sample stability under high flux of synchrotron beam and application of uniform magnetic field flux. Selected samples that exhibited good stability were further measured using circularly polarized X-rays. A series of three to ten HERFD-XAS and XMCD spectra were needed to achieve good signal-to-noise ratio. Average spectra were normalised to HERFD-XAS intensity at IE = 7116.8 eV.

Measurement time depends on the energy range and the energy step (measurement precision) as well as the single point acquisition time needed for gaining smooth spectra for the given concentration and type of nanoparticles. For instance, the total acquisition time for collection of RIXS and RIXS-MCD planes shown in Figure 1(d,e) was approx. 45 minutes. HERFD-XAS and XMCD spectra were gathered several times for each sample in various positions to avoid errors due to possible contamination or agglomeration and self-absorption. A typical HERFD-XAS scan (Figure 2a) takes 1-5 minutes at the energy step of 0.1 eV, while HERFD-MCD (Figure 2b) requires four fold longer acquisition.

Selective magnetization profiles were obtained as the field dependence of maximum emission intensity corresponding to  $Fe^{3+}T_d$  site (IE = 7114.1, EE = 6404.7 eV, see Figure 1(e)). Magnetic field was swept from positive to negative and back to positive direction. Averaged magnetization profiles probed at L and P helicity were respectively subtracted. The total acquisition time of the profile shown in Figure 3a (an average of six independent loops) was approx. 45 minutes.

### 5. Stability of liquid samples under X-ray irradiation

Liquid suspensions of SPION were inserted into thin-walled polyimide (Kapton) tubes of approx. 1 cm in length (inside diameter: 1mm; wall thickness: 50  $\mu$ m). These were sealed on both ends using silicon grease. Special care was taken to remove all the air from the tube interior. Such samples were mounted vertically on the goniometer and aligned to the incident synchrotron

beam. The interaction point was fixed in the geometrical centre of both Rowland spectrometer and the electromagnet. All the measurements were performed at room temperature.

In general, SPION suspended in BnOH showed significantly better stability under intense X-ray beam than that suspended in water. Nevertheless, both sudden changes and slow drift of scattered photon intensity have been observed in selected samples. This was related to the evaporation of solvent, formation of bubbles, and formation of quasi-solid deposit on the capillary wall. In order to minimize these effects, samples were therefore raised slowly relative to the incident X-ray beam during measurements. Unfortunately, disruptions related to solvent evaporation, especially pronounced in concentrated suspensions, were unpredictable and strongly decreased the efficiency of data collection.

During our study on selective magnetization profiles, intensity disruptions were also present due to change of suspension density at the interaction point, related to the dynamics of the nanoparticles caused by magnetic field sweep. However, these could easily be spotted by comparison of the profiles probed with opposite helicity. These led to additional inflection points (s-like deformation) or large intensity hysteresis in the averaged magnetization profiles. Such profiles were rejected from further analysis.

### 6. The origin of K pre-edge and the quantitative estimation of Fe site occupancy

Pre-edge structure of *K*-edge XAS reflects density of unoccupied 3d states of transition metals and their multiplet structure. In spinel oxides it consist of combined signal from tetrahedrally ( $T_d$ ) and octahedrally ( $O_h$ ) coordinated iron ions in various oxidation states. Thanks to line sharpening effect in RIXS,  $T_d$  and  $O_h$  sites can be distinguished and site occupancy can be determined. Transition to intermediate states in RIXS-MCD, which are split by the 3d spin-orbit coupling and the exchange field, are reached by left and right circular polarized X-rays with 100% selectivity. Thus, the magnetic contrast depends on the splitting of final states with different orbital and spin momenta. The effect is strong - of the order of 10-20% - in those systems that reveal well-defined pre-edge features and high spin polarization of the final states, as in the case of spinel and garnet iron oxides.

Considering that the experimental spectrum reflects a weighted average of the spectral shape of all the excited iron sites, the overall amplitude of the pre-edge with respect to edge jump in spinel iron oxide is:

$$P_{\text{spinel}} = (N_{\text{Td}}P_{\text{Td}} + N_{\text{Oh3}}P_{\text{Oh3}} + N_{\text{Oh2}}P_{\text{Oh2}}) / (N_{\text{Td}} + N_{\text{Oh3}} + N_{\text{Oh2}}),$$
(S1)

where  $P_{Td3}$ ,  $P_{Oh3}$ , and  $P_{Oh2}$  is the amplitude of the pre-edge peak of  $Fe^{3+}$  in tetrahedral ( $T_d$ ) site,  $Fe^{3+}$  in octahedral ( $O_h$ ) site, and  $Fe^{2+}$  in octahedral site, respectively.  $N_{Td}$ ,  $N_{Oh3}$ , and  $N_{Oh2}$  are the fractional occupations of the respective sites by iron ions. These are  $N_{Td} = N_{Oh3} = N_{Oh2} = 1$  for magnetite;  $N_{Td} = 0$ ,  $N_{Oh3} = 2$ ,  $N_{Oh2} = 0$  for normal spinel ferrite; and  $N_{Td} = N_{Oh3} = 1$ ,  $N_{Oh2} = 0$  for inverse spinel ferrite.

In the extensive experimental study by Westre *et al.* [4], it is shown that the pre-edge features of both  $Fe^{2+}$  and  $Fe^{3+}$  octahedral sites are similar in shape and amplitude. However, the maxima are shifted to lower photon energy with respect to the maximum of the pre-edge of  $Fe^{3+}$  tetrahedral site by approx. 1.7eV ( $Fe^{2+}$ ) and 0.5eV ( $Fe^{3+}$ ). Based on Ligand Field Multiplet calculations, Juhin *at al.* [5] determine the amplitude and shape of the K pre-edge for  $Fe^{3+}$  in the structure of garnet. Assuming that similar shapes and amplitudes are realised for iron sites in spinel and garnet iron oxides, the relative amplitudes of the pre-edge structures of octahedral sites at the position of the maximum of the tetrahedral site can be estimated by inspection of Figure 4(a,b) in paper [5]. The respective values are:

$$P_{Td} \approx 0.19,$$
  
$$P_{Oh3} \approx P_{Oh2} = P_{Oh} \approx 0.027,$$

as derived from the calculations broadened to account for the instrumental resolution (Gaussian, 1.0 eV FWHM) and lifetime broadening (Lorentzian, 0.4 eV FWHM). Similar conditions are expected for our HERFD-XAS measurements.

Assigning these values to equation S1 results in:

$$A_{pre} \approx (0.19N_{Td} + 0.027N_{Oh3} + 0.027N_{Oh2}) / (N_{Td} + N_{Oh3} + N_{Oh2})$$

where A<sub>pre</sub> is the amplitude of the pre-edge. This formula can be rewritten into:

$$A_{\text{pre}} \approx 0.027 \cdot (7.03N_{\text{Td}} + N_{\text{Oh3}} + N_{\text{Oh2}}) / (N_{\text{Td}} + N_{\text{Oh3}} + N_{\text{Oh2}}),$$

transformed:

$$A_{\text{pre}} \left( N_{\text{Td}} + N_{\text{Oh3}} + N_{\text{Oh2}} \right) / 0.027 \approx 7.03 N_{\text{Td}} + N_{\text{Oh3}} + N_{\text{Oh2}},$$

and simplified to:

$$A_{\text{pre}} \cdot (3-x) \cdot C \approx 7N_{\text{Td}} + 2N_{\text{Oh}}, \tag{S2}$$

where  $N_{Oh} = N_{Oh3} + N_{Oh2}$  is the fractional amount of iron ions in the octahedral sites, and *x* is defined by the stoichiometry of the ferrite sample, namely  $M_xFe_{3-x}O_4$  (M=metal). Constant C accounts for difference in experimental broadening and normalization. It can be derived from the spectrum of a spinel reference sample with known Fe distribution, e.g. Fe<sub>3</sub>O<sub>4</sub>.

#### 7. Volume magnetometry

Volume magnetization measurements were performed using vibrating sample magnetometer (VSM) LakeShore 7407. The volume of sample (suspension) was approx. 80 µl.

Room temperature magnetization profile of the water suspension of non-stoichiometric Zn ferrite nanoparticles was recorded by cycling the flux of external field from -1.2 to +1.2 T twice with a step rate of 0.005 T/s.

Figure S1 shows the temperature vs. magnetization dependence for the suspension of  $CoFe_2O_4$  nanoparticles in BnOH recorded at constant flux of external magnetic field of 0.2 T by warming up the frozen sample. The inflection of the profile at T ~ 260K is attributed to melting of the solvent, which may result in redistribution of the particles.



Figure S1. Temperature dependence of the volume magnetization of the suspension of  $CoFe_2O_4$ nanoparticles in benzyl alcohol.

### **References:**

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