

Dipole Interactions with Random Anisotropy in a Frozen Ferrofluid

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Glassy behavior (including hysteresis, irreversibility, a peak in the zero-field-cooled magnetization, and nonexponential relaxation) is observed in a quenched ferrofluid system consisting of 50-Å magnetite particles. An Arrott plot, M^2 vs H/M , shows clear features of random anisotropy similar to what is found in amorphous ferromagnets. We discuss the glassy behavior in terms of both the random anisotropy and the dipole interactions, and we contrast the unusual response of our system with canonical spin glasses.

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Magnetically disordered systems have been intensively studied in recent years [1]. In particular, spin glasses, with competing interactions, and random-field magnets, with random effective magnetic fields at the local sites, have been the focus of much attention. Very little work has been done on systems with dipole interactions largely because millikelvin temperatures are required in order to achieve ordering [2]. Recently, disordered systems with random magnetic anisotropy [3] have been investigated both theoretically and experimentally. Such systems involve magnetic moments with easy magnetization axes, due to local crystal fields, which are different from site to site. The theory [4] for such systems was originally developed in order to explain the unusual behavior of amorphous ferromagnets. Systems with random anisotropy plus competing interactions remain essentially unexplored. In this paper we report studies on a system which has both dipole-dipole interactions and local random anisotropy.

The experiments were performed on a ferrofluid, a solution of magnetic particles suspended in a nonmagnetic solvent [5] as shown schematically in the illustration in Fig. 1. For our sample the magnetic material is magnetite, Fe_3O_4 , with a mean particle diameter of 50 Å and a standard deviation of ± 16 Å. Each particle is a ferromagnetic microcrystal. In order to avoid clustering, each particle is coated with a ~ 20 -Å-thick nonmagnetic surfactant layer. The Curie temperature for bulk magnetite is ≈ 850 K [6], which is much higher than the freezing temperature of 210 K of the solvent, a hydrocarbon oil. For our particle size there is a single domain within the particle [5], and to a very good approximation we can take each whole grain as a rigid moment at low temperature. The average moment of each particle μ is about $3000\mu_B$, where μ_B is the Bohr magneton [7]. Earlier magnetization measurements of ferrofluid samples [8] involved much larger particles so that the moment was constrained to point along the easy axis of the particle. Thus, each dipole became immobilized at the freezing temperature of the solvent. In our system, by contrast, the dipoles can change their orientation below the freezing point of the solvent and the ground state is determined by the magnetic interactions between the dipoles.

The moments interact with one another through the magnetic-dipole interaction: $J_{ij} = \mu_i \mu_j (1 - 3 \cos^2 \theta_{ij}) / r^3$. The large μ_i moves the characteristic interactions from the millikelvin to the kelvin temperature range. This interaction can be either ferromagnetic or antiferromagnetic depending on the relative orientation of each dipole. This suggests that a disordered dipolar system may behave as a spin glass [2,9]. Inside each particle the crystal field creates easy axes for the magnetic moment of the grain. Electron microscopy has indicated that the particles in our sample are basically spherical so that shape anisotropy is unimportant. For temperatures slightly below 100 K, the crystal structure of magnetite changes from cubic to monoclinic and the system develops a uniaxial easy axis [10]. As the solvent freezes, each easy axis is frozen in a random orientation so that the only relaxation process is spin rotation relative to the particle. The spins experience a random anisotropy due to the frozen easy axes.

Our sample, sealed inside a small quartz tube with epoxy, was placed in a SQUID magnetometer and cooled in zero field from room temperature to a temperature below the freezing temperature of the solvent. During a

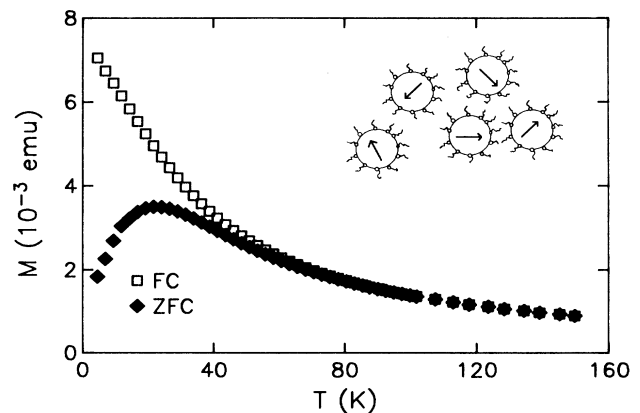


FIG. 1. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization vs temperature at $H = 10$ G. The illustration shows randomly oriented magnetite particles of median diameter 50 Å and a surfactant layer of ~ 20 Å.

measurement the magnetic-field variation is less than 0.05%. The fluid was examined by electron microscopy and no agglomeration was found.

The main part of Fig. 1 shows the magnetization M versus temperature T in a field $H=10$ G. The lower curve, marked ZFC (for zero-field cooled), was obtained by first cooling the system in zero magnetic field from 150 to 4.5 K. The magnetic field H is then applied and the magnetization is measured while the temperature is increased. The upper curve, marked FC (for field cooled), is obtained in a similar manner except that the sample is cooled in the measuring field. The two curves are the same for temperatures above about 80 K, but depart from one another at lower temperatures. The ZFC curve peaks at $T_{\max}=21$ K and the FC curve continues to increase with decreasing temperature. Both the fact that the two curves depart from one another at a temperature much higher than T_{\max} and the fact that the field-cooled magnetization continues to increase without saturation below T_{\max} distinguish this system from what is observed in canonical spin-glass systems. We presume that the distribution of particle size produces a broad peak in the ZFC curve instead of a sharp cusp as in a spin glass. Nanometer particles in an insulating medium also show a peak in the ZFC curve and an FC curve which continues to increase on lowering the temperature [11]. However, in those cases the peak in the ZFC curve is associated with the superparamagnetic blocking temperature which depends on the time scale of the measurement. The time dependence of the peak in our ZFC curve is considerably slower than what would be expected from superparamagnetic blocking and appears to saturate at long times. This indicates that even in the limit of infinite waiting times, the peak would occur at a finite temperature. In addition, as we explain below, the evidence suggests that our peak is due to interactions between the grains.

The peak in the ZFC curve is field dependent as shown in Fig. 2, where T_{\max} is plotted against H . To determine whether T_{\max} is a collective effect or simply the blocking temperature of a superparamagnet, the dependence of T_{\max} on dipole concentration was explored. Samples with different volume fractions of magnetite, $\varepsilon \equiv V_m/V$, were obtained by changing the amount of solvent. Thus, the distribution of particle sizes should be the same in all samples. Figure 2 also shows the H dependence of T_{\max} for the different concentrations $\varepsilon=0.002, 0.02$, and 0.04 . For low fields T_{\max} shifts nonlinearly to higher values with increasing concentration. All the curves merge at about a few hundred gauss; for fields larger than this value, T_{\max} decreases with increasing field for all the samples. The largest T_{\max} is 26 K, found in the most concentrated sample. In order to calculate the magnetic energy associated with this temperature we set $\mu H_0 = k_B T_{\max}$ and obtain $H_0=150$ G. This suggests that for fields larger than 150 G the magnetic energy dominates

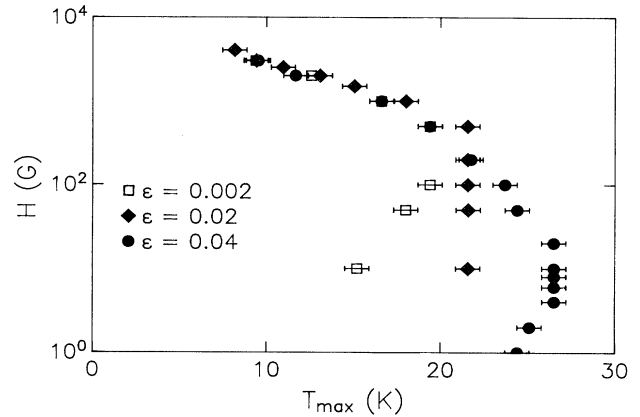


FIG. 2. H vs T_{\max} , the peak position in the ZFC curve, for three volume fractions ε of magnetite. At low fields the interactions dominate, with all curves merging at large H .

the interaction energy. In this regime the differences between the concentrations should be diminished. The field where the curves merge approximately coincides with H_0 and lends credence to the idea that for magnetic fields less than a few hundred gauss the interaction energy dominates the behavior.

It is worth comparing our results for $T_{\max}(H)$ with work on the canonical spin glasses Ag:Mn and Cu:Mn. In those materials, T_{\max} is roughly independent of H for small fields [12]. In contrast, for our samples we find an unusual increase in T_{\max} with increasing field at small H . Here, the application of an external field apparently increases the barriers to spin reorientation. In the spin glasses, the field dependence of the irreversible temperature T_{irr} , below which the ZFC and FC curves start to differ, is consistent with the de Almeida-Thouless line [12,13]. For the ferrofluid, the irreversibility starts very gradually far above T_{\max} and the irreversible temperature T_{irr} is difficult to specify.

In order to determine the anisotropy strength, we have measured hysteresis curves. Figure 3 shows the results at 4.5 K for the $\varepsilon=0.02$ mixture. We obtain the anisotropy constant K from the following relations: $K = \frac{1}{8}$ times the area of the hysteresis cycle [14] and the anisotropy for magnetite, $K_m = K/\varepsilon \approx 2.3 \times 10^4$ ergs/cm³. The temperature corresponding to the anisotropy energy D is $D/k_B = K_m V/k_B \approx 10$ K, where k_B is the Boltzmann constant. We are in the range $D/J \approx 1$ (we have used $J = 2\mu^2/r^3 \approx 5$ K to estimate the exchange interaction between two spins). The remanence is $M_r = 0.21M_0$, where M_0 is the saturation magnetization. For an assembly of noninteracting, randomly oriented single-domain particles one expects [15] $M_r = 0.5M_0$. Hadjipanayis and co-workers [16] pointed out that when there are ferromagnetic interactions in the system, $M_r > 0.5M_0$, but if there are antiferromagnetic interactions, $M_r < 0.5M_0$. The reduced M_r is further evidence for interactions which can lead to frustration.

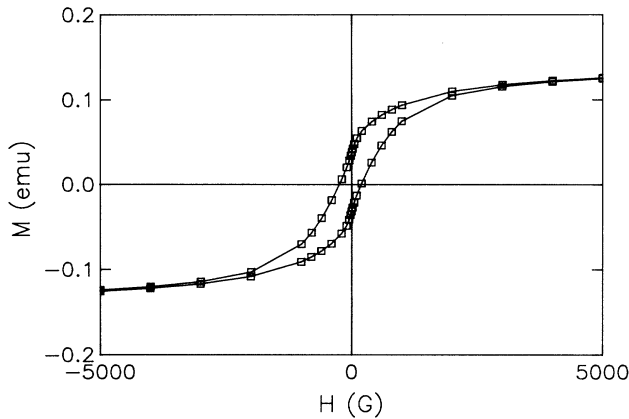


FIG. 3. Hysteresis curve at $T=4.5$ K for a sample with $\epsilon=0.02$ obtained by field cooling.

Aharony and Pytte [17] showed within a mean-field approach that for a system with ferromagnetic interactions the local uniaxial anisotropy will destroy the long-range order. In an Arrott plot, where M^2 is plotted against H/M , the curvature should change at a specific temperature. This temperature was found to be related to the onset of the glassy behavior. Although the Aharony-Pytte theory is only valid for weak anisotropy, a similar change of curvature was also found in amorphous ferromagnetic materials with both weak and strong anisotropy [3,18]. In all these materials the interaction among magnetic moments is basically ferromagnetic. No predictions exist for random anisotropic systems with competing interactions. We show in Fig. 4 an Arrott plot for our ferrofluid sample. A change of the curvature is obvious at $T \geq T_{max}$. A change of curvature in an Arrott plot is not unique to amorphous ferromagnets; it also occurs in a dipolar system with random anisotropy.

Magnetic relaxation results are presented in Fig. 5. The sample was cooled in a field of $H=100$ G from 150 to 15 K, at which point the field is cut to zero and the time decay of the thermoremanent magnetization (TRM) was recorded by the SQUID magnetometer. The data are well fitted by a logarithmic form. However, we note that similar $\ln t$ fits were observed over short time intervals in spin glasses, but were later found to be inadequate to describe the data over a large range [1]. From 10^2 to 10^4 sec the remanence decreases by only 20%, indicating that the relaxation time is much longer than a few hours. In the inset in Fig. 5 we show the logarithmic slope of the decay versus T . It peaks at $T < T_{max}$, as was also observed in studies of the Au:Fe spin glass [19], amorphous ferromagnets [16], and in the vortex state of high- T_c superconductors [20].

The logarithmic time dependence and the nonmonotonic temperature dependence for $M(t)$ presented in Fig. 5 are consistent with the predictions of a recent model [21] for nonexponential relaxation based on dipole-dipole interactions. We note that nonexponential relaxation may

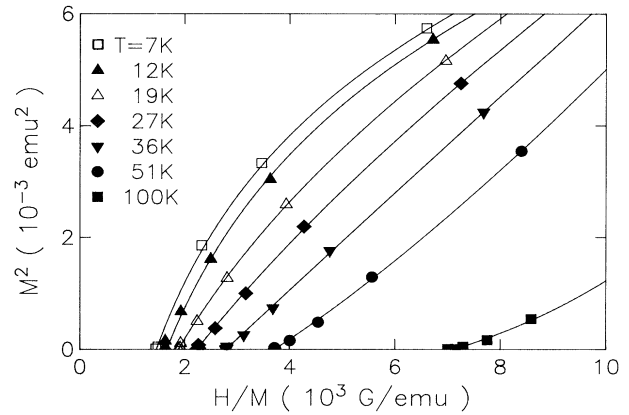


FIG. 4. Arrott plot, M^2 vs H/M for a sample with $\epsilon=0.02$, with a clear curvature change at $T \sim 36$ K, characteristic of a system with random anisotropy. Solid lines are guides to the eye.

also be associated with a distribution of relaxation times in the system, arising either (i) from competing interactions among magnetic moments and disorder giving rise to a multivalley structure in the free-energy surface or (ii) from the distribution of the anisotropy energies. When a magnetic field is turned off, each moment attempts to return to the easy-axis direction defined by the anisotropy energy. The Néel relaxation time for this process is $\tau_N = \tau_0 \exp(K_m V / k_B T)$, where $\tau_0 = 10^{-9}$ sec, and K_m and V are the anisotropy constant and volume for each particle, respectively [5]. The distribution of particle sizes produces a distribution of relaxation times. Using the value of K_m obtained from the hysteresis loop in Fig. 3, we find $\tau_N \approx 1.0 \times 10^{-8}$ sec for a particle with the average diameter occurring in our sample (50 Å) at $T=4.5$ K. A relaxation time longer than 10^4 sec would

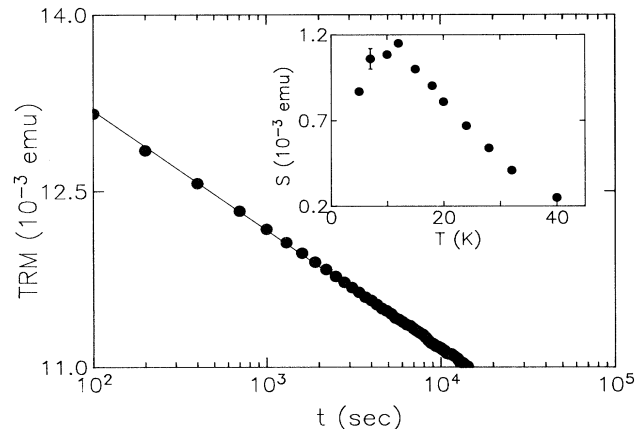


FIG. 5. Time decay of the thermoremanent magnetization for $H=100$ G, $T=15$ K. Within our time window, the decay can be fitted by a logarithmic form (solid line). Inset: The slope of the $\ln t$ fit, S , vs temperature. The peak in S is seen in many types of glassy systems.

require a particle with a diameter larger than 190 Å at $T=20$ K. Even if such large particles are present, their contribution to the magnetization is negligible. We conclude from the time dependence that the collective interaction [21] plays an important role in the glassy behavior.

Given that both the dipole interaction and the RKKY interaction [1] in metallic spin glasses are long range, one might expect that they should behave in a similar manner. Our experimental results indicate many common features between the dipole system and canonical spin glasses, i.e., irreversibility, hysteresis, a peak in the ZFC magnetization, and slow nonexponential relaxation. Hysteresis in our system is more reminiscent of what is found in Au:Fe spin glasses than what is seen in Cu:Mn spin glass. The difference between the two spin glasses is the presence of significant spin-orbit scattering in Au:Fe, which causes local anisotropy [14]. The hysteresis loop of Au:Fe has a smooth curve rather than an abrupt jump seen in the Cu:Mn spin glass [14]. This feature is another confirmation of random local anisotropy in our system.

There are two major differences between our system and a standard spin glass. First, we find a curvature change in the Arrott plot. von Molnar and co-workers [18] compared random-anisotropy and spin-glass properties in several amorphous rare-earth alloys. They found that for amorphous rare-earth ferromagnets the curvature changes at a specific temperature in the Arrott plot, and that this temperature is associated with the peak temperature in the zero-field-cooled magnetization. However, for the spin glass $\text{Gd}_{0.37}\text{Al}_{0.63}$, there is no curvature change in the Arrott plot from a temperature above T_g to temperatures below T_g , where T_g is the spin-glass transition temperature. The results shown in Fig. 4 indicate that our system behaves in this respect more like a random-anisotropy system than a normal spin glass. A second difference is that the FC curve of our quenched ferrofluid sample continues to increase with decreasing temperature, while for a spin glass the corresponding curve flattens off below the freezing temperature. Whether this increase in the FC magnetization below T_{max} , representing continuing degrees of freedom for the spins below the nominal ordering, is unique to dipolar systems with random anisotropy or a more general phenomenon is not understood.

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