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Ultrasmall CoFe_2O_4 magnetic nanoparticles in ferrofluids, influence of the synthesis on the magnetic anisotropies

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Abstract— The magnetic properties of cobalt ferrites nanoparticles prepared using three different processes (thermal decomposition, polyol or co-precipitation synthesis routes) are investigated by X-ray Absorption Spectroscopy and X-ray Magnetic Circular Dichroism. The relative repartition of cobalt and iron ions amongst the interstitial sites of the spinel structure is determined and correlated with their magnetic properties. The study reports on the influence of the synthesis method on the crystallographic order within a nanoparticle, and hence, on the magnetic anisotropy. **Index Terms—** Spinel, Ferrite, Nanoparticles, XMCD, Anisotropies

Introduction

Nanoparticles composed of ferrite nanospinels are used in various applications ranging from medicine to optical devices [1], [2]. Among these nanospinels, cobalt ferrite (CoFe_2O_4) is a promising material because in the nanosize range it presents a high magneto-crystalline anisotropy energy and a high magnetization saturation. These appealing properties are very sought after for hard record devices [3]. For such applications, beating the so-called superparamagnetic limit is one of the current biggest challenges. In this direction, various strategies have been developed such as multi-shell structuration, particle doping, or coordination of molecules to nanoparticles surfaces. However, it is well-known that the preparation route of magnetic nanoparticles can influence in many way their morphology, their chemical composition or their crystallographic structure which in turn strongly impact their magnetic properties. Among all possible synthesis routes, soft chemical synthesis has become a very convenient way to obtain magnetic ferrite nanospinels. Various synthesis processes have been developed to obtain ferrofluids with long-term stable nanoparticles. In this study we choose three different synthesis that are very common in the preparation of ferrofluids : (i) the co-precipitation process is a cost-effective and versatile synthesis that allows to obtain a large amount of nanomaterial, (ii) while nanoparticles obtain via the polyol process show original structures with enhanced magnetic properties but allows less control on the crystallographic structure and (iii) the thermal decomposition route is found to be a very effective method to prepare monodisperse nanoparticles with controlled morphology, although involving higher temperature and more expensive reactants. In the present paper, we investigate the magnetic properties of small CoFe_2O_4 nanoparticles obtained from these three different synthesis pathways. Using one of the synthesis process mentioned above, several groups have studied the magnetic properties of the nanoparticles obtained. Small spherical CoFe_2O_4 nanoparticles synthesized in polyol medium were found to have a saturation magnetization comparable to that of the bulk structure [4], [5]. Large coercive field were measured at 5 K on small CoFe_2O_4 nanoparticles prepared through high temperature decomposition route: Song and Zhang measured coercive field of 11 kOe on 6 nm CoFe_2O_4 nanoparticles [6] and Torres and co-workers measured a coercive field of 14 kOe on 5.7 nm large CoFe_2O_4 nanoparticles [7]. In this study, we want to emphasize the fact that magnetic anisotropies of comparable small size of CoFe_2O_4 nanoparticles are strongly modulated by the synthesis process. We propose hereby to investigate the magnetic anisotropies and crystallographic structures of small CoFe_2O_4 nanoparticles obtained with co-precipitation synthesis, polyol process and thermal decomposition route. Bulk CoFe_2O_4 crystallized in a spinel structure that belongs to the $\text{Fd}\bar{3}m$ space group. In the perfectly ordered spinel structure, all Co^{2+} ions occupied Octahedral symmetry sites while Fe^{3+} ions are equally distributed between Octahedral and Tetrahedral symmetry sites. X-ray Magnetic Circular Dichroism (XMCD) spectroscopy at

the $L_{2,3}$ edges is a unique tool to probe the 3d magnetic orbitals of the transition elements [8]. The method provides a chemical selectivity used to disentangle the magnetic signatures of the cobalt and iron. In addition, XMCD is also sensitive to the site symmetry of the element. The cationic distribution of Co and Fe between Octahedral (O_h) symmetry sites and Tetrahedral (T_d) symmetry sites in the spinel structure is determined with the investigation of the ultrasmall $CoFe_2O_4$ nanoparticles with XMCD. The influence of the synthesis on the crystallographic structure and the magnetic properties of the nanoparticles is thus revealed.

1 Experimental

1.1 Synthesis

Co-Coprec sample. The Cobalt-Iron nanospinels Co-Coprec were obtained by using a modified Massart's process [9]. It consists in precipitating Co(II) and Fe(III) hydroxydes followed by a heating at boiling temperature to obtain nanoparticles with a meansize of 11 nm. In order to obtain smaller nanoparticles, the Massart's process was slightly modified by adding complexing species (tartrate ions) in the mixture of cobalt and ferric nitrates before the addition of sodium hydroxide. The different steps of the synthesis are reported elsewhere [10].

Co-Acac sample. Following the route of thermal decomposition of metal precursors developed by Sun et al. [11], we have synthesized a second set of small nanoparticles of $CoFe_2O_4$ named Co-Acac. The different steps of the so-called "Acac" synthesis are reported elsewhere [12].

Co-Polyol sample. The third set of small particles of Cobalt-Iron nanospinels is obtained by using the polyol process [13] which consist in a forced hydrolysis of Fe(III) and Co(II) mixture in a polyol solution . Depending on the polyol used for the synthesis, the morphology of the nanoparticles obtained differs. When the reaction is realized in diethylene glycol (DEG) small spherical nanoparticles are obtained [14].

1.2 Methods

Chemical composition of cobalt and iron of the nanoparticles was measured by Atomic Absorption Spectrometry using Perkin Elmer Analyst 100 with a, air-acetylene flame at a mean temperature of $2300^\circ C$. Table 1 present the cationic concentrations of the cations of each sample is represented by the molar ratio X_M as detailed in eq. (1) below:

$$X_M = \frac{[Co]}{[Co] + [Fe]} \quad (1)$$

Nanospinels morphology and size were determined by Transmission Electron Microscopy (TEM) micrographs using a JEOL-100 CX2 (UPMC University). The analysis of the micrographs of more than 2000 particles leads to size histograms fitted with a log-normal distribution presented Fig.1.

Magnetisation vs. magnetic field at 4 K and 300 K and Magnetisation vs temperature measurements were recorded with a Vibrating Sample Magnetometer (VSM) using a Quantum Design PPMS. The saturation magnetization (M_S) values at 300 K and the blocking temperature (T_B) were herewith determined (Table 1).

X-Ray Absorption Spectroscopy (XAS) and X-Ray Magnetic Circular Dichroism (XMCD) measurements were recorded on the DEIMOS beamline at the French synchrotron facility SOLEIL. XAS and XMCD signals were recorded at the Co and Fe $L_{2,3}$ edges at 4 K under ultra-high vacuum (10^{-10} mbar) in the presence of a magnetic field up to 6.4 Tesla. The circularly polarized X-Rays are provided for XAS and XMCD measurements by an Apple-II HU52 undulator. The XMCD signals were recorded by flipping both the circular polarization (left and right helicity) and the external magnetic field (either + 6.4 T or -6.4 T). Each XMCD spectra was thereby acquired by taking the difference:

$$\sigma_{XMCD} = \sigma^- - \sigma^+ \quad (2)$$

$$\text{where } \sigma^- = [\sigma_L(H^+) + \sigma_R(H^-)] \quad (3)$$

$$\text{and } \sigma^+ = [\sigma_L(H^-) + \sigma_R(H^+)] \quad (4)$$

where σ_L (respectively σ_R) is the absorption cross section measured with left (respectively right) helicity. The measurements were performed on dried magnetic nanoparticles, therefore the XAS spectra were obtained by taken the isotropic absorption cross-section as :

$$\sigma_{XAS} = \frac{\sigma^- + \sigma^+}{2} \quad (5)$$

By following the variation of the XMCD intensity as a function of the external magnetic field, we measured the element specific magnetization curves at the energies corresponding to a specific minority site of the absorbing ion (707.98 eV for T_d Fe, 708.72 eV for O_h Fe, 776.56 eV for T_d Co and 777.55 eV for O_h Co). The EMPHU-65 (ElectroMagnet/Permanent Helical Undulator) undulator was used to record the element specific magnetization curves.

2 Results and discussion

2.1 Size, morphology and chemical composition

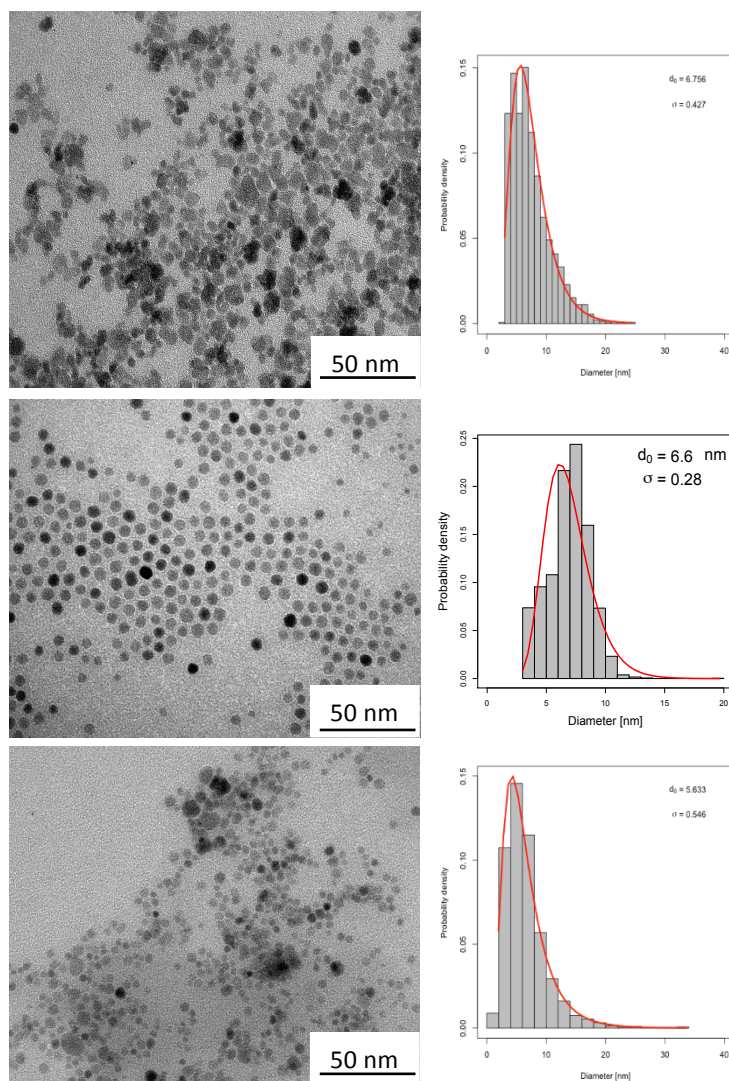


Figure 1. TEM micrographs and size distribution histograms of a) Co-coprec (6.7 nm), b) Co-Acac (6.6 nm) and c) Co-Polyol (5.6 nm) nanoparticles

Cobalt-Iron nanospinels from the different synthesis routes demonstrate similar mean sizes of 6.7 nm for the Co-coprec nanoparticles, 5.6 nm for the Co-polyol nanoparticles and 6.6 nm for the Co-acac nanoparticles. TEM micrographs show the dependence of the nanoparticles morphology with the synthesis process through which they were obtained. The co-precipitation synthesis leads to non-spherical nanoparticles with a high polydispersity ($\sigma = 0.43$). Nanospinels obtained with the polyol process are spherical but the sample is highly polydisperse ($\sigma = 0.55$). Cobalt-iron nanospinels synthesized with high temperature decomposition process are also spherical but the process allows to obtain monodisperse nanoparticles with narrower size distribution ($\sigma = 0.28$).

Sample	d_{TEM} nm	σ_{TEM} nm	X_M %	M_s $\mu\text{e.g}^{-1}$
Co-coprec	6.7	0.43	26.9	66
Co-polyol	5.6	0.55	8.2	51
Co-acac	6.9	0.27	27	59

Table 1. Physico-chemicals characteristics of Co-coprec, Co-polyol and Co-acac nanoparticles with d_{TEM} the mean diameter of the nanoparticles measured from TEM micrographs, σ_{TEM} the size distribution, X_M the cationic molar ratio, M_s the saturation magnetization measured at 300 K on the dried nanoparticles.

Assuming that the molar ratio X_M rely on 4 oxygens atoms, the X_M value expected for a stoichiometric crystallographic structure of CoFe_2O_4 is equal to 33%. From the absorption atomic spectroscopy measurements of Co and Fe concentrations, we obtain lower value of X_M for all cobalt-iron nanospinels obtained. The Co-coprec and Co-acac samples have similar composition with a molar ratio of 26.9 % for the co-coprec nanoparticles and of 27% for the Co-acac, while the co-polyol nanoparticles exhibit a very low molar ratio of 8.2 %. The crystallographic structures of the nanoparticles contain some lacuna, and the structure of the cobalt-iron nanospinels can be formulate as $\text{Co}_{\frac{8}{11}}\text{Fe}_{\frac{24}{11}}\blacksquare_{\frac{1}{11}}\text{O}_4$ for the Co-coprec and Co-acac samples and as XX for the Co-polyol nanoparticles.

2.2 Bulk magnetometry measurements

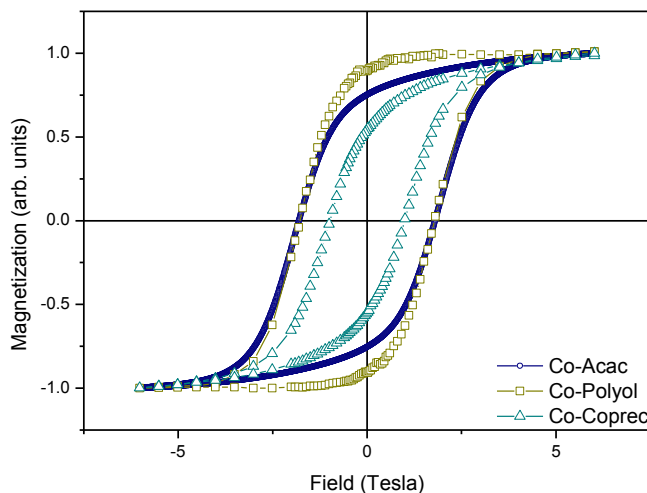


Figure 2. Bulk Magnetization curves measured on ferrofluids samples of Co-Acac (blue circle), Co-Polyol (dark-yellow square) and Co-Coprec (Dark cyan triangle) at 4 K.

We compare the magnetic properties of the Co-Coprec, Co-Acac and Co-Polyol nanoparticles. The nanoparticles from the different synthesis pathways do not exhibit the same saturation magnetization values M_s (Table 1). The Co-coprec nanoparticles have a saturation magnetization of $66 \text{ A.m}^2.\text{kg}^{-1}$, while the Co-acac and Co-polyol nanoparticles possess lower saturation magnetization of $59 \text{ A.m}^2.\text{kg}^{-1}$ and $51 \text{ A.m}^2.\text{kg}^{-1}$ respectively. The Figure 2 show the magnetization as a function of the applied magnetic field performed on the frozen phase of the ferrofluid samples (4 K) in zero field cooled. The temperature at which the measurements were performed is well below the blocking temperature of the nanoparticles and the magnetization vs applied magnetic field measurement result in hysteresis curve. The hysteresis curve of the Co-Coprec nanoparticles show a coercive field value of 0.99 Tesla that is one order of magnitude smaller than that of the Co-Acac and Co-Polyol nanoparticles. Magnetic coercivity of Co-Acac (1.77 tesla) and Co-Polyol (1.80 tesla) samples are quite similar, but the Co-Polyol nanoparticles show a

more pronounced remanence ratio than the Co-Acac nanoparticles.

2.3 XAS and XMCD measurements

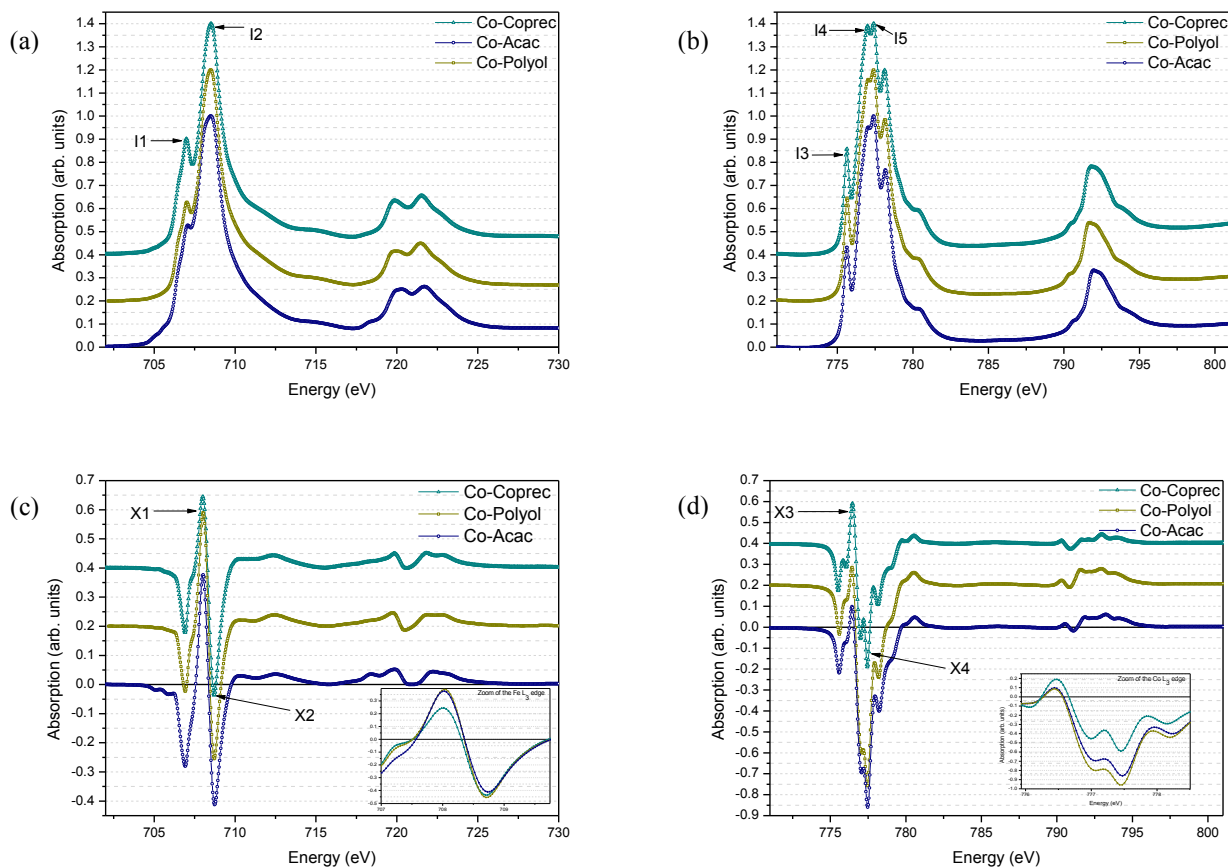


Figure 3. XAS and XMCD spectra measured at 4 K on the dried nanoparticles of Co-Coprec (dark cyan triangle), Co-polyol (dark yellow square) and Co-acac (blue circle) samples at the (a) Fe $L_{2,3}$ edges ((a) and (c)) panels and Co $L_{2,3}$ edges ((b) and (d)) panels

Figure 3. shows the XAS spectra measured at 4 K for the nanoparticles at Fe $L_{2,3}$ edges ((a)) and at the Co $L_{2,3}$ edges ((b)). The XAS spectra is very sensitive to the cationic distribution among the T_d and O_h sites. The magnetic properties investigated with bulk magnetometry measurements can be correlated to the magnetic contributions of the Co and Fe ions in T_d and O_h symmetry sites to the magnetization thanks to element specific XMCD measurements. Indeed, the L_3 edge of the XMCD signals is site sensitive and consists of a positive peak (X1 or X2) which can be related in the case of Fe^{3+} and Co^{2+} to the occupation of the cations of the T_d symmetry sites, and a negative peak (X3 or X4) which comes from the cations occupation of the O_h sites symmetry. XMCD spectra measured at the Fe $L_{2,3}$ edges in the Co-Coprec and Co-Polyol samples are very similar to the one measured in maghemite γ - Fe_2O_3 [15], which contains fully oxidized iron ions Fe^{3+} , while the Fe $L_{2,3}$ edges spectrum for the Co-Acac nanoparticles exhibit more intense feature at 705 eV characteristic of the presence of traces of Fe^{2+} ions in O_h sites [16] (Figure 3. (c)). XMCD signals display a positive peak when the magnetic moment are parallel to the external magnetic field and a negative peak when the peak is anti-parallel to the external magnetic field. The Fe L_3 edge signals exhibit a X1 peak opposite in sign to the X2 peak, and the Co L_3 edge signals exhibit a X3 peak opposite in sign to the X4 peak. This implies that the magnetic moments of the Fe^{3+} ions (respectively Co^{2+} ions) in T_d symmetry are coupled antiferromagnetically with the Fe^{3+} ions (respectively Co^{2+} ions) in O_h symmetry sites.

The X1/X2 ratio for Co-Polyol and Co-Acac samples are very close (respectively 0.86 and 0.93) which demonstrates that the distribution of Fe^{3+} among O_h and T_d symmetry sites is similar in both samples. The ratio is smaller for the Co-Coprec nanoparticles (0.56) which exhibit less Fe in T_d symmetry and more in O_h symmetry than the other samples.

The Co $L_{2,3}$ edges spectrum measured in the Co-Coprec nanoparticles is typical of a compound containing a mixture of T_d and O_h Co^{2+} [17]. The XMCD signal measured at the Co $L_{2,3}$ edges in the Co-Acac and Co-Polyol samples show that in both

samples, Co^{2+} ions are predominantly in O_h symmetry for these two samples with a very intense X4 peak signal (Fig.3). The preferential occupancy of O_h sites by Co^{2+} ions that is observed for the Co-Acac and Co-Polyol nanoparticles accompany a larger occupancy of the T_d sites by Fe^{3+} for these samples than for the Co-coprec. The smaller X1/X2 ratio of the Co-polyol nanoparticles compare to that of Co-acac nanoparticles can be assess to the defect of Co^{2+} in the crystallographic structure. This implies less Co^{2+} occupying O_h symmetry sites in favor of more Fe^{3+} cations occupying the O_h symmetry sites. Larger occupancy of O_h sites by Co^{2+} coincides with the greater values of coercive field observed with bulk magnetometry measurements. In the case of nanoparticles prepared with Acac and Polyol synthesis, the obtained inverse spinel structure with all Co^{2+} ions in O_h symmetry can be interpreted as the result of the high temperature ($>200^\circ\text{C}$) conditions used for the decomposition of the metal precursors in both processes, while the co-precipitation synthesis is carried out at lower temperature (100°C).

Conclusion

Ultrasmall magnetic nanoparticles of CoFe_2O_4 were obtained through three different synthesis processes. The cationic distribution determined from XMCD measurement in the three samples show that the Acac and Polyol processes allow to obtain nanoparticles with great coercive field that is by one magnitude order larger than from the Co-precipitation process. The coercivity is directly related to the presence of Co^{2+} in O_h interstitial sites explaining the enhanced magnetic properties exhibited by the nanoparticles from these synthesis. Acac and Polyol synthesis lead to an increased crystallographic order, with nanoparticles that have a structure closer to the bulk structure of CoFe_2O_4 . However, during the Acac synthesis some Fe^{2+} ions are formed.

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