Memory effects and magnetic interactions in a γ-Fe_2O_3 nanoparticle system

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The low-temperature dynamics of a magnetic nanoparticle system (γ-Fe_2O_3—alginate nanocomposite with average particle size around 4 nm) have been studied by superconducting quantum interference device measurements. Using different temperature and field protocols, memory phenomena in the dc magnetization and magnetic relaxation have been observed at temperatures below its blocking temperature T_B=37 K. However, aging experiments show an absence of any waiting time dependence in the magnetization relaxation. These observations indicate that the dynamics of this nanoparticle system are governed by a wide distribution of particle relaxation times which arise from the distribution of particle sizes and weak interparticle interactions. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1853898]

INTRODUCTION

The dynamics of magnetic nanoparticles systems has been a subject of considerable interest for the last several decades.[1] For a noninteracting assembly of single domain magnetic nanoparticles the Néel–Brown theory[2,3] predicts that each particle (superparamagnetic) moment thermally fluctuates between its easy magnetic anisotropy axes with a characteristics relaxation time τ being dependent upon the magnetic anisotropy, the particle size, the temperature, and applied magnetic field. The relaxation time increases with decreasing temperature and eventually becomes equal to the measuring time t_m at the blocking temperature T_B where the moment freezes. Even though these "freezing" processes are no longer independent when interparticle interactions are present, the dynamical properties are frequently described within this superparamagnetic model, and especially if the interactions are weak. When the interactions are sufficiently strong, there is a possibility of collective spin-glass-like behavior in random interacting systems or even long-range magnetic ordering. Observations of critical slowing down,[4] a divergent behavior of the nonlinear susceptibility,[5] aging, and relaxation in the low-frequency ac susceptibility[6] have been cited as evidence for distinguishing between archetypal spin-glass behavior and simple superparamagnetic relaxation phenomena.

In a recent paper Sun *et al.*[7] reported observing memory effects in the dc magnetization and the magnetic relaxation of an interacting magnetic nanoparticle system ($Ni_{81}Fe_{19}$). Furthermore, the authors indicate that the observed memory effects were consistent with the existence of a low-temperature spin-glass phase. In this paper analogous experiments were performed on a system of very weakly interacting γ-Fe_2O_3 nanoparticles and similar memory effects were observed. Only the absence of any aging effect in the dc magnetization on this nanoparticles system appears to distinguish its properties from the characteristics of spin glasses.

EXPERIMENTAL DETAILS

The samples used in the experiments were prepared by using cross-linked gels of alginic acid.[8] This technique allows gels to be prepared containing different amounts of iron oxide. X-ray powder diffraction patterns on the samples indicated that the synthesized magnetic nanoparticles are single phase with an average particle size of 4 nm. dc magnetization measurements were performed using a quantum design model MPMS-5S SQUID (SQUID—superconducting quantum interference device) magnetometer from 5 to 300 K.

The saturated magnetic moment at 5 K, obtained by extrapolation to $1/H=0$, was 22 emu/g. Since the saturation magnetization of bulk γ-Fe_2O_3 is 87.4 emu/g,[9] the volume concentration of particles is about 7%, which could lead to potential interparticle interactions.

RESULTS AND DISCUSSION

The field-cooled (FC) and zero-field-cooled (ZFC) magnetizations were measured as a function of temperature (5–300 K) and magnetic field (1–5000 Oe). Figure 1 shows the temperature dependence of the magnetization $M(T)$ for the sample of γ-Fe_2O_3 nanoparticles taken in ZFC and FC

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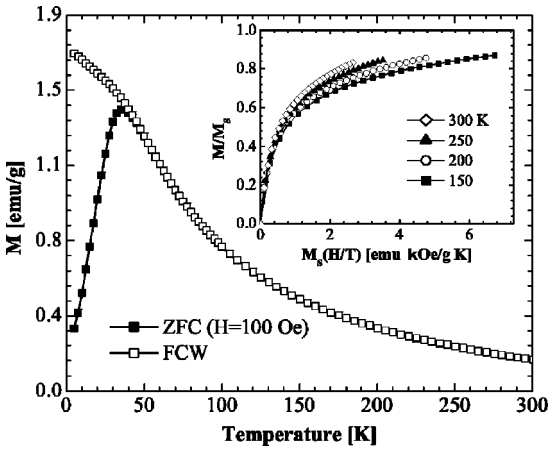

FIG. 1. Zero-field cooled (ZFC) and field-cooled (FC) magnetizations upon warming in a magnetic field of 100 Oe. The inset displays the reduced magnetization M/M_s vs $M_s(H/T)$ at high temperatures $T=150$, 200, 250, and 300 K.

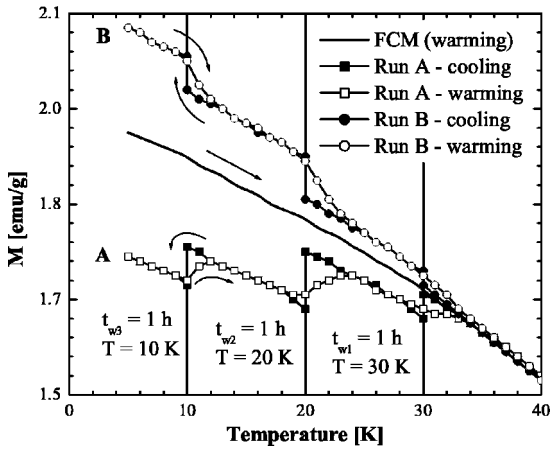

FIG. 2. The FC magnetization vs temperature with intermittent stops at $T=30$, 20, and 10 K during cooling. Run *A* was measured for $H=100$ Oe with the field reduced to 0 Oe at each stop. Run *B* was measured for $H=100$ Oe with the field increased to 200 Oe at each stop. The solid symbols were measured during cooling with the intermittent stops of 1 h while the open symbols are measured during continuous heating. The solid line is the FC magnetization without any stops during warming.

conditions at a magnetic field $H=100$ Oe. The curves exhibit the main features of a superparamagnetic system: the ZFC curve has a characteristic maximum at the blocking temperature $T_B=37$ K and paramagnetic behavior above T_B, while the FC curve below T_B continues to increase with decreasing temperature. The superparamagnetic behavior of the sample was confirmed by the magnetic hysteresis measurements (the inset to Fig. 1). Above the blocking temperature the $M(H)$ curves are described by the Langevin function with a log-normal size distribution of nanoparticles[10] of mean diameter $D_{vm}=3.4$ nm (300 K) and standard deviation $\sigma=0.42$. However, the superparamagnetic scaling law $M\sim H/T$ was not strictly followed, which is consistent with a weakly interacting system of nanoparticles. Below T_B the system exhibits hysteretic behavior characteristic of a freezing of the nanoparticle magnetic moments.

The dynamics of the FC magnetization in this nanoparticle system were studied following the approach used by Sun *et al.*[7] The sample was cooled in $H=100$ Oe from 200 K down to 5 K at a constant cooling rate of 1 K/min; the magnetization was then measured during warming and is shown in Fig. 2 as the reference curve. The sample was subsequently cooled again at the same rate and the magnetization was recorded during the cooling, but now with stops at $T=30$, 20, and 10 K for identical waiting times $t_w=1$ h (run *A*). The magnetic field was turned off at the beginning of the stop and then set again to 100 Oe at the end of the waiting time before the cooling process resumed. The cooling curve is shown in Fig. 2 as solid squares. After reaching the lowest temperature of 5 K, the sample was reheated at the rate of 1 K/min in $H=100$ Oe and the magnetization was recorded again (open squares). The system remembered its thermal history and demonstrated a memory effect as the warming curve exhibits magnetization steps at 10 K, 20 K, and 30 K, identical temperatures where the system was intermittently stopped during the cooling process. In the second run B, the sample was cooled in $H=100$ Oe with stops at $T=30$, 20, and 10 K for the same waiting times $t_w=1$ h, but the magnetic field was increased from 100 to 200 Oe during the stops (solid circles) and then decreased back to 100 Oe after the waiting time. This cooling process produced magnetization steps in the opposite directions in the magnetization curve as compared to run *A*. The magnetization recorded during the reheating process shown as open circles in Fig. 2 exhibits the steplike structure as well.

The effects of temperature and field change on the time evolution of the ZFC and thermoremanent magnetization (TRM) were also studied using the protocols from Ref. 7. In the ZFC relaxation measurements the sample was cooled down to $T=15$ K in $H=0$. After applying a magnetic field $H=100$ Oe the relaxation of the magnetization was recorded for a time period $t_1=4000$ s. The sample was then cooled down to $T=10$ K in the same magnetic field and the magnetization was measured for another 4000 s time period t_2. Finally the sample was heated back to $T=15$ K and the magnetization was measured for a time period t_3 (=4000 s). This entire relaxation measurement is displayed in Fig. 3(a). The initial logarithmic increase in the magnetization observed at 15 K almost stops during the temporary cooling to 10 K, and then the magnetization continues to increase after returning to 15 K. The inset in Fig. 3(a) indicates that the relaxation process during t_3 is essentially a continuation of the process during t_1. A similar resumption in the relaxation of the ZFC magnetization occurred at 15 K after reducing the field from 100 Oe to 0 Oe during t_2 of the temporary cooling to 10 K and then increasing the field to 100 Oe and heating the sample back to 15 K (not shown).

Memory effects were also observed for the field-cooled process by measuring the time evolution of TRM. Figure 3(b) shows the TRM as a function of time at 15 K for a time t_1, cooling to 10 K for t_2, and then returning to 15 K. Again the magnetization essentially resumes its logarithmic relaxation as seen in the inset. It should be further noted that these memory effects in the magnetic relaxation have only been observed after a temporary cooling and not after a temporary heating (figure not shown), similar to the results reported by Sun *et al.*[7] on an interacting nanoparticle system.

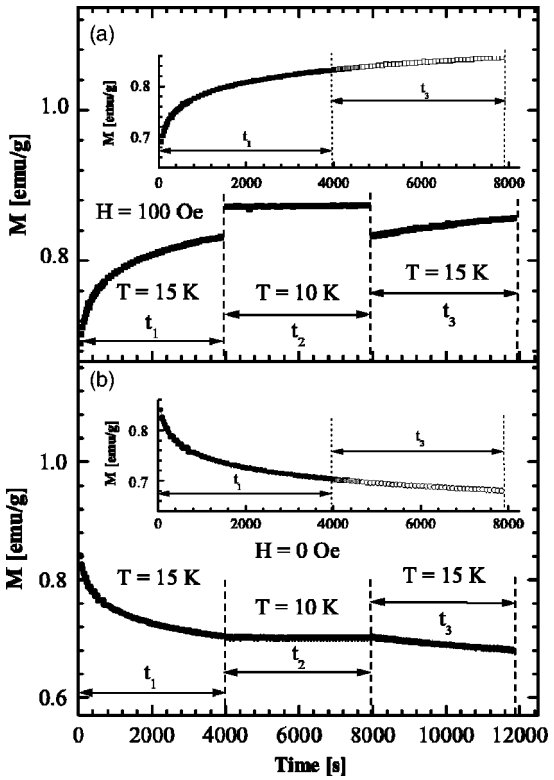

FIG. 3. (a) The ZFC magnetic relaxation measurement at 15 K with a decrease in the temperature to 10 K for 4000 s. (b) The TRM relaxation measurement at 15 K with a decrease in the temperature to 10 K for 4000 s. The insets show the data as a function of total time spent at $T=15$ K.

The observed memory effects on the interacting nanoparticles system[7] were thought initially to be solely a characteristic of spin glasses and the asymmetric response with respect to negative/positive temperature change consistent with the hierarchical model of the spin-glass phase.[11] It has since been shown[12] that such memory effects are also present in superparamagnetic systems and can even be reproduced by using only a model of *isolated* nanoparticles with a temperature-dependent distribution of relaxation times. Moreover, the dynamics of archetypal spin-glass systems are generally characterized by an "aging" dependent behavior, i.e., the ZFC (and TRM) magnetic relaxation is dependent upon the time elapsed after the system was quenched.[13,14] In such experiments the sample is first cooled to a temperature below the spin-glass transition temperature. Then after a waiting time t_w, a dc field is applied (or cutoff) and the time evolution of magnetization is recorded. The relaxation for a spin-glass system exhibits a clear dependence on the waiting time t_w as the relaxation for systems with infinite equilibration times must scale with the only relevant time scale in the experiment, the waiting time t_w. However, no such waiting time dependence was measurable in the ZFC and TRM magnetic relaxations on our γ-Fe_2O_3 nanoparticle system. Neither were any memory effects detectable with a stop during cooling in zero field, which is another characteristic found in spin-glass systems.[15] Instead, the relaxation effects in the γ-Fe_2O_3 nanoparticle system appear to be controlled simply by thermally activated dynamics of individual superparamagnetic particles. This has been subsequently confirmed[16] by using a simple bistable model with a broad distribution of particle sizes (similar to the approach of Ref. 12) to study the dynamics of this system. Indeed, most of experimentally observed memory effects are qualitatively reproduced including the absence of a waiting time dependence. Thus, the dynamics of noninteracting or weakly interacting magnetic nanoparticles can be distinguished from genuine spin-glass behavior by selecting the appropriate protocols by including aging-dependent studies in the ZFC magnetization process.

In summary, using different temperature and field protocols, memory effects in the dc magnetization and magnetic relaxation similar to those observed in spin-glass systems have been observed in weakly interacting system of γ-Fe_2O_3 nanoparticles at temperatures below its blocking temperature. However, aging experiments show an absence of any waiting time dependence in the magnetization relaxation due to a field change after field cooling or zero-field cooling processes. This observation discriminates the dynamics of our nanoparticle system from the behavior of a classical spin glass, where frustration and disorder lead to an aging dependence of the system's magnetic response. Moreover, the dynamics of this nanoparticle system are consistent with the dynamical properties expected from a wide distribution of particle relaxation times arising from a broad distribution of particle sizes.

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