Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Magnetism and Magnetic Materials 289 (2005) 118–121
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Experimental evidence of surface effects in the magnetic dynamics behavior of ferrite nanoparticles

E.C. Sousa[a], C.R. Alves[a], R. Aquino[b], M.H. Sousa[b], G.F. Goya[c], H.R. Rechenberg[c], F.A. Tourinho[b], J. Depeyrot[a,*]

[a]*Complex Fluids Group, Instituto de Física, Universidade de Brasília, Caixa Postal 04455, 70919-970 Brasília (DF), Brazil*
[b]*Complex Fluids Group, Instituto de Química, Universidade de Brasília, Caixa Postal 04478, 70919-970 Brasília (DF), Brazil*
[c]*Instituto de Física Universidade de São Paulo, Caixa postal 66318, 05315-970 São Paulo (SP), Brazil*

Available online 26 November 2004

Abstract

The magnetic dynamics behavior of copper and nickel ferrite nanoparticles used in the magnetic fluid elaboration and with mean sizes between 3.5 to 10.4 nm is investigated by measurements of magnetic hysteretic properties and zero field cooling (ZFC) susceptibility. The dependence of the irreversibility field, inversely proportional to the particle size, clearly indicates that the magnetic anisotropy of our particles finds its origin on the surface layer.

PACS: 75.50.Mm; 75.40.Gd; 75.30.Pd

Keywords: Magnetic liquids; Magnetic naoparticles; Spinel ferrites; Surface effects; Magnetic dynamics

1. Introduction

Magnetic ferrite nanoparticles are currently very promising new materials in technological applications and also in the design of new magneto-pharmaceuticals [1]. From a more fundamental point of view, these applications require the knowledge of how the properties of magnetic systems differ from bulk ones when the size decreases to the nanometric range. At this scale, the spatial confinement induces finite size effects of the magnetic core and the existence of an interface leads to an incomplete and distorted atomic surrounding in the surface shell [2]. As an example, significant deviations of the Bloch law were predicted and observed due to finite size effects [3]. Moreover, surface spin canting, non-saturated magnetization curves, freezing of surface spin in a disordered state and surface anisotropy are one of the most current experimental manifestations of surface effects [4]. In this work, we investigate the magneto-dynamic properties of copper- and nickel-based spinel ferrite nanoparticles used in the elaboration of electric double layered magnetic fluids (EDL-MF) [5]. Our measurements point the main role played by surface spins in the thermal activated relaxation and in high field irreversibility.

2. Experimental details

The investigated spinel $CuFe_2O_4$ and $NiFe_2O_4$ nanoparticles are prepared by hydrothermal coprecipitation, in alkaline medium, of a ferrite stoichiometric mixture of aqueous solutions of $CuCl_2$ and $NiCl_2$ with

*Corresponding author. Tel.: +55 61 307 2900; fax: +55 61 307 2363.
E-mail address: depeyrot@fis.unb.br (J. Depeyrot).

0304-8853/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2004.11.035

Table 1
Blocking temperature T_B, anisotropy energy E_A and effective constant K_{eff} deduced from susceptibility temperature dependence measurements

	d_{XR} (nm)	T_B (K)	E_A (10^{-20} J)	K_{eff} 10^5 J m^{-3}	K_S(10^{-4} J m^{-2})
$CuFe_2O_4$	3.5	40.6	1.40	6.24	3.6
	7.5	104.2	3.60	1.63	2.0
	10.4	156.8	7.00	1.19	2.1
$NiFe_2O_4$	4.3	51.0	1.76	4.23	3.0
	5.9	132.3	4.50	4.19	4.1
	7.7	195.5	6.74	2.82	3.6
	8.9	175.5	6.05	1.19	1.8

$FeCl_3$ [5]. Then, in order to ensure the chemical thermodynamical stability of acidic colloidal dispersion, the nanoparticles are submitted to a hydrothermal (100 °C) treatment with ferric nitrate that induces the formation of a protective shell, rich in iron, surrounding the ferrite core [6]. Afterwards, the resulting magnetic nanocrystals are peptized in aqueous medium leading to EDL-MF. Samples based on different mean sizes are obtained directly during the coprecipitation process, by changing the velocity of adding the reagents, in the case of $NiFe_2O_4$ nanoparticles. A colloidal size sorting method [7], which also reduces the polydispersity typically below 0.2, is used for $CuFe_2O_4$ samples.

All our experiments are made on powder samples obtained after evaporation of the liquid solution. X-ray diffraction (XRD) measurements are carried out using a Rigaku/Geigerflex powder diffractometer using Cu-Kα radiation and the nanoparticle mean size (see Table 1) is deduced from the Scherrer formula applied to the main reflections of the diffraction pattern. Investigations of the magnetic behavior of our nanosized material use two different experiments. Both are performed by first cooling the samples from room temperature in zero applied field (ZFC processes) to the temperature of 5 K. Then, hysteresis loops are obtained in a vibrating sample magnetometer in fields up to 90 kOe . Moreover, measurements as a function of the temperature are carried out in a superconducting quantum interference device (SQUID) magnetometer (Quantum design). In this case, after the ZFC process, a field of 100 Oe is applied and the variation of the susceptibility is measured with increasing temperature.

3. Results and discussion

Fig. 1 presents typical results obtained for both samples: a hysteresis loop measured at 5 K for $NiFe_2O_4$ nanoparticles based on smallest mean size (4.3 nm) and the temperature dependence of the susceptibility for our size-sorted $CuFe_2O_4$ nanoparticles. We will first analyze the latter data.

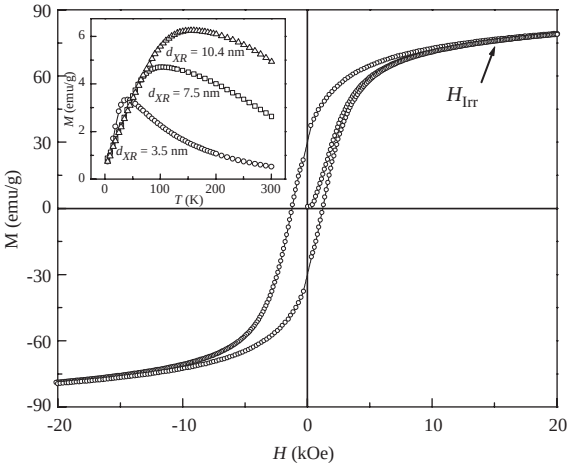

Fig. 1. Hysteresis loop at 5 K of $NiFe_2O_4$ nanoparticles (4.3 nm). The inset displays the thermal variation of the ZFC susceptibility for all $CuFe_2O_4$ samples.

The ferrimagnetic nanoparticles are superparamagnetic [1] and their magnetic behavior can be first described following the Néel model of relaxation [8]. In such a context, each single-domain particle bears a magnetic moment μ that can thermally fluctuate, overcoming the anisotropy energy barrier between the two easy directions. In the presence of very low field and for uniaxial anisotropy, the characteristic time associated to this process is well described by a Néel–Arrhenius law [4] $\tau = \tau_0 \exp(E_A/k_B T)$, where τ_0 is of the order of 10^{-9} s, E_A being the anisotropy energy, T the temperature and k_B the Boltzmann constant. Thus, the outcome of a measurement of magnetic properties depends on the measuring time related to each experimental technique. The blocking temperature T_B is defined as the temperature for which the measuring time is equal to the

relaxation time. For magnetic measurements, $\tau \approx 100\,s$ and then, $E_A \approx 25 k_B T_B$ provides an experimental estimate of the anisotropy energy.

The inset of Fig. 1 indicate a superparamagnetic behavior of $CuFe_2O_4$ nanoparticles. Indeed, when an ensemble of individual particles is frozen without applied field, the magnetic moments are randomly oriented and the resulting magnetization is zero. With increasing temperature, the magnetic moments can fluctuate and then align in the direction of the field, leading to an increase of the total magnetization. Above the blocking temperature superparamagnetic behavior sets in, leading to a decrease of the total magnetization. The presence of a maximum in the ZFC susceptibility curve is therefore associated to the transition between superparamagnetic and blocked behavior. Moreover, the transition is not sharp as a consequence of the size distribution. Our results (see the inset of Fig. 1) evidence that as the nanocrystal mean size increases, the blocking temperature is shifted towards higher temperatures, reflecting as expected, larger anisotropy energy. Similar results are obtained with $NiFe_2O_4$ nanoparticles.

Table 1 lists, for both nanomaterials, the values of the measured blocking temperature and the deduced anisotropy energy. Table 1 also presents the values of the effective magnetic anisotropy constant, calculated by considering that the total anisotropy is proportional to the particle volume, and the value of the resulting surface constant $K_S = K_{eff} d/6$, d being the particle diameter. Both values are extracted using the XRD mean size. It is worth to underline the large values of the effective constant deduced here, especially when compared to the first-order magneto-crystalline anisotropy constant of bulk $CuFe_2O_4$, equal to $2.1 \times 10^4\,Jm^{-3}$ and of bulk $NiFe_2O_4$ equal to $1.1 \times 10^4\,Jm^{-3}$. The one order of magnitude difference between both determinations, associated with the increase of the effective value with decreasing size, constitute a fingerprint of the surface anisotropy domination in the magnetic behavior of the investigated nanoparticles. Moreover, the values found for K_S are in good agreement with values found for maghemite nanoparticles of similar mean sizes [9].

Let us now analyze the typical hysteresis loop presented in Fig. 1 and more specifically the field above which the cycle is reversible (loop closure) H_{irr}. For each sample, this field is determined from similar M vs. H cycles recorded at 5 K and then, H_{irr} is plotted in a double logarithmic representation as a function of the XRD mean size (see Fig. 2). As it can be seen, the values obtained for both kinds of samples, composed of different spinel ferrite material lie on a master curve, a result that therefore supports a common surface structure and is related with the surface treatment done during the chemical synthesis of our nanoparticles. Indeed, measurements of the the surface charge density performed in similar samples of magnetic fluids made of different ferrite nanoparticles strongly support such hypothesis [10]. In a very near future we will explore this behavior using electrochemical experiments. Moreover, a fit using a d^{α} power law would give in double logarithmic plot a straight line of slope α. The full line in Fig. 2 corresponds to the best fit and leads to $\alpha \approx -1$, showing therefore that the irreversibility field is inversely proportional to the reference particle size, a result which indicates surface-related phenomena [11]. Indeed, as in Ref. [11], the irreversibility field is well compared with the effective internal field $H_{eff} = 2E_A/\mu_0\mu$, which maintains the magnetic moment in the easy magnetization direction. Thus, if the anisotropy energy is mainly proportional to a surface contribution, H_{irr} only can scale with $1/d$. Finally, the theoretical model developed in Ref. [4] for 2.5 nm sized $NiFe_2O_4$ particles show that with surface spin disorder, the surface anisotropy results in irreversibility up to more than 10 kOe, a value in excellent agreement with our experimental measurements.

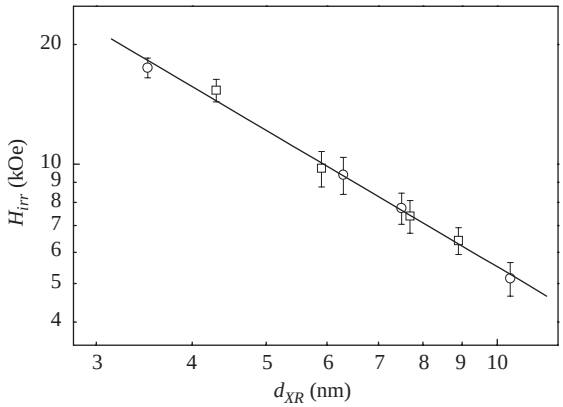

Fig. 2. Mean particle size dependence of the irreversibility field H_{irr}. □: Ni ferrite, ◯: Cu ferrite. Straight line: best double-logarithmic fit (slope = −1).

In conclusion, our experimental determination of the single-domain anisotropy energy and the irreversibility field of Ni and Cu ferrite nanoparticles have provided direct evidence for the importance of surface effects for the magnetic behavior at the nanometric size scale.

Acknowledgments

We acknowledge the Brazilian agencies CNPq, FAPESP, FINATEC and CAPES through the contract of cooperation PROCAD/CAPES no. 0054/01-1.

References

[1] J.F. Deux, C. Riviere, F. Gazeau, J. Roger, E. Allaire, F. Boudghene, J.B. Michel, D. Letourneur, Circulation 108 (17) (2003) 2497.
[2] R. Perzynski, Yu.L. Raikher, in: D. Fiorani (Ed.), Surface Effects in Magnetic Nanoparticles, Kluwer, Dordrecht, to appear in 2004.
[3] P.V. Hendriksen, S. Linderoth, P.A. Lindgard, Phys. Rev. B 48 (1993) 7259.
[4] R.H. Kodama, J. Magn. Magn. Mater. 200 (1999) 359.
[5] M.H. Sousa, F.A. Tourinho, J. Depeyrot, G.J. da Silva, M.C.F.L. Lara, J. Phys. Chem. B 105 (2001) 1168.
[6] M.H. Sousa, Thesis, University of Brasília and University of Paris, 2003.
[7] R. Massart, E. Dubois, V. Cabuil, E. Hasmonay, J. Magn. Magn. Mater. 149 (1995) 1.
[8] L. Néel, Ann. Geophys. 5 (1949) 664.
[9] F. Gazeau, E. Dubois, J.-C. Bracri, F. Boué, A. Cebers, R. Perzynski, Phys. Rev. E 65 (2002) 031403.
[10] A.F.C. Campos, Thesis, University of Brasilia, 2004.
[11] D. Fiorani, A.M. Testa, F. Lucari, F. D'Orazio, H. Romero, Physica B 320 (2002) 122.