

Memory Effects in an Interacting Magnetic Nanoparticle System

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We have performed a series of measurements to study the low temperature dynamics of an interacting magnetic nanoparticle system. The results obtained demonstrate striking memory effects in the dc magnetization and magnetic relaxation that support the existence of a spin-glass-like phase in interacting magnetic nanoparticles. Moreover, we observe an asymmetric response with respect to temperature change that supports a hierarchical picture, rather than the droplet model discussed in other works on nanoparticle systems.

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Magnetic nanoparticles have attracted considerable interest due to their significance in technological applications as well as for the fundamental physics [1–3]. The isolated noninteracting magnetic nanoparticle is known to behave as a giant spin and its dynamics are described by “superparamagnetism” [4]. One important and more practical subject concerns the behavior of an assembly of magnetic nanoparticles, which is in general a disordered system with random anisotropy and competing interparticle interactions. When the interparticle interactions become significant such systems may have a rich variety of magnetic configurations resulting from competing energy terms and may display unusual experimental phenomena. Previous studies have shown that glassy behavior appears when the concentration of the particles is high [5–8]. In particular, aging and memory phenomena, which are thought to be typical characteristics of spin-glass dynamics, have been observed in low-frequency ac susceptibility or low-field magnetization measurements on frozen ferrofluids [9–12] and discontinuous metal-insulator multilayers [13]. While these effects were discussed in the context of a droplet model, the nature of the low temperature phase for a system of interacting magnetic nanoparticles remains controversial. To properly address this issue, further experimental evidence is required. In this study, we performed a series of new experiments on an interacting magnetic nanoparticle system and observed striking memory effects in the dc magnetization and magnetic relaxation that go beyond those observed previously. Such effects indicate that the organization of the metastable states that develops below a blocking temperature is similar to the hierarchical picture proposed for spin glasses.

The samples in this study are permalloy ($\text{Ni}_{81}\text{Fe}_{19}$) nanoparticles prepared in an inert gas condensation system. A 2 in. magnetron sputtering gun with a permalloy target was used to create a plasma. A high pressure of

inert gas causes the sputtered atoms to nucleate and form clusters. The clusters are then extracted by a pressure difference through a series of apertures and collected on SiO_2 substrates placed in this path. By controlling the sputtering time we can make the clusters form a monolayer of nanoparticles with the required density. The structure and morphology of the particles were examined by transmission electron microscopy. The particles have spherical shape and the size distribution is peaked around 6 nm. The area coverage of the particles is about 25%, which introduces strong interparticle interactions. dc magnetization measurements were performed by using a quantum design superconducting quantum interference device magnetometer from 10 to 300 K. In order to obtain enough magnetic signal, we used a stack (eight pieces) of as-prepared film instead of a single piece. The magnetic fields are applied parallel to the film plane.

Figure 1 shows the zero-field cooled (ZFC) and field cooled (FC) magnetization curves in a 50 Oe field for the studied sample. The ZFC curve peaks at $T_{\text{max}} = 78$ K, which corresponds to the blocking temperature T_B . The FC curve continues to increase with decreasing temperature. The two curves depart from one another at a temperature much higher than T_{max} . As also seen in frozen ferrofluids, these facts distinguish the particle system from a conventional spin-glass system where the FC magnetization departs from the ZFC magnetization just at T_{max} and shows a plateau below T_{max} . The inset shows the M - H curves at both high and low temperatures. Below the blocking temperature hysteresis appears. The ZFC peak and the hysteresis below T_B are general characteristics of magnetic nanoparticle systems.

We now focus on the phase below the blocking temperature. In order to gain new information on the low temperature dynamics, we employed a new approach in the FC magnetization measurement. First, we cool the sample in a 50 Oe magnetic field from 200 down to 10 K at

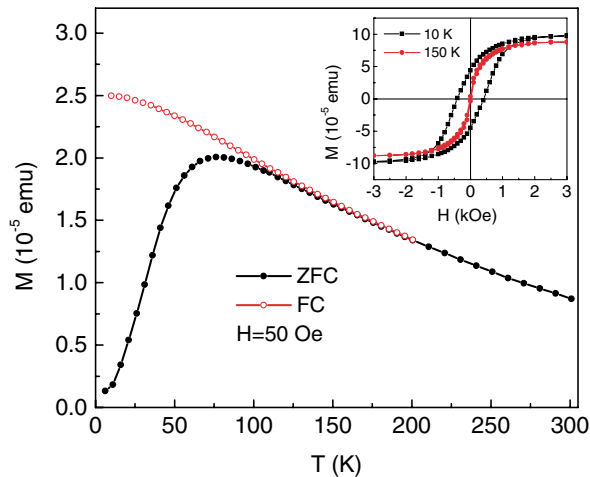


FIG. 1 (color online). Temperature dependence of the dc magnetization in a 50 Oe field for both ZFC and FC processes. The inset shows the M - H curves below and above the blocking temperature.

a constant cooling rate of 2 K/min; then we heat it back continuously at the same rate and record the magnetization. The obtained $M(T)$ curve is referred to as the reference curve and is shown as a solid line in Fig. 2. We then cool the sample at the same rate again and record the magnetization with cooling, but now temporarily stop at $T = 70, 50, 30$ K for a waiting time $t_w = 4$ h, respectively. During t_w , the field is also cut off to let the magnetization relax downward. After each stop and wait period, the 50 Oe field is reapplied and cooling is resumed. This cooling procedure produces a steplike

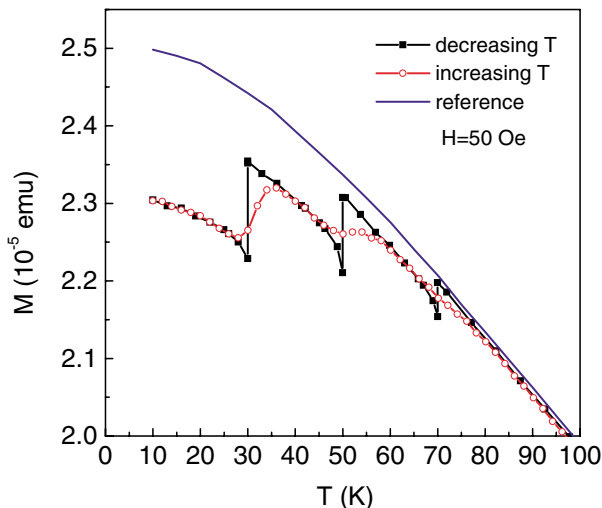


FIG. 2 (color online). Memory effect in the dc magnetization. The solid line is measured on heating at a constant rate of 2 K/min after FC in 50 Oe (reference curve). The solid squares are measured during cooling in 50 Oe at the same rate, but with stops of 4 h duration at 70, 50, and 30 K. The field is cut off during each stop. The open circles are measured with continuous heating at the same rate after the previous cooling procedure.

$M(T)$ curve and is shown as solid squares in Fig. 2. After reaching the base temperature 10 K, the sample temperature is raised continuously at the 2 K/min rate in a constant 50 Oe field and the magnetization is recorded again. A striking result is that the $M(T)$ curve obtained in this way, shown as open circles in Fig. 2, also exhibits a steplike shape. As the temperature increases continuously, the magnetization has an upturn around 30 K, and then at only a few kelvins above, it recovers the previous $M(T)$ curve measured on cooling. Similar, though less dramatic, behavior is observed around other stopping temperatures, $T = 50$ and 70 K. In a word, the system remembers its thermal history when the temperature is returned—a “memory” effect. To confirm this unusual behavior, we repeated the same measurement scheme but with a smaller temperature sweeping rate of 0.5 K/min. The result is basically the same except that the magnetization value is relatively higher.

For a relaxation process by simple thermal activation, the FC magnetization is expected to decrease monotonically with increasing temperature due to increasing thermal fluctuations. The memory behavior seen in interacting permalloy nanoparticles indicates that the low temperature dynamics are far beyond the simple scenario of thermal activation over constant energy barriers. Instead, the memory effect implies that relaxation at lower temperatures has little or no influence on the state at higher temperatures.

In order to test this argument, as well as to verify the memory effect, we examined the magnetic relaxation itself and studied the influence of a temperature change on the relaxation behavior. In these relaxation measurements, both the ZFC and FC methods are used. In the ZFC experiment, the sample is cooled down to $T_0 = 30$ K in zero field. Then a 50 Oe field is applied and the magnetization is recorded as a function of time. After a time t_1 , the sample is quenched in constant field to a lower temperature, $T_0 - \Delta T = 22$ K, and the magnetization is recorded for a time t_2 . Finally the temperature is turned back to T_0 and the magnetization is recorded for another period t_3 . Figure 3(a) shows the relaxation curve with the ZFC method. When the field is first turned on, following an immediate jump, a slow logarithmic relaxation takes place. During the temporary cooling, the relaxation becomes very weak. When the temperature returns to T_0 , the magnetization comes back to the level it reached before the temporary cooling. Moreover, by plotting the data points during t_3 vs $t - t_2$, we find that the relaxation curve during t_3 is a continuation of the curve during t_1 (insets in Fig. 3). Correspondingly, the FC experiment, in which the sample is cooled to $T_0 = 30$ K in a 50 Oe field and the relaxation is measured after the field is cut off, gives consistent results [shown in Fig. 3(b)]: the state of the system before temporary cooling is recovered when the temperature returns (memory effect) and the relaxation curve during t_3 is on the continuation of the curve during t_1 . Therefore, in a more straightforward way, these

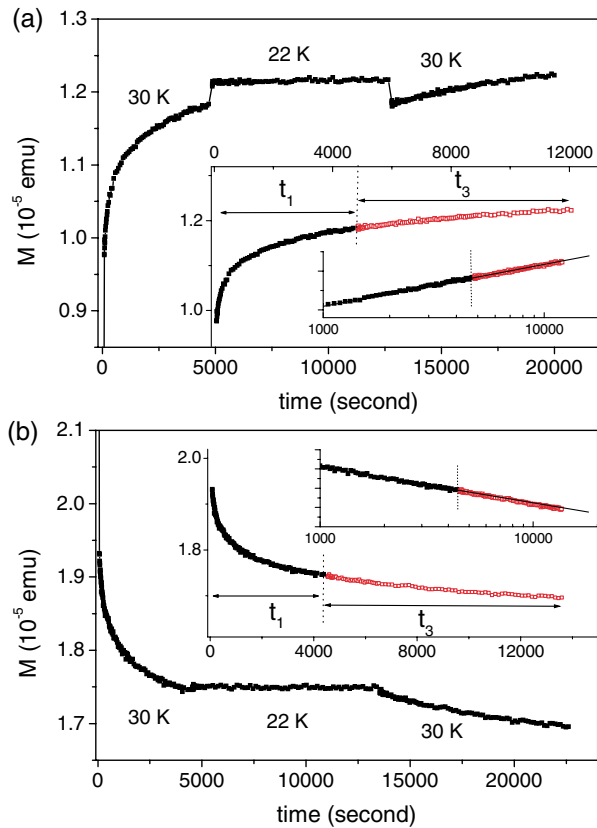


FIG. 3 (color online). Magnetic relaxation with temporary cooling for (a) the ZFC method and (b) the FC method. The insets plot the same data vs the total time spent at 30 K. The relaxation curve during t_3 is the continuation of the curve during t_1 .

experiments demonstrate the memory effect in interacting magnetic nanoparticles.

We note that there is an imperfection in these experiments. Because the relaxation at 22 K is almost halted in such measurements, i.e., no real relaxation happened at the lower temperature, one may argue that the memory and the continuation seem to be natural consequences. To avoid this ambiguity, we performed another class of relaxation measurements in which, during the temporary cooling, we intentionally changed the field to force the system to relax at the lower temperature. As shown in Fig. 4, during the temporary cooling at 22 K, the magnetization makes a large jump followed by a remarkable relaxation with opposite sign due to the turning on [Fig. 4(b)] or turning off [Fig. 4(a)] of the applied field. Amazingly, even after such strong opposite relaxation at 22 K, the magnetization returns to the level it reached before the temporary cooling when the temperature and the field are restored. Again, the relaxation curve during t_3 is the continuation of the curve during t_1 , as plotted in the insets of Fig. 4 with a logarithmic time scale. These results unambiguously confirm the memory effects. In addition, they prove the argument that the relaxation at lower temperatures has no influence on the state at higher temperatures.

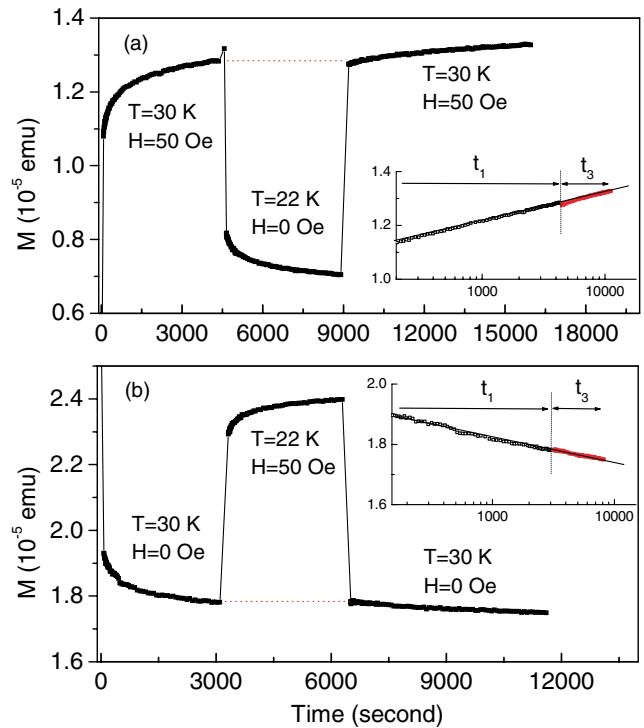


FIG. 4 (color online). Magnetic relaxation with temporary cooling and field change for (a) the ZFC method and (b) the FC method. The memory effect is unambiguously confirmed. The insets demonstrate that the relaxation curve during t_3 is the continuation of the curve during t_1 .

The interesting memory effects seen in the interacting permalloy nanoparticles provide us illuminative information about the nature of the low temperature phase. For real spin-glass systems, memory phenomena in low-frequency ac susceptibility have been widely observed [14,15]. Though the full understanding of the nature of spin glass is still open to question, these memory effects have been discussed with a droplet model [16] or a hierarchical model [17,18]. In the hierarchical model, a multi-valley structure is organized on the free-energy surface at a given temperature. The free-energy valleys (metastable states) split into new subvalleys with decreasing temperature and merge with increasing temperature. This hierarchical picture naturally provides the observed memory effects. When the system is quenched from T to $T - \Delta T$, each free-energy valley splits and develops a set of subvalleys. If ΔT is large, the barriers separating the main valleys become too high to be overcome during the finite waiting time t_2 , with relaxation occurring only within the subvalleys of each set. Therefore, the relative occupation among different sets remains unchanged during the stay at $T - \Delta T$. As the temperature is returned to T , the newly born subvalleys and barriers merge back to the previous free-energy landscape. Thus, relaxation at $T - \Delta T$ has not contributed to the evolution at T . Based on the above understanding, the observed memory effects in the present study may imply that a hierarchical organization of the metastable states exists in interacting magnetic

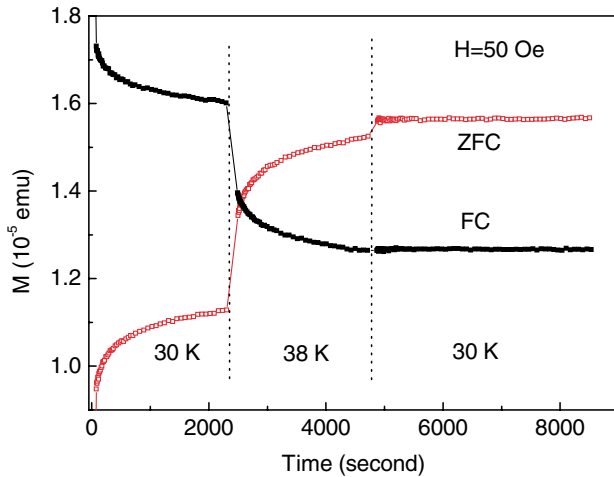


FIG. 5 (color online). Magnetic relaxation with a positive temperature cycling. The relaxation is reinitialized at the higher temperature and no memory effects appear after temperature returns.

nanoparticles. Since the hierarchical organization requires a large number of degrees of freedom to be coupled [19], it could not be produced by the independent behavior of individual particles and consequently highlights the significant role played by interparticle interactions. More importantly, for the first time, the memory effect with a field change (Fig. 4) indicates that the hierarchical configuration is preserved even when under a considerable magnetic field change (50 Oe in this case).

Unlike the droplet model, which should be symmetrical with respect to heating and cooling [16], the hierarchical model predicts that the relaxation would be fully initialized only upon heating and no memory effect would appear after a temporary heating. We test this by introducing a positive temperature cycling. As seen in Fig. 5, the temporary heating reinitializes the relaxation in both ZFC and FC processes. When temperature returns, the magnetization does not restore to the level before the temporary heating—no memory effects. Such an asymmetric response with respect to negative/positive temperature change favors the hierarchical model. Though a previous study [10] showed symmetric response in the out-of-phase component χ'' of ac susceptibility, it is obtained only after introducing an effective extra time. Another reason to account for this discrepancy could be that with χ'' one can explore only the very beginning of the aging regime while the dc relaxation provides access to a larger time window in the aging regime [20].

The various memory effects as well as the aging phenomena reported so far support the view of a spin-glass-like phase in interacting magnetic particles. Nevertheless, the “glassy phase” in magnetic particle systems should be distinguished to a certain extent from an ordinary spin-glass phase, as evidenced by the difference in the FC magnetization curve between two systems. One important issue is that the magnetic moment of a nano-

particle is several orders larger than an atomic spin. The spin flip time for magnetic particles is much longer than that of an atomic spin in an ordinary spin glass, and it depends exponentially on the particle size. Therefore, even a small distribution of the particle size could give a broad range of relaxation times, which may partially contribute the observed glassy phenomena.

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