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Exchange Bias Properties and Surface Spin Freezing in Magnetic Nanoparticles

F. G. Silva[a], R. Aquino[b,*], J. Depeyrot[a], F. A. Tourinho[c], V. Dupuis[d], R. Perzynski[d]

[a]*Complex Fluids Group, Instituto de Física, Postal box 04455, 70919-970, Brasília-DF ,Brazil*
[b]*Complex Fluids Group, Faculdade UnB Planaltina, Postal box 04455, 70919-970, Brasília-DF ,Brazil*
[c]*Complex Fluids Group, Insituto de Quimica, Postal box 04455, 70919-970, Brasília-DF ,Brazil*
[d]*PECSA, Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France*

Abstract

ZFC and FC magnetization measurements versus field are carried out on manganese ferrite based nanoparticles with a mean diameter of 3.3 nm. The exchange bias field determined from the field shift of hysteresis loops, decreases as the cooling field increases. Magnetization measurements performed at constant applied field H as a function of temperature allows us to separate two H-dependent contributions. One is associated to the well ordered core which inflates as the field increases and the other is related to surface spins frozen in a disordered structure. The thermal dependence of this disordered surface contribution decreases exponentially with a freezing temperature T_f, which decreases as the applied field increases.

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1. Introduction

Magnetic Nanoparticles (NP's) have been the target of research for many years from both, theoretical and experimental points of view. This interest is mainly due to their unique and striking features, which make them suitable for a large range of applications [1,2]. In particular much attention has been given to NP's with a magnetic core/shell structure because of their finite-size and surface effects [3]. In previous studies [4,5,6], the manganese ferrite NP's studied here, as the NP's based on other ferrites have been shown to have a "core-shell" magnetic structure. It consists of a well-ordered ferrimagnetic core surrounded by a surface layer of spins randomly frozen in a spin glass-like manner. Field and size dependencies of this disordered contribution have been studied by Mössbauer spectroscopy. These studies have shown a progressive spin alignment along the ferrite core [6], quantifying the under-field variations of the shell thickness and the unidirectional exchange through the core-shell

* Corresponding author. Tel.:+55-61-33072900; fax +55-61-33072900.
E-mail address: reaquino@unb.br.

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interface with a constant K_{Ea}=2.5x10^{-4} J/m^2, which is close to the one expected for a ferromagnetic/ antiferromagnetic (FM/AFM) interface.

This exchange coupling between the ordered core and the disordered surface let suspect exchange bias properties for these manganese ferrite NP's as - for core/shell nanoparticles consisting of a FM core/AFM shell, or - at core/shell interfaces involving either a ferrimagnetic (FI) structure (FI/AFM, FM/FI) or a spin-glass one [7,8].

In this context, we present here magnetization measurements under different cooling field conditions, in order to probe the exchange bias properties of our NP's and the thermal evolution of their magnetic surface contribution, which is deduced from high field magnetization.

2. Experiment

The $MnFe_2O_4$ based NP´s are prepared by hydrothermal coprecipitation and then, dispersed in acid medium, thanks to a surface treatment which provides iron enrichment at the nanoparticle surface. A chemical core/shell model allows deducing the nanoparticle volume fraction [9]. The crystalline structure, as well as the mean diameter (3.3 nm), are determined from X-ray diffraction patterns.

Previous under-field Mössbauer measurements performed on $NiFe_2O_4$ based NP´s show that the fraction of disordered spins decreases while the applied field increases [5]. A possible interpretation is a shift-out of the core-shell interface due to the gradual alignment of the spins in the shell along the applied field and thus along the core direction. A linear extrapolation of these data shows that the complete alignment of spins would require a field around 60 T for nickel ferrite NP's of similar mean size when compared to the 3.3 nm NP's as studied here [5]. In this paper, magnetization measurements are carried out using both SQUID and VSM devices. The thermal dependence of Zero Field Cooling (ZFC) magnetization is obtained from 5 to 300 K under an applied field varying between 2 T and 8 T. ZFC and FC (Field Cooled) hysteresis loops are taken at 5K, with two different FC conditions. Our magnetic fluid sample is diluted enough and presents the structure of a gas of individual particles at room temperature [10], structure which is frozen-in by the temperature quench of the sample in the SQUID or in the VSM.

3. Results and Discussion

The shape of the ZFC magnetization loop (see figure 1a) corresponds to a typical disordered and frustrated system. Indeed for coherent reversal of ordered core spins the hysteresis loop would be a perfect square [3]. 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 (see figure 1b). Figure 1(b) presents a magnification of the hysteresis loop around the coercitive fields and allow to determine the exchange bias field value, through $H_{ex}=(H_{right}+H_{left})/2$ H_{right} and H_{left} being the points where the loop intersects the field axis. The Exchange Bias fields (in absolute values) are $\mu_0 H_{ex}$=6x10^{-3} T and $\mu_0 H_{ex}$= 1,1x10^{-3} T for cooling field, $\mu_0 H_{cool}$= 1 and 5 T respectively. This exchange bias phenomenon is expected to depend on the strength of the cooling field H_{cool}. For low cooling field values, the exchange bias field first 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 a maximum in the H_{ex} variations is usually considered as an effective depinning threshold, above which magnetic interactions are overcome by the Zeeman coupling [11]. Figure 1(b) illustrates this higher field behavior as we observe a decrease of the hysteresis shift when the cooling field increases from 1 to 5 T.

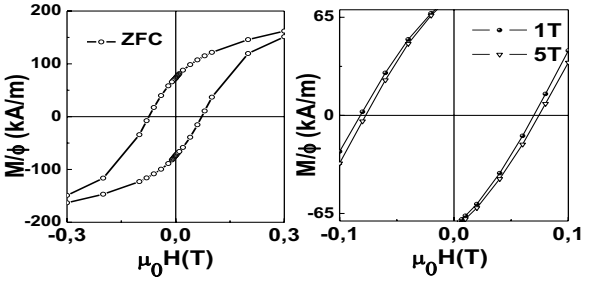

FIG. 1: (a) ZFC and FC (1T) hysteresis loop. (b) Shift of the hysteresis loop under two cooling field conditions.

ZFC magnetization measurements of the magnetization temperature dependence of "gas-like" diluted dispersions of independent nanoparticles allow separating the core and surface contributions. Figure 2 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 [4, 12] written at constant H:

$$m(T) = m(0)\left[1 - BT^{\alpha}\right] + \Delta m(T) \qquad (1)$$

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 4 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 in these 3.3 nm NP's. The confinement modifies the magnetization decrease caused by thermal excitation of spin waves in the magnetically ordered particle core [13]. This core contribution is therefore expected to be independent on the field strength. However a core magnetization m(0) as T tends to zero is found to be 230 kA/m at $\mu_0 H = 2T$ and 310 kA/m at $\mu_0 H = 8T$. The relative increase $\Delta m(0)/m(0)$ could be associated to a reduction $\Delta e = d_{RX}\Delta m(0)/6m(0)$ of the shell thickness of the order of 0.17 nm, in quantitative agreement with the under-field Mössbauer measurements of [5] on Ni ferrite nanoparticles of comparable size. It should thus be ascribed to a core inflation as the field increases.

At low temperatures, the magnetization variations m(T) at constant H 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 Δm(T) is well accounted for by a reduced exponential behavior $\Delta m(T) \propto \exp\left(-T/T_F\right)$ [4]. The inset of Figure 2 shows that the thermal variations of the surface magnetization normalized to its value at 5 K also depends on the field strength, while keeping the same exponential shape with a field-dependent T_f.

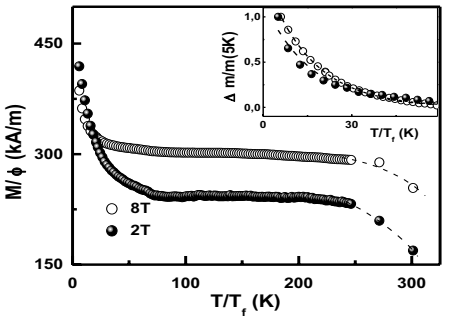

FIG. 2: High Field Magnetization Thermal Dependence, the inset shows the reduced exponential behavior of surface contribution for the magnetization at 2T and 8T.

The fitted values of the freezing temperature T_f decrease, from 22 K to 12 K, while increasing $\mu_0 H$ from 2 to 8T. 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 core-shell interface.

4. Conclusion

We have shown that the FC hysteresis loop of magnetic nanocolloid presents a negative exchange bias which decreases (in high fields) as the cooling field increases. This behavior is associated to the alignment along the field direction of disordered surface spins. The thermal variations of the magnetization are also field-dependent. At high temperatures, the modified Bloch law is well followed using a magnetization $m(0)$ which decreases as H decreases, associated to a reduction of the shell thickness. The low temperature contribution reflects the freezing of surface spins and is well described with a freezing temperature T_f, decreasing as H increases.

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