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Ferromagnetic resonance in Ni–Zn ferrite nanoparticles in different aggregation states

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ABSTRACT

Ferrite nanoparticles of composition $Zn_{0.5}Ni_{0.5}Fe_2O_4$ were synthesized by forced hydrolysis in polyol from the corresponding zinc, nickel and iron acetates. By varying the preparation conditions, different aggregation states were obtained, ranging from isolated nanoparticles with average diameter of 5 nm, to clusters of some 20 nm, formed as well by nanoparticles with average diameter in the 5 nm range, as confirmed by X-ray diffraction and high resolution transmission electron microscopy. Ferromagnetic resonance measurements exhibited a ferrimagnetic behavior for both aggregation states at 77 K; at 300 K, however, isolated nanoparticles showed a superparamagnetic behavior while clustered ones remained ferrimagnetic with a broad linewidth. These results are interpreted on the basis of interactions between nanoparticles.

1. Introduction

Magnetic nanoparticles (MNPs) have a clear fundamental importance, as well as a strong technological interest, ranging from fields as diverse as medicine applications to potential high density magnetic recording memories, and soil treatments. They exhibit very different macroscopic magnetic properties when compared with their bulk counterpart. Most of these differences are due to the effects of the small scale, leading to a significant increase in the fraction of atoms on the surface, as compared with those in the particle. In the case of MNPs, the effects of mutual magnetic interactions have to be added, in a complex way, to those of the reduced dimensions [1].

The synthesis of nanoparticles (NPs) by means of the forced hydrolysis of the acetates of the corresponding metals in a polyol [2,3] is a very convenient method to obtain spinel ferrite NPs in the 5 nm range. By varying the preparation conditions, different aggregation states can be obtained, ranging from monodisperse NPs to clusters formed by many NPs. In this paper, we present an investigation of the effects of these aggregation states on the ferromagnetic resonance response (FMR) of Ni–Zn ferrites. The observed resonance fields and linewidths clearly show the influence of the aggregation state.

2. Experimental techniques

Ferrite nanoparticles of composition $Zn_{0.5}Ni_{0.5}Fe_2O_4$ were synthesized by forced hydrolysis in a polyol (diethylenglycol) from the corresponding zinc, nickel and iron acetates [2,3]. By varying the preparation conditions, in particular by changing the strength of boiling and mechanical stirring during synthesis, two different aggregation states were obtained: isolated nanoparticles with average diameter of 5 nm, for strong boiling and stirring, or sample "A", to clusters of some 20 nm, formed as well by nanoparticles with average diameter in the 5 nm range, or sample "B", for gentle boiling and stirring. The X-ray diffraction pattern of samples was obtained in a Panalytical XperPro diffractometer equipped with a multichannel detector (X'celerator), using Co K_α radiation. High-resolution transmission electron microscopy (HRTEM) observation was performed by means of a JEOL 100-CX transmission electron microscope operating at 100 kV. A Quantum Design MPMS-5S SQUID magnetometer was used for magnetic characterization in the temperature range of 4.2–330 K. The thermal zero field cooling (ZFC) and field cooling (FC) susceptibility variations were measured under a 200 Oe dc field. A JEOL JES-RES 3X Spectrometer was used for the ferromagnetic resonance measurements, operating in the X-band (8.8–9.8 GHz) at room temperature (300 K), and at the liquid nitrogen point (77 K). Dried compact powders of samples A and B were used for FMR measurements.

3. Experimental results

X-ray diffraction (XRD) characterization showed a single spinel phase, well crystallized in both cases. Sample A showed broad diffraction peaks, see Fig. 1; a calculation by means of the Scherrer relationship led to a particle size of ~7 nm. In the case

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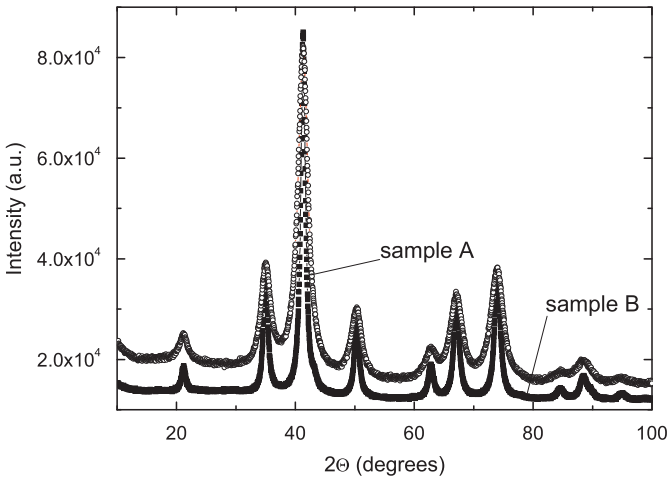

Fig. 1. X-ray diffraction patterns of both samples, which showed a single spinel phase. Sample A exhibited broad diffraction peaks, while B sample showed narrower peaks.

of sample B, XRD peaks appeared narrower, associated with an apparent particle size of ~20 nm.

High-resolution transmission electron microscopy (HRTEM) confirmed that sample A is formed by isolated nanoparticles in the 5–8 nm diameter range, while sample B is made of clusters with a size of ~20 nm, made of nanoparticles with individual sizes also in the 5 nm range. Additionally, HRTEM showed that there is an epitaxial arrangement of nanoparticles within clusters, i.e., there is a good agreement of crystal planes between neighboring nanoparticles. This was confirmed by a Fast Fourier Transform (FFT) study of electron diffraction patterns, Fig. 2(b), which showed a clearly textured structure.

ZFC–FC magnetization studies (Fig. 3) exhibited clearly different behaviors; a blocking temperature separating the ferrimagnetic phase from the superparamagnetic phase at ~36 K was observed in sample A, while sample B showed a complex plot with a blocking temperature at about 100 K and a discontinuity or "kink" at 58 K. This feature can be the result of the contribution of different aggregation states in sample B, i.e., clusters with different numbers of nanoparticles ranging from a few nanoparticles, up to a few tens.

Fig. 4(a) shows the hysteresis loops of sample A at 5 and 300 K. At 5 K, a ferrimagnetic loop is observed, with a saturation magnetization (M_s) of 93 emu/g and a coercive field (H_c) of 62 Oe (inset at left). M_s is slightly lower than the magnetization of the bulk (~113 emu/g [4]), while H_c (more clearly observed in the left upper inset) is about half the anisotropy field (H_K~125 Oe [4,5]), which can be expected for nanoparticles in the single domain range. At room temperature, the magnetization as a function of applied field exhibits a superparamagnetic shape with no coercive field (right lower inset in Fig. 3(a)), in good agreement with ZFC–FC measurements (Fig. 3).

Fig. 4(b) shows the hysteresis results of sample B. At 5 K, nanoparticle clusters exhibited also a ferrimagnetic hysteresis loop, with M_s and H_c values slightly larger than those for sample A (coercive fields are also more evident in the amplified insets of Fig. 4(b)). At room temperature, sample B displayed a general behavior associated with a ferrimagnetic ordering, with a coercive field of about 20 Oe, in contrast with sample A.

The ferromagnetic resonance (FMR) of both samples was investigated in the X-band (9.45 GHz) at 77 K and at room temperature. Both samples showed broad linewidths in plots of the derivative of power absorption (dP/dH) against applied field, especially for applied magnetic fields above the resonance field, as shown in Fig. 5

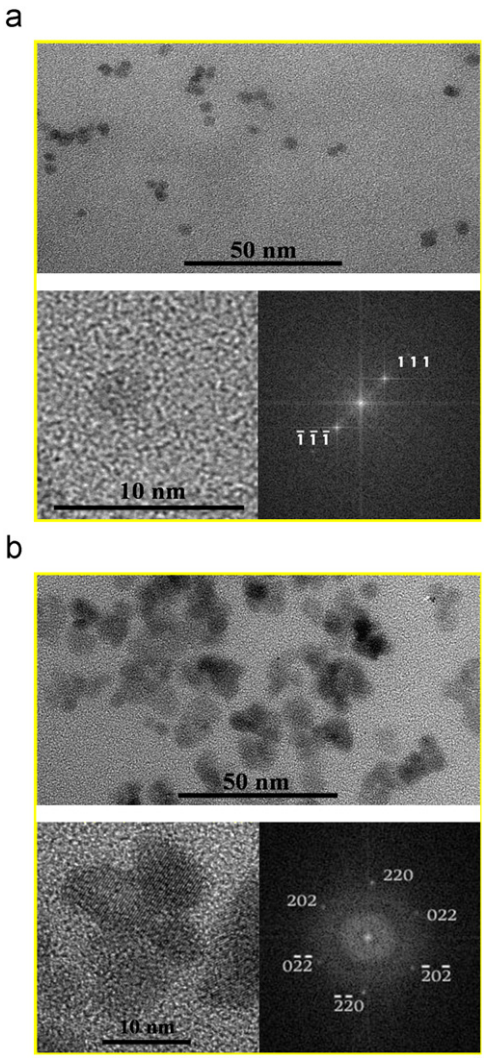

Fig. 2. Micrographs (TEM, HRTEM and FFT) of (a) sample A showing isolated NPs and (b) sample B showing NP clusters with a preferential crystal.

for $T=77$ K. The resonance field of sample A, $H_{res}=2382$ Oe, is larger than that of sample B ($H_{res}=1696$ Oe). At 300 K, Fig. 6, sample A exhibited a narrow linewidth ($\Delta H=$ 253 Oe), while sample B showed a linewidth with a larger value ($\Delta H=497$ Oe).

The broadening of resonance lines can be interpreted in terms of a random distribution of the anisotropy axis [6]. This effect has also been observed in bulk ferrites [7] and it is probably more significant in these materials because most ferrites possess cubic anisotropy. This is confirmed by the fact that sample A at 300 K is superparamagnetic, and therefore showed the narrowest line (see Fig. 6). The resonance field of sample A for both temperatures is larger than that of sample B; this trend can account for by the epitaxial character of clusters in sample B. This crystal ordering leads to an increase of the internal field (which can be considered as formed by the contributions of exchange field, H_x, anisotropy field, H_K, etc.), and thereby a decrease in the value of the external field, H_{res}, needed to satisfy the Larmor relation $\omega=\gamma H$, where ω is the angular frequency, γ the gyromagnetic ratio and H the total magnetic field $H=H_{res}+H_x+H_K+\ldots$ In the paramagnetic (and also in the superparamagnetic) phase, $H=H_{res}$, since there is no contribution from any internal field.

The epitaxial character of clusters in sample B can explain the ensemble of differences as compared with the monodispersed

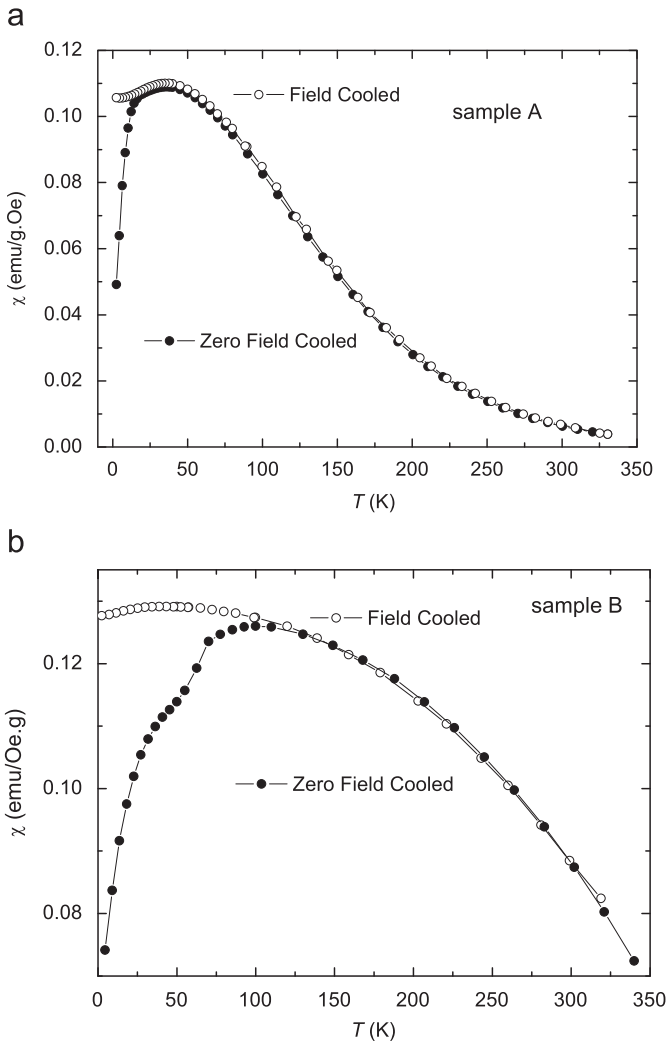

Fig. 3. Magnetization studies (zero field cooled–field cooled, ZFC–FC) in (a) sample A and (b) sample B.

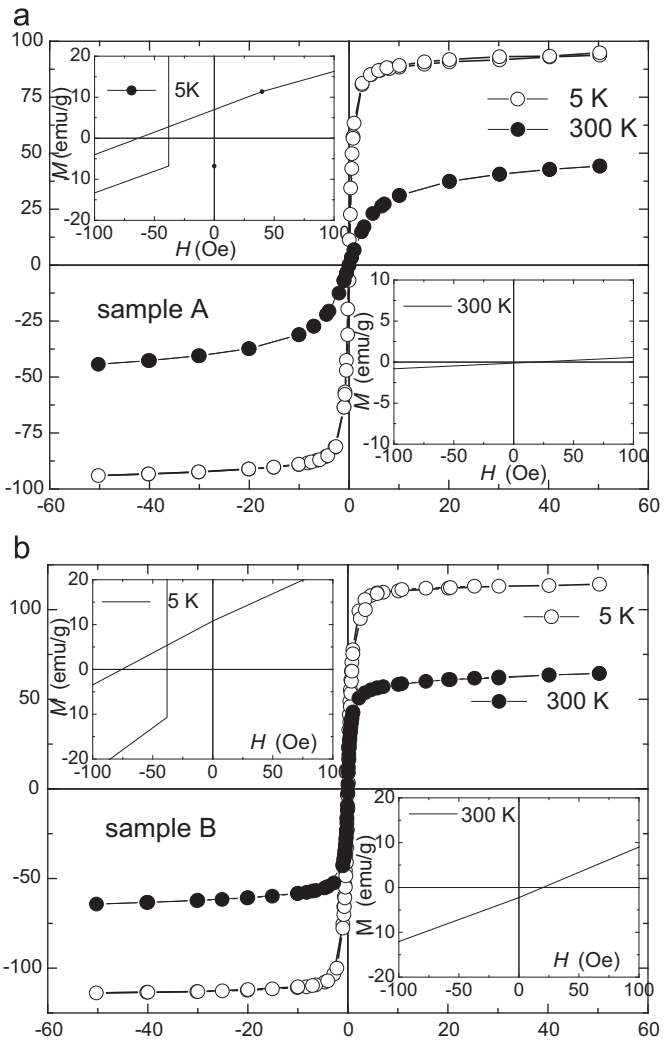

Fig. 4. Hysteresis loops of samples, at 5 and 300 K: (a) sample A and (b) sample B. In insets, results are plotted in the very low fields to show the coercive field for each sample and temperature. Note the difference in scale.

NPs of sample A. X-ray diffraction, Fig. 1, showed a narrowing of diffraction lines for sample B, in spite of being formed by NPs of the same size (about 5 nm). Clusters in sample B retain the ferromagnetic ordering up to room temperature, as showed by hysteresis loops and ferromagnetic resonance measurements. These results point to a significant exchange interaction between adjacent NPs, as well as a probable decrease in demagnetizing fields as well. To our knowledge, there are no theoretical works on this subject.

Finally, there seems to be an inconsistency in the results, since the blocking temperature of sample A is 36 K; however, at 77 K (Fig. 1), sample A exhibited an FMR pattern closer to a ferrimagnetic state than to a superparamagnetic phase. This can be explained in terms of the differences in the time window, or the time scale of the experimental techniques (in this case, between SQUID and FMR experiments [8]). For macroscopic measurements such as the direct determination of the magnetization, the measurement time is on the order of 100 s [9]. For microscopic measurements such as Mössbauer spectroscopy or ferromagnetic resonance the time window is much smaller, in the range of 10^{-9}–10^{-7}. If the relaxation time τ of NPs is shorter than the measuring time t_m, spins can oscillate randomly during measurement and lead therefore to superparamagnetic behavior with zero resulting magnetization. In the opposite case, i.e., $\tau > t_m$, the sample appears as blocked (ordered).

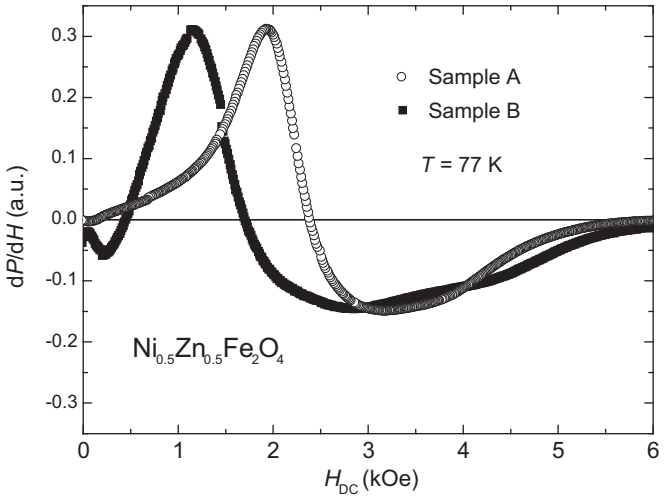

Fig. 5. Ferromagnetic resonance for both samples at 77 K.

In FMR experiments, where the absorption is measured by the microwave field (not by the slowly sweeping field), the time window is about 10^{-12} smaller than in SQUID experiments, and

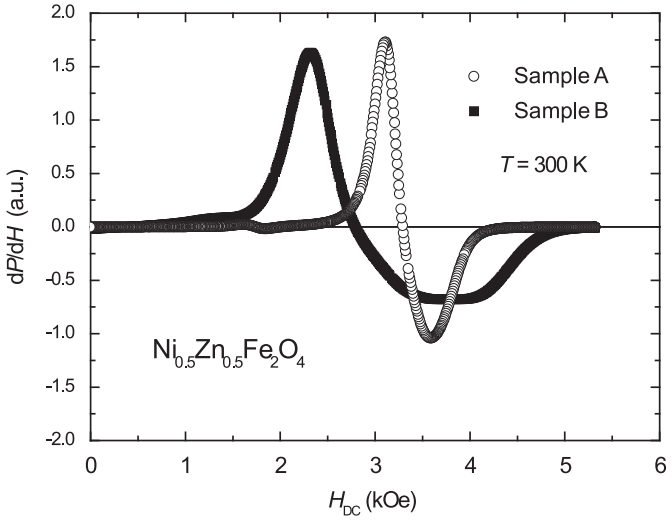

Fig. 6. Ferromagnetic resonance results from the two types of samples, obtained at room temperature.

therefore it shows an ordered magnetic structure for considerably higher temperatures.

4. Conclusions

We have shown that by varying the preparation conditions of ferrite nanoparticles by the forced hydrolysis in a polyol method, it is possible to produce significant differences in their aggregation state, from monodisperse nanoparticles to clusters formed by tens of NPs. These clusters exhibited an epitaxial character which has a considerable impact on all the observed properties in this work. In particular, by comparing with the monodispersed NPs, the blocking temperature of clusters increases above room temperature and the resonance field, as measured in FMR experiments, decreases. These results are consistent with the assumption that there exists an exchange interaction between the NPs in the clusters. Finally, an explanation based on the differences between measuring time and relaxation time was proposed to account for the differences observed in the blocking temperature, as determined by ZFC–FC and FMR measurements.

Acknowledgment

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