Exchange bias properties and surface spins freezing in ferrite nanoparticles of magnetic nanocolloids

F G Silva[1], R Aquino[2],V Dupuis[4], J Depeyrot[1], F A Tourinho[3] and R Perzynski[4]

[1]Complex Fluids Group, Instituto de Física, Universidade de Brasília (DF), Brazil
[2]Complex Fluids Group, Faculdade UnB Planaltina, Universidade de Brasília (DF), Brazil
[3]Complex Fluids Group, Instituto de Química, Universidade de Brasília (DF), Brazil
[4]PECSA, Université Pierre et Marie Curie , Paris, France

E-mail: depeyrot@fis.unb.br

Abstract. We investigate magnetic nanocolloids based on 3.3 nm sized particles of manganese ferrite. The observation of shifted hysteresis loops after cooling the sample in high fields indicates the existence of a coupling between the ferrimagnetic ordered core and the disordered surface layer. The exchange bias field, determined from the field offset from the origin, decreases as the cooling field increases. Zero field cooling measurements of the thermal dependence of the high field magnetization allow separating two contributions. One is associated to the well ordered core and the other is related to surface spins frozen in a disordered spin glass like structure. As the applied field increases the freezing temperature decreases from 23 K to 12 K.

1. Introduction

Nanoscale magnetic particles present unique and striking features which make them suited for a large number of applications in quite a diverse range of fields from engineering to biomedicals [1]. A challenge for these applications is the production of magnetic nanoscale materials with controlled particle size and polydispersion. Indeed the magnetic and magneto-optics properties of ferrite nanoparticles are deeply affected by a complex competition between interface and finite size effects, which arises from the spatial confinement at nanoscale. Much attention has therefore been given to particles with magnetic core/shell structure from both, experimental and theoretical point of view [2]. Although many studies involving core/shell structures consist of a ferromagnetic (FM) core , and an antiferromagnetic (AF) shell, several studies have also been reported on core/shell interfaces involving a ferrimagnetic (FI) structure (FI/AFM, FM/FI) or a spin-glass (SG) [3, 4]. More particularly, exchange bias properties have shown that it does exist exchange coupling between the ordered core spins and the disordered surface ones. In this context, we investigate magnetic nanocolloids designed with nanoparticles based on $MnFe_2O_4$ core protected by γ-Fe_2O_3 shell [5]. Previous investigations of their magnetic properties support the so-called magnetic core-shell model, in which a well-ordered ferrimagnetic structure within the inner region of the particle is surrounded by a surface layer of spins randomly frozen in a spin glass-like manner [6, 7]. The thermal dependence of the magnetization has been characterized by Bloch-like variations of the core and an exponential-like decrease of the surface contribution related to a freezing temperature T_f. Field and size dependencies of this disordered contribution

have been studied by Mössbauer spectroscopy measurements have shown, in the presence of an external field, a progressive spin alignment along the ferrite core. In this context, we will show that the magnetic properties of our investigated nanoparticles are governed by a peculiar balance between exchange interaction and local anisotropy at the shell/core interface.

2. Experimental Details

Magnetic nanocolloids based on $MnFe_2O_4$ are elaborated following basically three fundamental steps. The first step is the nanoparticle hydrothermal coprecipitation which determines their crystallographic structure, mean size and size distribution. After the coprecipitation step the obtained nanoparticles are washed in acidic medium and in order to ensure the thermodynamical stability of the particles the precipitates are boiled with a 0.5 $mol/LFe(NO_3)_3$ solution. In the final step the precipitated is washed in acetone and after evaporating the solvent, the nanoparticles are redispersed in acidic medium. The protective $Fe(NO_3)_3$ treatment provides iron enrichment at the nanoparticle surface resulting in a heterogenic chemical composition. A chemical core/shell model [5] has been recently proposed to deduce the nanoparticle volume fraction (ϕ) from the molar concentration of iron and Manganese ions determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The crystalline structure of the synthesized nanoparticle is determined by X-ray diffraction experiment performed at the Brazilian Synchrotron Light Laboratory (LNLS) using the D12A-XRD1 beam line. The average lattice parameters are calculated from the five ([220], [311], [422], [511] and [440]) most intense diffraction lines appearing between $20 < 2\theta < 130$, while the mean crystalline size d_{XR} is deduced by means of the Scherrer formula applied to the [311] line. The spinel structure (Fd3m space group) is confirmed and the mean size diameter of our $MnFe_2O_4$ ferrite nanoparticle is $3.3nm$.

Magnetization measurements were carried out using a Superconducting Quantum Interference Device (SQUID) magnetometer and a Vibrating Sample Magnetometer (VSM). The Zero field cooling magnetization thermal dependence curves are obtained using applied fields varying between 2 T and 8 T in a temperature range from 5 to 300 K. Hysteresis loops are taken at 5K, in zero field and two different field cooling conditions. Furthermore our magnetic fluid sample is sufficiently diluted, $\phi = 1,5\%$ to consider the colloidal dispersion as a gas of individual particles.

3. Results and Discussion

Figure 1 displays the amplified hysteresis region of 5K magnetization loops obtained after zero field and field cooling processes. The squareness of the zero field curve indicates a typical disordered and frustrated system, since for coherent reversal of ordered core spins the hysteresis loop would be a perfect square [2]. Thus, it is the progressive alignment of surface spins along the field direction that dominates the reversal behavior of the particle moment. When the sample is cooled in the presence of 1T field the hysteresis loop is left shifted showing a negative exchange bias related to the coupling between the ferrimagnetic ordered core and the disordered surface layer. The inset of Figure 1 presents the magnified left branch of the hysteresis cycles and allow to determine the exchange bias field value, through $H_{ex} = -(H_{rigth} + H_{left})/2$, H_{rigth} and H_{left} being the points where the loop intersects the field axis. The reversal of the surface spins triggers the reversal of the core and the exchange bias field is then quantitatively related to the net local exchange fields of the interfacial shell spins that act on the particle core. This exchange bias phenomenon is expected to depend on the strength of the cooling field H_{cool} [8]. First, for low cooling field values, the exchange bias field increases when H_{cool} increases due to the enhancement in the alignment degree of the core spins. For higher cooling field values the Zeeman coupling between the field and surface spins increases until dominating the magnetic interactions inside the particles, then leading to a decrease of the exchange bias field. The

presence of the maximum in the H_{ex} variations is considered as an effective depinning threshold above which magnetic interactions are overcome by the Zeeman coupling [9]. Figure 2 illustrates this higher field behavior: we observe a decrease of the shift of the hysteresis as the cooling field increases from 1 to 5 T.
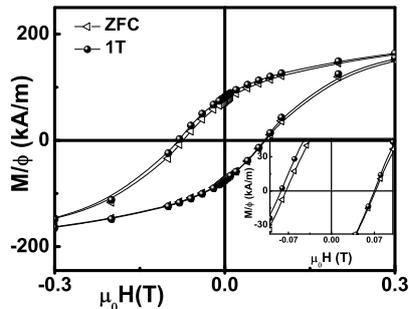

Figure 1. ZFC and FC (1T) hysteresis loop. The inset displays the exchange bias field.
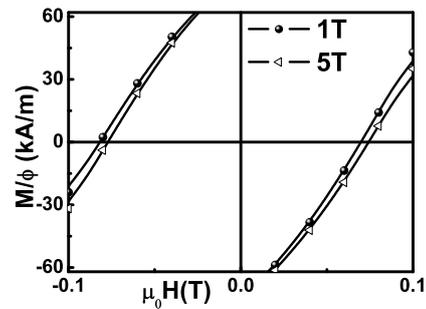

Figure 2. Shift of the hysteresis loop under two cooling field conditions.

Recent results of in-field Mössbauer spectroscopy, obtained with nanoparticles of magnetic nanocolloids based on nickel ferrite, enlighten the magnetometry measurements presented here [10]. Indeed, field and size dependencies of the disordered contribution have been extracted from spectra and show a progressive alignment of the surface spins along those of the ferrite core. As the external field increases, both the thickness of the disordered surface layer and the mean canting angle decreases. Then, for larger field strength, the volume fraction of misaligned spins is smaller and the volume fraction of ordered core spins is larger. As an example, when the external field strength increases from 2 T to 8 T, the fraction of canted spins decreases from approximately 70 % to 45 %. Hence, the exchange coupling is expected to be smaller for high cooling field values since the surface disorder is less pronounced.

ZFC magnetization measurements of the magnetization temperature dependence of "gas-like" diluted dispersions of independent nanoparticles allow separating the core and surface contributions. Figure 3 presents the high field magnetization obtained at $\mu_0 H = 2T$ and $\mu_0 H = 8T$ as a function of the temperature. In both cases, we can describe the thermal variations of the magnetization according to the following equation [6, 11]:

$$m(T) = m(0)[1 - BT^{\alpha}] + \triangle m(T). \tag{1}$$

At high temperatures, the smooth variations are well reproduced by the first term which corresponds to a modified Bloch's law accounting for the thermal dependence of the core contribution. The exponent α, determined as in reference [6] by fitting a log-log representation of $m(0) - m(T)$, is found to be approximately equals to 2. This large value, compared to the 3/2 bulk reference, is attributed to the spatial confinement at nanoscale which modifies the magnetization decrease caused by thermal excitation of spin waves in the magnetically ordered particle core [12]. It is therefore expected to be independent on the field strength. m(0) is the magnetization as T tends to zero and is found to be 230 kA/m and 310 kA/m for $\mu_0 H = 2T$ and $\mu_0 H = 8T$ respectively. This result could also be associated to finite size effects since at large field, the volume fraction of ordered core spins would also be larger.

At low temperatures, the magnetization variations are dominated by the progressive freezing of disordered surface spins. This is characterized by the steep upturn of the magnetization

thermal variation observed at temperatures lower than 70 K. Whatever the field strength, the surface contribution to the total magnetization $\triangle m(T)$ is well accounted for a reduced exponential behavior $\triangle m(T) \propto \exp^{-T/T_f}$. The inset of Figure 3 displays the thermal variations of the surface magnetization normalized to its value at 5 K. The fitting procedure allows the determination of the freezing temperature T_f.
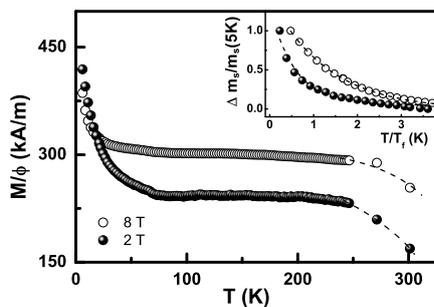

Figure 3. Temperature dependence of the high-field magnetization. The inset shows the reduced exponential behavior of the surface contribution.
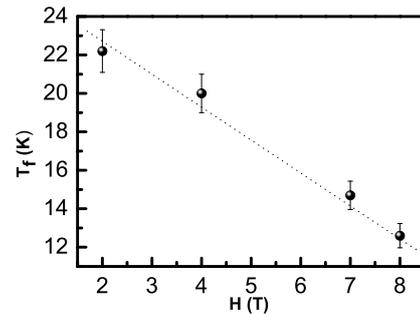

Figure 4. Freezing temperature as a function of the applied field.

Figure 4 indicates that the deduced values of T_f decreases with increasing applied fields. It shows that the energy $k_B T_f$, intimately related to the superexchange interactions which pin the interacting spins in the frozen disordered layer, is smaller for large applied field. That well agrees with a smaller exchange bias field for larger cooling field and the observed progressive alignment of the surface spins along their core counterparts. It therefore suggests a delicate balance between exchange interaction and local anisotropy at the shell-core interface.

In summary, we have shown that the field Cooling hysteresis loop of magnetic nanocolloid present a negative exchange bias which depends on the cooling field strength. It is associated to an exchange coupling the ferrimagnetic ordered core and disordered surface layer spin-glass like. The thermal dependence of the magnetization is well accounted by the sum of two contributions; the hight temperature region is dominated by the core variation modified due to finite size effects. The low temperature contribution reflects the freezing of surface spins and is well described by a reduced exponential behavior with a freezing temperature T_f, which decreases as the applied field increase.

3.1. Acknowledgments

References

[1] Elaissari E 2008 *Colloidal Nanoparticles in Biotechnology* (Oxford: John Wiley and Sons)
[2] Labarta A, Batlle X and Iglesias O From finite-size and surface effects to glassy behaviour in ferrimagnetic nanoparticles *Surface Effects in Magnetic Nanoparticles* pp 105–137
[3] Salazar-Alvarez G, Sort J, Surinach S, Baro M D and Nogues J 2007 *Journal of the American Chemical Society* **129** 9102–9108
[4] Eftaxias E, Vasilakaki M and Trohidou K N 2007 *Modern Physics Letters B* **21** 1169–1177
[5] Gomes J A, Sousa M H, Tourinho F A, Aquino R, Silva G J, Depeyrot J, Dubois E and Perzynski R 2008 *The Journal of Physical Chemistry C* **112** 6220–6227
[6] Aquino R, Depeyrot J, Sousa M H, Tourinho F A, Dubois E and Perzynski R 2005 *Phys. Rev. B* **72** 184435
[7] Alves C R, Aquino R, Depeyrot J, Cotta T A P, Sousa M H, Tourinho F A, Rechenberg H R and Goya G F 2006 *Journal of Applied Physics* **99** 08M905

[8] Vasilakaki M and Trohidou K N 2009 *Physical Review B* **79** 144402

[9] Del Bianco L, Fiorani D, Testa A M, Bonetti E and Signorini L 2004 *Phys. Rev. B* **70** 052401

[10] Rechenberg H R, Sousa E C, Depeyrot J, Sousa M H, Aquino R, Tourinho F A and Perzynski R 2008 *Hyperfine Interactions* **184** 9–14

[11] Shendruk T N, Desautels R D, Southern B W and van Lierop J 2007 *Nanotechnology* **18** 455704 (6pp)

[12] Linderoth S, Balcells L, Labarta A, Tejada J, Hendriksen P V and Sethi S A 1993 *Journal of Magnetism and Magnetic Materials* **124** 269–276