

PROGRAMMA SHORT TERM MOBILITY – ANNO 2009

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Titolo del programma: Correlation between magnetic properties (saturation magnetization, exchange bias, magnetic anisotropy and spin canting) and cationic distribution in spinel metal oxide nanoparticles

Final Report

1. Introduction

During the stage at the Laboratoire de Physique de l'Etat Condensé (UMR CNRS 6087 of the University of Le Mans, France) the atomic environment of Fe in different samples of spinel metal oxides (γ -Fe₂O₃, CoFe₂O₄, MnFe₂O₄) has been studied. Using ⁵⁷Fe Mössbauer Spectroscopy the hyperfine magnetic structure has been correlated to magnetic properties (saturation magnetization, exchange bias, magnetic anisotropy and spin-canting) previously studied by static magnetic measurements performed in the laboratory of Institute of Structure of Matter in Rome. (Paragraph 3) In addition, spectra in absence of magnetic field at different temperature have been performed in order to study the blocking in systems of interacting nanoparticles, in the timescale of Mössbauer experiments (paragraph 4).

Nevertheless during the stay in Laboratoire de Physique de l'Etat Condensé more than 80 Mössbauer spectra were performed, in this report we will discuss only the most relevant results. A semi-qualitative interpretation of the Mössbauer data will be given and a preliminar comparison with magnetization measurements and structural characterization, previously carried out, will be performed. Indeed, in the next future, further efforts will be made in order to refine the fitting procedure and to better understand the hyperfine magnetic structure of the materials.

2. Experimental

Transmission Mössbauer Spectrometry was carried out using a ⁵⁷Co(Rh) source in the constant acceleration mode. Zero-field Mössbauer spectra have been recorded at different temperature in the range 4.2-300 K using a bath cryostat while the in-field Mössbauer spectrum has been obtained at 10 K using a cryomagnetic device, where an external field of 8T was applied parallel to the γ -beam. Spectra were analyzed by means of a least-squares program MOSFIT¹ and the isomer shift values were quoted relative to that of metallic α -Fe at 300 K.

3. Correlation between magnetic properties and cationic distribution in spinel metal oxide nanoparticles

The magnetic properties of nanosized particles of spinel ferritic oxides are a subject of great interest both for application purposes and for basic research. The most relevant features of the size reduction are superparamagnetism, finite-size effects and the presence of non-collinear spin structure (spin-canting). Spin-canting is more likely in surface spins, but it can occur in the particle core, too²⁻⁴. Interface exchange coupling between a magnetically ordered core and magnetically disordered surface shell with high anisotropy may give rise to the “*exchange bias*” (EB) phenomenon^{5, 6}. EB modifies the effective anisotropy of the systems, inducing an extra unidirectional contribution to the magnetic anisotropy; this gives rise to the horizontal shift of the hysteresis loop (H_{ex}) observed when the sample is cooled in an applied magnetic field. Besides, in $MeFe_2O_4$ ferrites, where Me is a divalent cation, a further variant is given by the distribution of cations in the tetrahedral and octahedral sites of the close packed oxygen structure (Figure 1), as it

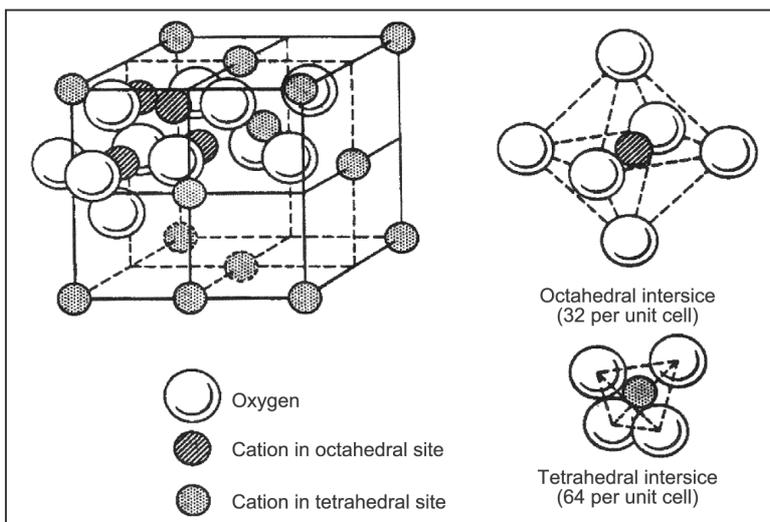


Figure 1: Schematic Representation of the Spinel Structure

may affect the alignment of the moment of the different ions. Magnetic interactions among nanoparticles as well as their magnetic structure play an important role in the physics of these systems. Thus, the magnetic behaviour of assemblies of ferrite nanoparticles is due to a complex interplay of all such effects. For this reason, Mössbauer measurements, especially in high magnetic field, become fundamental to obtain information about cationic distribution and magnetic disorder (fraction of canted spins and canting angle).

3.1 CoFe₂O₄ nanoparticles prepared by a self combustion technique

A series of CoFe₂O₄ nanopowders were prepared at the laboratory of Chemistry Department at Cagliari University through a novel sol-gel autocombustion method. The samples were characterized by XRD, TEM, N₂- Physisorption, DC magnetization measurements and Mössbauer spectroscopy at room temperature in zero field⁷.

Sample	XRD average particle size (nm)	Ms 5K emu/g	Ms 300K emu/g
A	19±1	74.8	65.9
B	22±1	70.0	56.2
C	18±1	76.3	67.4
D	10±1	99.4	82.7

Peculiar differences have been noticed as regards the saturation magnetization values (M_s) deduced from the hysteresis loops (Table 1). In fact, the samples A, B and C exhibit M_s values lower than that of bulk cobalt ferrite (93.9 emu/g at 5 K and 80.8 at 298K), while the M_s value of sample D is well above it. On the other hand, on the basis of particle size, just the opposite behaviour would have been expected, as lower saturation magnetization is usually observed in smaller particles, presumably due to a larger spin-canting effect.

In order to better understand the relation between spin-canting, saturation magnetization and particles size, Mössbauer spectra in 8T at 10 K were performed on sample D (figure 2)

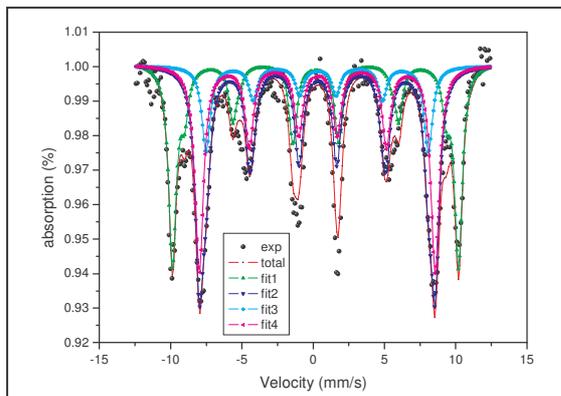


Figure 2: Mössbauer spectrum recorded at 10 K, in an external magnetic field of 8T, on CoFe₂O₄ nanoparticle (sample D)

As expected, the spectra are clearly resolved in two main six-lines components. Lines 2 and 5 have non-zero intensity and this suggests a non-collinear spin structure, i.e. some of the spins are not aligned parallel or antiparallel to the external magnetic field⁴. The first fitting was performed with four components. This indicates a high degree of inversion, that could explain the increase of saturation magnetization observed in this sample.

3.2 Nanochains of Maghemite ($\gamma\text{Fe}_2\text{O}_3$)

Another system investigated in the framework of this collaboration was a system constituted by $\gamma\text{Fe}_2\text{O}_3$ nanoparticle prepared by a wet chemistry method in the chemical Laboratory of Chemistry Department at the University of Cagliari.⁸ High-Resolution TEM analysis (previously performed in the University of Cagliari) had revealed the presence in the samples of needle-shaped particles, each formed by aggregates of nanocrystals arranged in nanochains. The mean nanocrystals size, extracted from XRD measurements, was $\sim 5 \text{ nm}^8$.

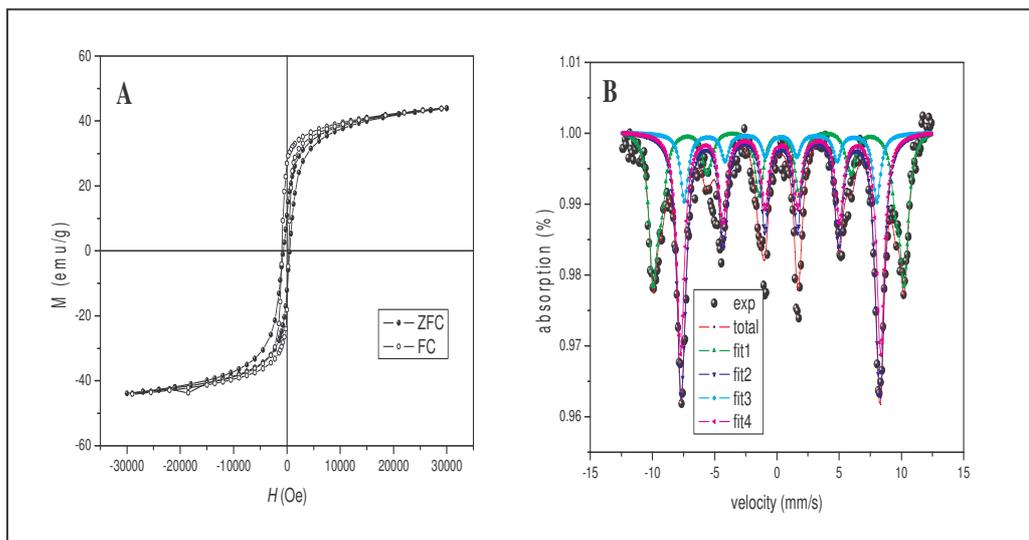


Figure 3: A. Hysteresis loop after zero field cooling (full symbols) and field cooling (empty symbols) on $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles; B. Mössbauer spectrum recorded at 10 K, in an external magnetic field of 8T, on D samples.

Hysteresis measurements at low temperature (5K) showed a non-saturating character until 3T. The magnetization extrapolated at high field was $\sim 49.8 \text{ A m}^2 \text{ Kg}^{-1}$ whereas the coercive field was 0.06 T. In order to get information about the magnetic structure of nanoparticles, Mössbauer spectrum in high magnetic field (8T) at low temperature (10 K) was performed (Figure 4b).

The Mössbauer spectra indicated the presence of a high fraction of canted spins, probably located on the particle surface. This is in agreement with the picture according which the exchange bias was due to the presence of frozen canted surface spins exchange coupled with a ferrimagnetically ordered core.

In addition, Mössbauer investigations suggested a highly inverted magnetic structure, opening interesting perspectives in the study of the correlation between spin canting and inversion degree.

4. Spin Glass like behaviour of magnetic nanoparticles

The magnetic behavior of a nanoparticles assembly varies with the morphology of the particles (particle size and shape) and is also strongly affected by interparticle interactions. The magnetic interactions can be due to dipolar coupling and exchange coupling among nanoparticles surface atoms and play a fundamental role in the physics of these systems.⁹ Disorder and strong competing interactions lead an assembly of nanoparticles to a long range magnetic ordered state with spin glass-like features.¹⁰⁻¹² Mössbauer spectroscopy and magnetization measurements have significantly different time scales and for this reason the blocking temperatures estimated by the two techniques differ considerably. On the contrary in the case of a transition from a superparamagnetic state to a spin-glass like (or Superspin glass) state, the transition temperatures deduced by the two techniques are very close to each other. Therefore, the simultaneous application of Mössbauer spectroscopy and magnetic investigations is a powerful tool to investigate the effect of magnetic interactions on superparamagnetic relaxation.¹⁰

4.1 Superspin glass behaviour in MnFe₂O₄ nanoparticles

MnFe₂O₄ nanoparticles were prepared by microemulsion technique.¹³

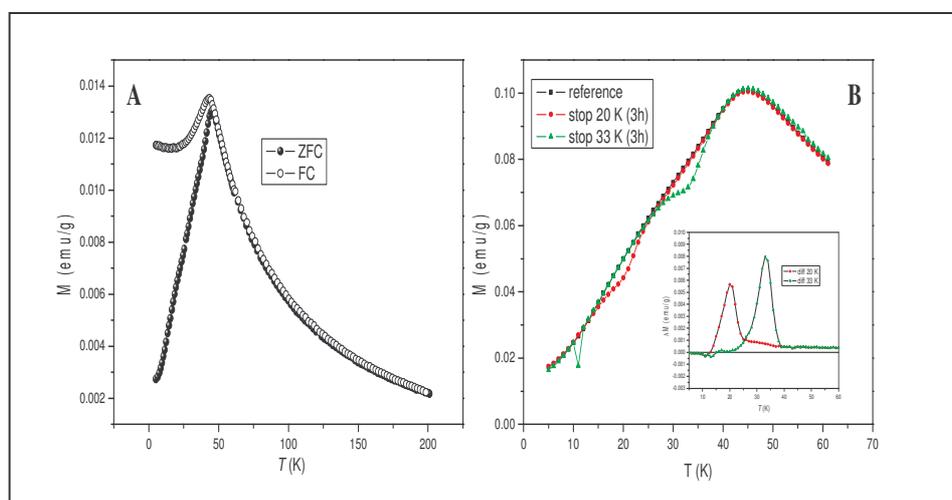


Figure 4: A: Zero Field Cooled – Field Cooled magnetization measurements in external magnetic field of 5 mT of the MnFe₂O₄ nanoparticles system ; B.: Reference and memory ZFC magnetization; memory curves are recorded after cooling the samples at zero field and stopping for 3 h and 20 K and 33 K.

Mean crystallite size obtained by XRD was 2 nm, whereas the mean particle size value obtained from a BET measurement (~4 nm, corresponding to a 278 m²/g specific area) evidenced an incipient particle aggregation.¹³ A superspin glass (SSG) behaviour was deduced by ZFC/FC magnetization curves, showing a sharp maximum at $T_{\max} \sim 40$ K (Figure 4a). The SSG behavior was

confirmed by memory experiments (figure 4b), carried out according to the ZFC protocols at 20 K and 33 K.¹⁴

Figure 5 shows Mössbauer spectra for MnFe₂O₄ nanoparticles in zero applied magnetic field at different temperature. At low temperature, the spectra showed magnetically split sextets, but with increasing temperatures there is a gradual collapse of the six lines to a doublet component because of the fast superparamagnetic relaxation of the nanoparticles. The blocking temperature in Mössbauer spectroscopy (T_B^M) can be defined as the temperature at which 50% of the spectral area is magnetically split. The values of T_B^M was around 40K. As we already mentioned, for non-interacting superparamagnetic nanoparticles, the blocking temperatures estimated from Mössbauer spectroscopy and magnetization measurements, differs considerably because the different time scales of the two techniques. Using the Néel equation¹⁵, the ratio between the two blocking temperatures is given by:

$$\left(\frac{T_B^M}{T_B^m} \right) = \frac{\ln(\tau_m / \tau_0)}{\ln(\tau_M / \tau_0)} \quad (1)$$

Where τ_m , τ_M are the time scale of magnetization measurements and Mössbauer spectroscopy, respectively. The value of τ_0 is in the range $\approx 10^{-10} - 10^{-12}$ for ferromagnetic nanoparticles.⁴ By substituting $\tau_m = 100$ s and $\tau_M = 5 \times 10^{-9}$ s, we find a ratio T_B^M/T_B^m in the range 4-7. Because of the particle size distribution, the temperature of the maximum, T_{max} , in ZFC magnetization curves may be larger than the blocking temperature T_B by a factor $\beta=1-2$. Therefore one would expect a T_B^M/T_{max} ratio close to 2-7.

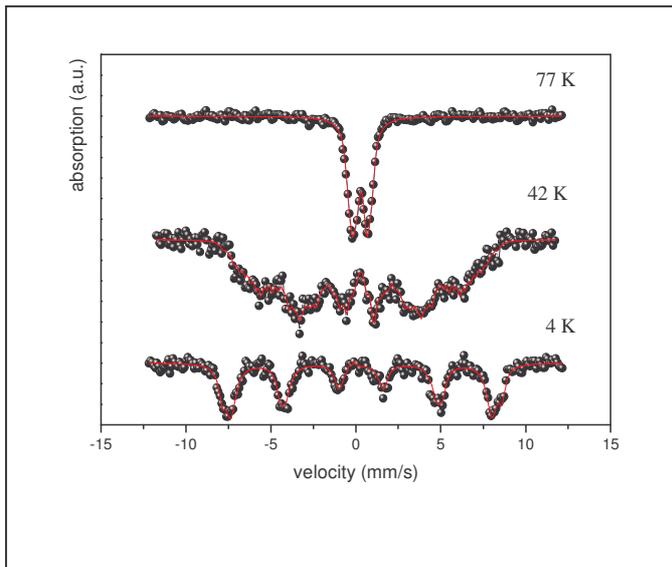


Figure 5: Mössbauer spectra in zero magnetic field recorded at different temperatures of the MnFe₂O₄ system

In MnFe₂O₄ samples the freezing temperature detected by Mössbauer spectroscopy is close to T_{max} deduced by ZFC magnetization measurements ($T_B^M/T_{max} = 1/1.25$). The almost identical

temperatures of T_{\max} and T_B^M indicated that this temperature is correlated to a transition from a superspin glass state to a superparamagnetic state.^{10, 15}

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