Anomalous magnetic relaxation in ferritin

Jonathan R. Friedman,* U. Voskoboynik,† and M. P. Sarachik
Physics Department, City College of the City University of New York, New York, New York 10031
(Received 18 February 1997; revised manuscript received 3 July 1997)

We report measurements in natural horse-spleen ferritin that provide a detailed mapping of the blocking temperature, T_B, as a function of magnetic field over a broad range up to 20 kOe. Unlike most superparamagnetic materials where it decreases with applied field, T_B *increases* with increasing field at small fields, reaching a maximum at ≈3 kOe before exhibiting the expected decrease. The hysteresis loops are anomalously ''pinched'' near zero field. Both observations are consistent with an effective energy barrier that is smaller at zero field than in small finite fields. This may arise from tunneling between pairs of states on opposite sides of the anisotropy barrier that are in resonance in zero magnetic field, regardless of particle size. However, direct measurements of the magnetic viscosity yield ambiguous results, leaving open other possible explanations. [S0163-1829(97)06441-2]

Quantum tunneling of magnetization has been the focus of renewed interest with the recent discovery[1,2] of resonant tunneling between spin states in the molecular-magnet Mn_{12} acetate. The magnetic relaxation rate in Mn_{12} was found to increase markedly whenever the applied magnetic field brings spin states on opposite sides of a potential barrier into resonance. These results have now been confirmed,[3,4] and recent experiments have found similar effects in other systems of magnetic molecules.[5,6]

The mesoscopic spin-10 magnetic subunits in Mn_{12} are each made of 12 strongly superexchange-coupled Mn ions. It would be interesting to observe similar effects in macroscopic systems where the magnetic entities are composed of a larger number (thousands) of spins. Molecular magnets such as Mn_{12} consist of magnetic entities that are nominally identical and, therefore, have resonances at well-defined values of field. This is not the case for most other ensembles of small magnetic particles, which generally have a distribution of moments, anisotropies, and potential barriers. In such systems one expects there to be resonances for some particles at any given field, smearing out the effect and thereby making it unobservable. The only resonance that all particles have in common is the one at zero field, where spin-up and spin-down levels are degenerate, and all pairs of states on opposite sides of the anisotropy barrier are in resonance, regardless of particle size. Thus, one expects to observe resonant tunneling effects only near zero applied field in systems containing a distribution of magnetic sizes.

Horse-spleen ferritin is in many ways an ideal laboratory for searching for resonant tunneling. It is a superparamagnet that consists of an iron-storage protein with an antiferromagnetic core of diameter <8 nm such as $(FeOOH)_8$ $(FeOPO_3H_2)$. Although the magnetic cores are broadly distributed in size in natural ferritin, the maximum cluster size is limited by the volume of the protein cage; moreover, since each is contained within a protein molecule, the interaction between clusters is relatively small. Also, because ferritin is antiferromagnetic, the net spin of a cluster is relatively small, allowing for a sizable energy spacing[7] between levels corresponding to different spin projections within the total-spin manifold. This material has captured the interest of chemists, biologists, and most recently, physicists. In particular, there have been reports of quantum tunneling of the magnetization in monodispersed[8] and polydispersed[9] samples. Indeed, Awschalom *et al.*[8] have reported the observation of coherent tunneling between degenerate spin ground states in zero applied field, an effect that is inherently resonant in nature.

In this paper, we report detailed measurements of the blocking temperature of natural horse-spleen ferritin over a broad range of magnetic fields. We find that the blocking temperature initially *increases* as the field is raised, in agreement with the earlier measurements of Gider *et al.*,[10] before exhibiting the decrease expected in high magnetic fields.[11] Moreover, the hysteresis loops exhibit an unusual ''pinched'' shape. These observations are consistent with an effective energy barrier that is smaller in zero field than in small finite fields, implying anomalously fast relaxation in zero field, similar to effects seen in magnetic molecules. We also report direct measurements of the magnetic viscosity that show an anomaly near zero field. However, absence of a reliable normalization procedure makes these data difficult to interpret.

The magnetization of 100 μL samples of horse-spleen ferritin (100 mg/ml) obtained from Sigma Chemicals was measured in a commercial Quantum Design magnetometer equipped with a 5.5-T magnet. Ferritin that was progressively diluted by the addition of horse-spleen apoferritin (50 mg/ml) or 0.15*M* NaCl solution gave results that were substantially the same as the undiluted form, indicating that interparticle interactions do not play a significant role in the temperature and field range of our measurements.

The behavior of the blocking temperature, T_B, is shown in Fig. 1. Data are obtained in the usual manner: after cooling the sample in zero field, the magnetization is measured in different fixed magnetic fields as the temperature is increased. Typical curves are shown in Fig. 1(a) for 100, 300, and 500 Oe; the maximum of each curve corresponds to T_B at that field. Note that the maximum exhibits an unexpected shift to higher temperature as the field is increased from 100 to 500 Oe. T_B plotted as a function of magnetic field in Fig.

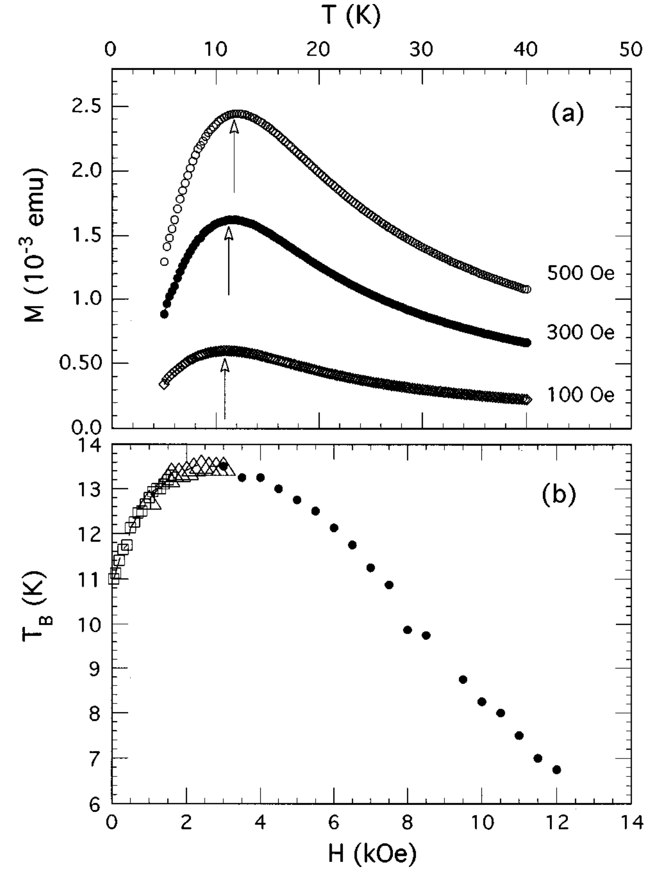

FIG. 1. (a) For natural horse-spleen ferritin cooled in zero field, the magnetization as a function of temperature measured in different fixed magnetic fields. (b) The blocking temperature, T_B [corresponding to the maxima of the curves in (a)] as a function of magnetic field. Different symbols refer to different samples.

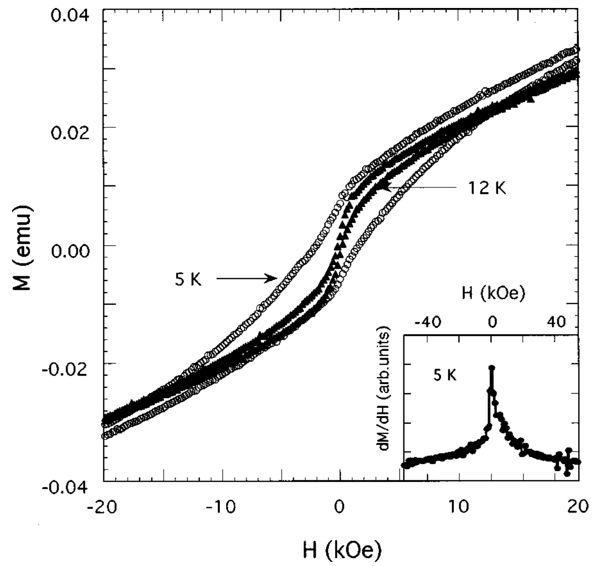

FIG. 2. Magnetization vs magnetic field of natural ferritin at 5 and 12 K. The inset shows the derivative of the hysteresis loop at 5 K, indicating a peak at zero field.

1(b), increases to a maximum temperature of about 13.5 K at ≈3 kOe, and then decreases rapidly for higher magnetic fields.

One expects a monotonic reduction in the energy barriers with magnetic field, and a consequent decrease of the blocking temperature with increasing field. The initial *increase* of T_B as the magnetic field is raised is unexpected and implies that the effective energy barrier is *smaller* in zero field than it is in magnetic fields up to 7 kOe (see Fig. 1). Moreover, it implies that the magnetic relaxation should be faster in zero field than in small finite fields. Support for this conjecture is provided by the hysteresis loops shown in Fig. 2. Both at 5 and 12 K, the hysteresis shows an anomalous ''pinched'' shape near zero field. Ordinary magnetic hysteresis loops are widest at zero field and exhibit an inflection point at the coercive field. In contrast, for ferritin dM/dH is largest near zero field, as shown in the inset to Fig. 2 for data taken at 5 K. This anomaly again implies that the relaxation rate is unexpectedly rapid in small fields relative to the rate at higher fields.

An anomalous field dependence of T_B and pinch-shaped hysteresis loops are both signatures of the resonant tunneling found in Mn_{12} molecules. In the case of Mn_{12} direct measurements of the relaxation rate showed a marked increase in magnetic relaxation at the resonant fields, providing unambiguous evidence of resonant tunneling at these fields. The magnetic subunits in Mn_{12} are all identical in size so that the relaxation is a nearly exponential function of time, making determination of the relaxation rate relatively easy. In polydispersed materials such as our ferritin samples, the relaxation is logarithmic and a single relaxation time cannot be extracted. Instead the relaxation is characterized by the magnetic viscosity, defined as $S = dM/d(\ln t)$.

The viscosity of ferritin was measured after cooling a sample to 5 K in a field of -5 kOe, and then abruptly changing the field to a value between -1 kOe (in the same direction) and 4 kOe (in the opposite direction). For several values of final magnetic field, Fig. 3(a) shows the magnetization plotted as a function of time on a logarithmic scale. The straight lines indicate that the magnetization is roughly proportional to ln$t$ for the range of parameters of our experiments, as is generally found and expected in materials that have a broad distribution of energy barriers. The slope of these lines gives the magnetic viscosity S, which is plotted as a function of the final-field value H in Fig. 3(b). There is clearly an anomalously sharp increase in the viscosity that occurs near zero field. It is difficult to compare viscosity data taken at different fields, since the subset of magnetic particles contributing to the relaxation depends on the field. Many empirical normalization procedures were tried, but all resulted in qualitatively similar results to those in Fig. 3(b).

The behavior of the blocking temperature (Fig. 1) and the shape of the hysteresis loops (Fig. 2) both imply that the magnetic relaxation is greater in zero field than it is in small finite magnetic fields in either direction. On this basis, one would expect the magnetic viscosity to display nonmonotonic behavior near $H = 0$. In contrast, the data of Fig. 3 show no hint of any nonmonotonic behavior. It is possible that using a proper normalization scheme, requiring a detailed knowledge of the distribution of energy barriers in the sample, might reveal nonmonotonic behavior. However, without a clearly defensible procedure for normalizing these

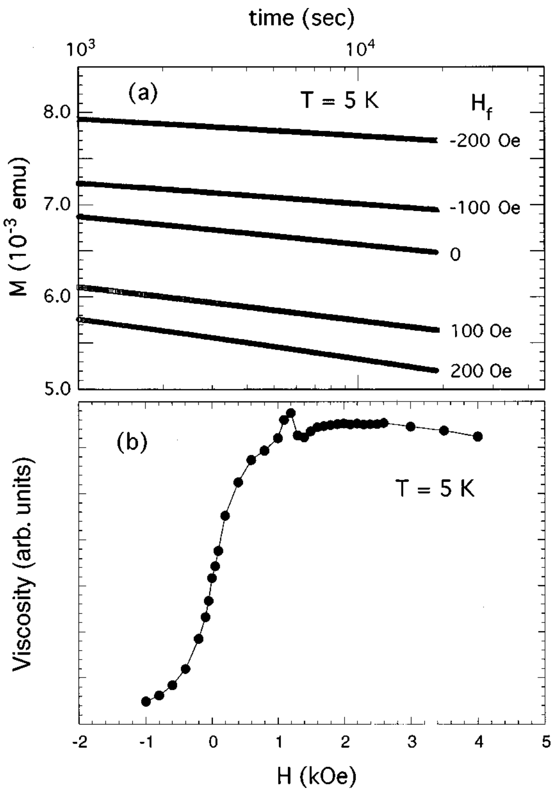

FIG. 3. (a) Magnetization as a function of ln$t$. After cooling to 5 K in a field of 5 kOe, the field was abruptly changed to different final values, H_f, between 1 and -4 kOe. (b) Magnetic viscosity, $S=dM/d(\ln t)$, vs H_f.

data, and in the absence of demonstrated nonmonotonic behavior around $H=0$, it is not possible to draw any firm conclusions from the viscosity data about the field dependence of the relaxation rate of ferritin.

The anomalous decrease of T_B for small magnetic fields and the pinched hysteresis loops suggest an explanation in terms of resonant tunneling similar to that found in magnetic molecules. As noted above, in a material with a random distribution of magnetic sizes, the resonant condition for tunneling would occur for all particles simultaneously *only* at $H=0$. However, there are other possible explanations for the observed anomalies: an unusual size distribution of magnetic clusters, or perhaps uncompensated surface spins,[12] may play a role. A similar field dependence of T_B has been found in quenched ferrofluids of Fe_3O_4,[13] where it was attributed to interparticle interactions, as well as in γ-Fe_2O_3.[14] In these FeO materials numerical estimates indicate that the effect cannot derive from tunneling. In a recent paper, Sappey *et al.*[15] have argued that the anomalous field dependence of the blocking temperature in γ-Fe_2O_3 and ferritin can be attributed to a change in the distribution width with magnetic field. This mechanism does not appear, however, to explain the pinched hysteresis loops or the anomaly in the viscosity near zero field. Since the submission of this paper, Tejada *et al.*[16] have confirmed many of the findings presented above and, in addition, shown that the viscosity is peaked at zero field using a different experimental procedure. They interpret their results as evidence for resonant tunneling.

To summarize: (a) in agreement with earlier reports[10,11] magnetization measurements on natural ferritin indicate an unusual dependence of the blocking temperature, T_B, on magnetic field; (b) unlike most superparamagnetic materials where the blocking temperature decreases with applied field, T_B *increases* with increasing field at small fields to a maximum value at ≈ 3 kOe, before decreasing in the manner one expects. Our measurements provide a detailed mapping of T_B over a broad range of magnetic field for natural horse-spleen ferritin. The hysteresis loops are anomalously ''pinched'' near zero field. Both observations are consistent with an effective energy barrier that is smaller at zero field than in small finite fields and suggest that resonant tunneling may be responsible. However, the results of magnetic viscosity measurements are ambiguous, mainly due to the absence of a well-defined normalization procedure. Additional detailed measurements of the viscosity near $H_{\rm final}=0$ would be of interest, as would measurements of the blocking temperature in magnetic fields much smaller than those used in our experiments.

We thank Eugene Chudnovsky, Javier Tejada, and Eric Vincent for valuable discussions. We thank Jaili Li for help in sample preparation and characterization, and Marilyn Gunner for valuable advice and discussions. This work was supported by the U. S. Air Force Office of Scientific Research under Grant No. F49620-92-J-0190.

*Present address: Physics Department, State University of New York at Stony Brook, Stony Brook, NY 11794.
†Bronx High School of Science. Current address: Cornell University, Ithaca, NY 14853.

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