Spin-glass-like characteristics of extremely small $\gamma$-Fe$_2$O$_3$ nanoparticles

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Abstract. Magnetic measurements on small $\gamma$-Fe$_2$O$_3$ particles (diameter $D \sim 3$nm) have been carried out. Features in the zero-field-cooled and field-cooled magnetization data and the high-field irreversibility in the low-temperature hysteresis curve are found to be consistent with a collective thermal blocking process. The dynamical properties, studied by ac magnetic susceptibility measurements, suggest the occurrence of a spin-glass like transition with a critical exponent $\nu = 8.0 \pm 0.8$. This finding is also supported by the $H^{2/3}$-dependence of the temperature transition ($T_g$) which is consistent with the Almeida-Thouless critical line $(3/2 \sim H^{2/3})$ of canonical spin glasses.

1. Introduction
Maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticles represent an interesting material platform for many areas of science and technology [1]. Hence, the fine control of the size-dependent magnetic properties of the nanosized component is of great importance to achieve desired properties for a specific application.

In comparison with the bulk counterpart, it is well known that small magnetic particles show peculiar features such as reduced saturation magnetization, no saturating behaviour in a rather high fields, and irreversibility. These are usually attributed to the random canting of the spins at the particle surface [2]. Moreover, the occurrence of surface structural defects and the incomplete coordination of superficial metal-ions are determinant for the magnetic behaviour of small magnetic particles [3]. Concentrated composite samples containing relatively large $\gamma$-Fe$_2$O$_3$ particles (mean size $\sim 10$nm) have been reported to show a superspin-glass behaviour [4]. Characteristic static and dynamic features of spin-glass behaviour with reasonable critical exponents have been determined close to the temperature of the superspin-glass transition in such nanoparticles [4]. In the present work, the magnetic properties of small $\gamma$-Fe$_2$O$_3$ nanoparticles (mean size $\sim 3$nm) are reported and the possibility of a transition to a spin-glass phase is discussed based on ac susceptibility measurements.

2. Experimental details
The $\gamma$-Fe$_2$O$_3$ nanoparticles were synthesized by the chemical co-precipitation method. The nanoparticles used in this work were not embedded in any template. The phase formation and the average size (~3nm) of the particles were determined from X-ray diffraction and electron microscopy data. Details of the synthesis route and structural characterization will be published elsewhere. The magnetic properties of these $\gamma$-Fe$_2$O$_3$ nanoparticles were studied by ac and dc magnetization measurements using a commercial PPMS system (VSM and ACMS options) in the range of temperatures from 5 to 320K and magnetic fields up to 90 kOe.

3. Results and discussion

Figure 1 shows the temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves. In the high temperature-region both curves show the typical Curie-Weiss behaviour. However, when the temperature is decreased, a clear separation between both curves is observed, starting at ~230K. At $T_{\text{max}}$=99K the ZFC curve shows a maximum while the FC curve keeps growing up to the maximum at $T_2$=68K, decreasing slightly below this temperature, as shown in the inset of Figure 1. The slight decrease observed in the FC curve is characteristic of spin glass systems.

![Figure 1](image_url)

**Figure 1.** Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves obtained with magnetic field $H=20$ Oe for the $\gamma$-Fe$_2$O$_3$ nanoparticles. The inset shows the slight decrease of the FC curve.

Magnetization (M) vs. field (H) curves obtained at 5K and 300K are shown in figure 2. The curve obtained at 5K shows hysteresis behaviour (irreversibility) which survives in applied fields up to ~50 kOe, but the 300K-curve does not show any hysteresis. The feature observed for the high-temperature curve is expected since at temperatures well above $T_{\text{max}}$ the system must be in the superparamagnetic state. However, for temperatures below $T_{\text{max}}$ the irreversibility may be associated with the blocking process of the magnetic particles and therefore irreversibility must survive until the applied field surpasses the anisotropy field (around the value of the coercive field $H_c$~840 Oe at $T=5K$). However, from our data the irreversibility remains up to the field ~50kOe as observed in the 5K-curve. On the other hand, both curves show a steady increase of the magnetization in the high magnetic field region, consistent with a disordered spin state. Saturation magnetization ($M_s$) of 32 emu/g for $T=5K$ can be estimated using the law of approach to magnetic saturation [6]. This saturation magnetization value is smaller than the value expected for bulk $\gamma$-Fe$_2$O$_3$ (~80 emu/g) [2] and suggests the occurrence of disordered spin states. These features are size-dependent since saturation value of ~80emu/g with no high-field irreversibility was determined for $\gamma$-Fe$_2$O$_3$ particles of ~10nm (data not shown here).
In order to additionally characterize the dynamic nature of the observed disordered spin behaviour, ac susceptibility (χ) measurements were carried out. Figure 3 shows the thermal dependence of the in-phase component (χ′) obtained at various excitation frequencies (ω). χ′ vs. T curves show a broad maximum whose broadening is thought to be related to the natural dispersion of grain size distribution. The maximum position shifts to higher temperatures as the frequency is increased. Similar features are observed in the out-of-phase component (χ″). The thermal relaxation of the magnetic particles can be described by the Arrhenius law: \( \tau = \tau_0 \exp(E_a/k_B T) \), where \( \tau \) is the relaxation time, \( \tau_0 \) is the characteristic time (usually in the range \( \sim 10^{-9} - 10^{-13} \) s), and \( E_a \) is the energy barrier. Assuming the temperature of the χ′ maximum, as the temperature representing the onset of the freezing process (T_g(ω)) a good linearity is obtained in the ln(ω) vs. 1/T_g plot, but generating an unphysical value for \( \tau_0 \sim 10^{-20} \) s. This result suggests that the relevant activation energy is temperature dependent, as expected for strongly interacting particles [7]. In order to test the existence of a spin-glass transition the critical slowing down law given by: \( \nu \omega \tau^{z} T_{g}^{-1/3} \), where \( z \) is the dynamical critical exponent and \( \nu \) is the critical exponent related to the correlation length, has been used in our analysis. A good linearity is obtained in the log-log plot as shown the inset of Fig. 3 which provides \( z \nu = 8.0 \pm 0.8 \). This value is consistent with that the value expected for atomic spin glasses [8] and for strongly interacting γ-Fe_2O_3 particles with mean size of D~9nm [4]. The claimed spin-glass transition is additionally corroborated by the relative variation of T_g per frequency decade, \( (\Delta T_g / T_g) / \Delta \log(\omega) \sim 6 \times 10^{-5} \), falling in the range of values of well known spin glasses, such as (Eu_{0.6}Sr_{0.4})S [5].

The effect of the DC magnetic field (H) upon the cusp position of χ′ has been also studied. The cusp position shows a shift to lower temperatures as the field strength increases (data not shown here), indicating that the onset of the spin-glass state decreases as H is increased. A careful data analysis indicates that T_g(ω) follows an H^{2/3}-dependence in the low-field region (H<500 Oe). This dependence corresponds to the de Almeida Thouless-line [9] and evidences the existence of a spin-glass phase for T<T_g. A spin-glass like state was reported for 9-10nm γ-Fe_2O_3 nanoparticles [4,10], whose origin has been assigned to the formation of a magnetically frustrated surface layer favored by the broken chemical bounds and symmetry lattice breaking. Reports on γ-Fe_2O_3 nanoparticles with a mean size of D~8nm indicate a thickness of the surface layer of d~1 nm [3] and that layer increases in thickness as the particle size decreases. Considering a surface layer thickness around d~1nm for our sample, the
spin disorder might extend throughout the whole nanoparticle volume, in which case the spin-glass like behavior is associated with the magnetic frustration of spins in the whole nanoparticle.

Figure 3. In-phase component of the ac susceptibility as a function of the temperature varying the excitation frequency. The inset shows the log-log plot of the critical slowing down law.

4. Conclusions
Small $\gamma$-Fe$_2$O$_3$ nanoparticles (with D~3nm) are found to show high-field irreversibility in the hysteresis curve at low temperatures. The cusp of the ZFC and the feature observed in the low-temperature part of the FC curve suggest the occurrence of a collective blocking process in the system. The frequency dependence of the cusp observed in the $\chi'$ vs. T curve provides a critical exponent $\nu = 8.0\pm0.8$, consistent with a spin-glass like phase for $T<T_g$. This result is additionally supported by the $H^{-2/3}$ dependence of the temperature transition ($T_g$) which is consistent with the AT-critical line.

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