Nonlinear temperature variation of magnetic viscosity in nanoscale FeOOH particles

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Temperature variations of the magnetization and magnetic viscosity S in 30-Å particles of FeOOH are reported. An average blocking tempeature $\overline{T}_b = 47$ K is determined for this system from the temperature variation of the difference susceptibility between the field-cooled and zero-field-cooled cases. The measured decrease of $\overline{T}_b$ with applied field is used to determine an average magnetic moment $\simeq 7150\mu_B$ per particle. The relaxation data of the magnetization $M(t)$ follow the equation $M(t)/M(\tau_0) = 1 - S\ln(t/\tau_0)$, from which temperature variation of S is determined for the range 2 to 200 K. Below 7 K, S is temperature independent signifying quantum tunneling. Above 7 K, initially S increaes linearly with T, but the variation becomes increasingly nonlinear, reaching an apparent maximum at $\overline{T}_b = 47$ K. The temperature variation of S is characteristic of a phase transition at $\overline{T}_b$ since the data fits well the equation $S = A|(T-\overline{T}_b)/\overline{T}_b|^{-\nu}$ with $A = 0.040(0.0076)$ and $\nu = 1.10(1.29)$ for $T > \overline{T}_b (T < \overline{T}_b)$. An average energy barrier $\langle U \rangle = 2140$ K and $\tau_0 = 5\times10^{-12}$ s are also estimated from the analysis of the data.

I. INTRODUCTION

Recently, the phenomenon of magnetic relaxation in nanoscale magnetic particles has received considerable attention, partly because of the prediction[1,2] and subsequent observations of quantum tunneling of the magnetization at low temperatures in a variety of systems.[3–8] In a complex system with a distribution of the particle sizes and barrier heights, it is found that the time dependence of the magnetization $M(t)$ should follow the equation[2,3]

$$M(t) = M(t_0)[1 - S\ln(t/\tau_0)] , \quad (1)$$

where S is the magnetic viscosity, τ_0 is a constant, and $M(t_0)$ is the magnetization at an initial time t_0. For quantum tunneling, S becomes temperature independent below a crossover temperature T_c whereas above T_c it is expected to follow the equation

$$S = k_B T/\langle U \rangle , \quad (2)$$

where $\langle U \rangle$ is the average energy barrier which determines the blocking temperature T_b in the static $M(T,H)$ studies according to the equation[2,3,9]

$$T_b \simeq \langle U \rangle / 30k_B . \quad (3)$$

The energy barrier U is believed to result from the magnetic anisotropy constant K so that $U = KV$ where V is the volume of the particle. For a system with a particle size distribution, a distribution of U and hence T_b is expected. A temperature-independent S in the liquid-helium temperatures, followed by a linear temperature dependence above T_c, has been observed in a number of systems.[3–8]

In this paper, we report the results of a detailed study of the temperature dependence of the magnetic viscosity coefficient S in 30-Å ferrihydrite (FeOOH) particles. In recent papers[10,11] magnetic, Mössbauer, and electron spin resonance studies in this system showed it to be a superparamagnetic system for temperatures $T \geq 100$ K with distinct anomalies observed near 50 K. However the significance of the changes observed near 50 K were not fully understood. In the results reported here we have covered the temperature region from 2 to about 200 K for magnetic relaxation studies. By making measurements at several fields and from the observation of the temperature variation of S, we infer that the temperature of about 47 K represents the average $\overline{T}_b$ for this system. Also, our observations show that on approach to $\overline{T}_b$, from both below and above, S attains a maximum value, a behavior characteristic of a phase transition. Such an apparent singular behavior of S around $\overline{T}_b$ has not been reported so far in any other system. Below $T_c \sim 7$ K, we observe a temperature-independent S, characteristic of quantum tunneling. The details of these results and discussion including comparison with theoretical predictions wherever possible, are presented below.

II. EXPERIMENTAL DETAILS AND RESULTS

All the measurements reported here were carried out on the commercial Nanocat sample of FeOOH.[12] Transmission electron microscopy measurements of this sample show it to contain particles of average diameter of about 30 Å.[13] In earlier papers[10,11,13] details of the crystal structure of the particles and electronic state of Fe^{3+} have been given. The magnetic measurements reported here were carried out on a superconducting quantum interference magnetometer (Quantum Design Model MPMS). For relaxation studies of the magnetization, the sample was cooled to the desired temperature in a field H_1 $(=+100$ Oe). Then after the temperature becomes stable, the field was switched to H_2 $(=-100$ Oe). As soon as H_2 becomes stable, M was measured as a function of time (at about 60-s intervals) for about an hour. The above protocol follows the procedures employed by other researchers.[3] After completing these measurements, the sample is then warmed to far above T_b in zero field, cooled again in H_1 to the new temperature and procedure was repeated.

The temperature dependence of the magnetic susceptibility $\chi = M/H$, in applied field $H = 100$, 500, 1000 and 2000 Oe, is shown in Fig. 1. The two sets of data correspond to the ZFC (zero-field-cooled) and the FC (field-cooled) configurations. Here in the ZFC case, the sample is cooled in zero field to 5 K, H is then applied and M measured with increasing temperatures whereas in the FC case, the sample is cooled to 5 K in the applied field H followed by data collection with increasing temperatures. The data for the ZFC case shows a broad peak at a temperature T_p (marked by arrows in Fig. 1) whose position shifts to lower temperatures as H is increased. The broad peak and the separation of χ between the ZFC and the FC cases has been observed in a variety of systems of magnetic particles.[3–8,10] For this system, $T_p \simeq 100$ K for $H = 100$ Oe and we have shown that for $T \geq 100$ K, M scales as H/T signifying superparamagnetism.[10] In literature, T_p is usually associated with the blocking temperature T_b. However, we argue later that for particles of different sizes, the average $\overline{T}_b$ is lower than T_p and T_b represents the temperature above which nearly all the particles are deblocked.

In Fig. 2, we have plotted the difference susceptibility $\chi_{FC} - \chi_{ZFC}$ against temperature for the four H values shown in Fig.1. This difference represents the irreversible part of the magnetization when the sample is cooled in H and consequently it should be related to the remanent magnetization M_r. To verify this, we show in Fig. 3 M_r vs temperature for the sample cooled in $H = 2000$ Oe to 5 K, then H is turned to zero (residual field is about 1 Oe) followed by measurements of M_r vs temperature. It is generally argued[9] that the temperature at which M_r falls to half its value at $T \to 0$ K represents the average blocking temperature $\overline{T}_b$ for the system and dM_r/dT represents the distribution of the blocking temperatures. From Fig. 3, we see that for $H = 2000$ Oe, $\overline{T}_b \simeq 25$ K using both criteria. From Fig. 2, a similar value is obtained using the difference susceptibility $\chi_{FC} - \chi_{ZFC}$ for $H = 2000$ Oe. This use of the difference susceptibility to measure the average $\overline{T}_b$ for a system does not seem to have been exploited before.

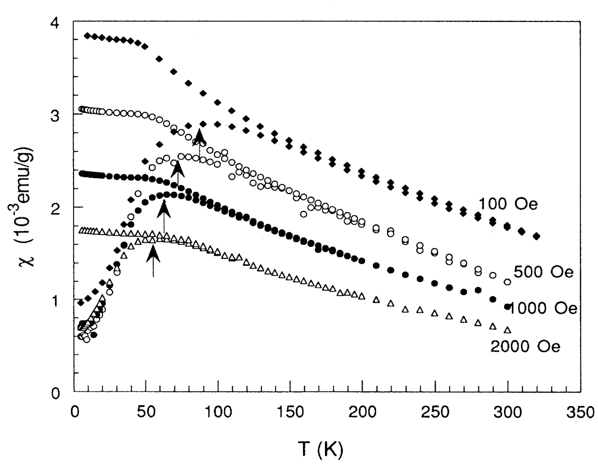

FIG. 1. Temperature dependence of the susceptibility $\chi = M/H$ at four applied fields. The upper (lower) set of data are for the field-cooled (zero-field-cooled) cases. The arrows mark the position of the peak zero-field-cooled susceptibilities.

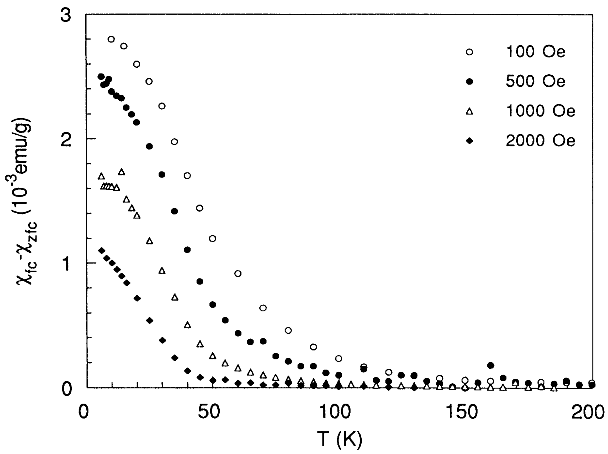

FIG. 2. The difference susceptibility $\chi(\mathrm{FC}) - \chi(\mathrm{ZFC})$, determined from Fig. 1, is plotted against temperature for four applied fields.

Using the data of Fig. 2 and the above procedures, the variation of $\overline{T}_b$ with the applied field H is shown in Fig. 4 where the solid line is a theoretical fit. We will return to the discussion of this data later. For $H = 100$ Oe, $\overline{T}_b \simeq 44$ K, a value about half the magnitude of T_p where the ZFC susceptibility peaks for $H = 100$ Oe. It is our view that T_p does not represent the average T_b but the temperature above which nearly all the particles of various sizes are deblocked and act as superparamagnets. This is clearly seen in the scaling of M as H/T for $T \geq 100$ K.[10] Thus in complex systems, a distinction between T_p and $\overline{T}_b$ needs to be clearly made.

Next we present the data on the relaxation studies with the protocol $H_1 = 100$ Oe and $H_2 = -100$ Oe as described earlier. In Fig. 5, we show the plots of the magnetization M vs $\ln t$ at several representative temperatures. The linear behavior of M against $\ln t$ shows that the data fit Eq. (1) with slope $= -M(t_0)S$ so that the magnitude of magnetic viscosity S can be determined from the slopes using the initial $M(t_0)$. The temperature variation of S

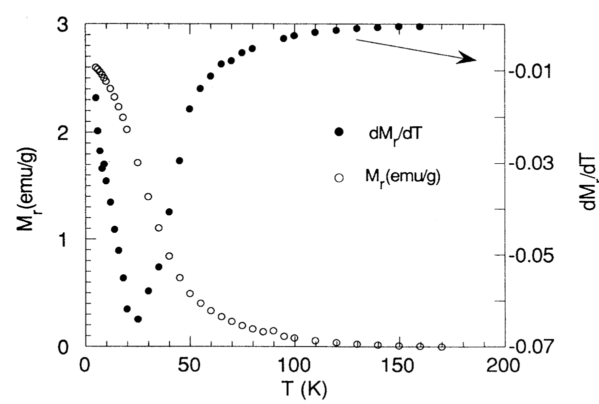

FIG. 3. The remanent magnetization M_r and calculated dM_r/d_T vs temperature for a sample cooled in $H = 2000$ Oe.

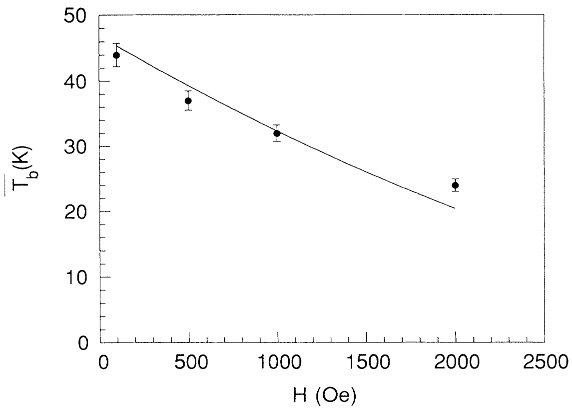

FIG. 4. Measured average blocking temperature $\overline{T}_b$ against applied field H. The solid line is Eq. (4).

from this analysis is shown in Fig. 6 in the temperature range of 2 to 200 K. The remarkable result, not reported so far in any other system, is that S peaks at $\overline{T}_b$. We also note that whereas for $T < \overline{T}_b$, M remains positive (but decreases with time) when field is switched from $+100$ to -100 Oe, for $T > \overline{T}_b$, M becomes negative on the field switching (followed by increase in its magnitude with time). These observations are easily understood if the coercive field H_c approaches zero as T_b is approached from below (or $H_c < 100$ Oe at $\overline{T}_b$). We have not carried out a detailed temperature dependence of H_c. However at 10 K, $H_c \simeq 1500$ Oe.

The details of the behavior of S vs temperature for the lower-temperature region is shown in Fig. 7. Below about 7 K, S becomes nearly temperature independent signifying the onset of the region of quantum tunneling of the magnetization, reported recently in other systems also.[3–8] Thus $T_c \simeq 7$ K for this system. Above T_c, in a

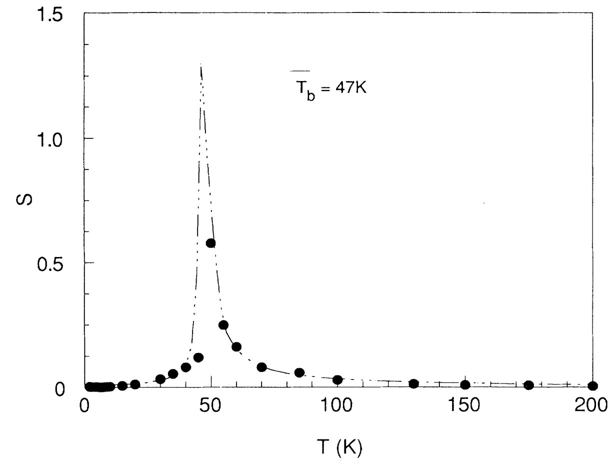

FIG. 6. Temperature variation of the magnetic viscosity S. Dotted lines are fits to Eq. (5) with parameters given in the text.

limited temperature range a case can be made for the expected linear temperature variation [Eq. (2)] due to thermal effects for $T \ll \overline{T}_b$. However, as shown in Fig. 6, the temperature variation of S over an extended temperature range is nonlinear. To the best of our knowledge, a theory does not yet exist with which the results of Fig. 6 can be compared.

Another way to verify the logarithmic scaling for very long times can be achieved by plotting M/M_0 vs $T\ln(t/\tau_0)$, as suggested by Labarta *et al.*[14] Such a representation of our data is achieved by choosing $\tau_0 = 5\times10^{-12}$ s, as shown in Fig. 8 for selected temperatures between 10 and 45 K. A good universal curve is obtained, allowing the relaxation behavior to be extrapolated to times that are otherwise experimentally inaccessible.

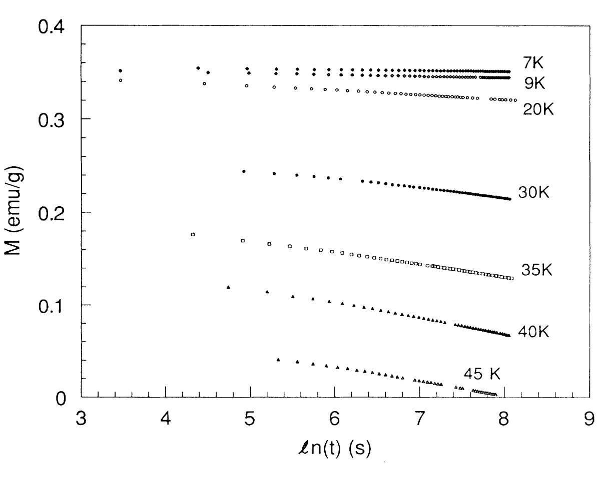

FIG. 5. Time dependence of the magnetization $M(t)$ at several representative temperatures, according to Eq. (1).

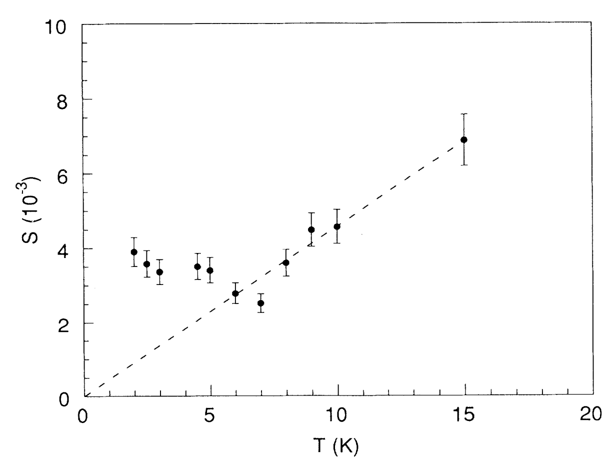

FIG. 7. Details of temperature variation of S for lower temperatures. The linear variation expected from Eq. (2) above 7 K is indicated.

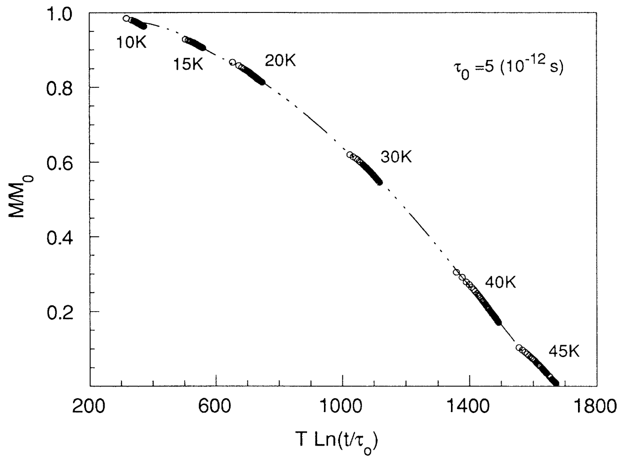

FIG. 8. Plot of reduced magnetization M/M_0 vs $T\ln(t/\tau_0)$ using the relaxation data at several temperatures indicated.

III. DISCUSSION

The variation of $\overline{T}_b$ with applied H in Fig. 4 can be understood using the argument that H lowers the energy barrier $\langle U \rangle$ to the new value $\langle U \rangle - \mu H + \mu^2 H^2/4\langle U \rangle$.[9] Then using Eq. (3) viz. $\langle U \rangle \simeq 30 k_B \overline{T}_b$, we can write

$$\overline{T}_b(H) = T_b(0)\{1-(\mu H/60 k_B T_b(0)]\}^2 , \tag{4}$$

where μ is the average magnetic moment of the particles. The solid line in Fig. 4 is fit to Eq. (4) with $T_b(0)=47$ K, and $\mu = 0.48 k_B$. Although the fit to the data is quite good, additional experiments will be carried out in the future to test Eq. (4) over an extended range of magnetic fields. The $\mu = 0.48 k_B$ yields $\mu = 7146\mu_B$ as the magnetic moment of the average superparamagnetic particles of FeOOH. Let us compare this number with the one calculated from the known structural information of the particles. Although particles are not spherical, for simplicity we assume them to be and to have a diameter of 30 Å.[10] Using $5.9\mu_B$ as the moment of the Fe^{3+} ions separated by a distance of about 3 Å,[13] total moment per particle neglecting surface spins is calculated to be $\simeq 2925\mu_B$. This number is 41% of the above calculation using Eq. (4), a reasonable agreement considering that the volume of the particles is not accurately known.

The calculation of the energy barrier $\langle U \rangle$ can be done at least two ways. First using $\overline{T}_b = \langle U \rangle / 30 k_B$ yields $\langle U \rangle = 14.10$ K with $\overline{T}_b = 47$ K. Second from the linear fit in Fig. 7 and using Eq. (2), we find $\langle U \rangle = 2140$ K, a result about 50% higher than the first calculation. Considering that the interparticle interactions are not included in the above calculations, the semiquantitative agreement obtained here is quite reasonable. The interparticle interactions can affect the calculation of T_b.[15]

Next we consider the temperature dependence of S over the extended temperature range to 200 K (Fig. 6). The temperature variation of S on approach to $\overline{T}_b$ is characteristic of the singular behavior traditionally observed for certain variables near a phase transition. Consequently we have fitted the data to the equation

$$S = A\,|(T-\overline{T}_b)/\overline{T}_b|^{-\nu} \tag{5}$$

for both above and below $\overline{T}_b$. The dotted curve in Fig. 6 is fit to Eq. (5) with $\overline{T}_b = 47$ K with the following parameters: $A = 0.040$ (1), $\nu = 1.10$ (3) for $T > \overline{T}_b$, and $A = 0.0076$ (2) and $\nu = 1.29$ (5) for $T < \overline{T}_b$. In making this fit, $\overline{T}_b$ was also allowed to vary in 1° steps and it was found that $\overline{T}_b = 47$ K gives the best overall fit with the above parameters. (The quoted uncertainties are in the last decimal place.) Although, at present, there is no theoretical basis for Eq. (5), the good agreement obtained in Fig. 6 demonstrates that there must be some truth to the validity of Eq. (5). We hope that this paper will encourage theoretical developments about the critical behavior of S around $\overline{T}_b$.

In Eq. (1), $1/\tau_0$ represent the attempt frequency for the relaxation rate $1/\tau = (1/\tau_0)\exp(-U/k_B T)$ of the individual particles for the barrier height U. It is the distribution of the barrier heights for a complex system which leads to Eq. (1). For a measuring time $\tau = 10^2$ s usually used the static M measurement, and $\tau_0 = 5\times 10^{-12}$ s estimated in Fig. 8, leads to $U = 30.6 k_B T_b$. In Eq. (3) and throughout this paper, we used the factor 30 (instead of 30.6) for simplicity. The point to note here is that the magnitude of τ_0 affects the magnitude of this factor which is often quoted to be anywhere between 25 and 32. Our magnitude of τ_0 is in excellent agreement with the recent measurements of Dickson *et al.*[9]

IV. CONCLUSIONS

The primary conclusions of this paper are as follows. First, for a complex system consisting of distribution of particle sizes, an average blocking temperature $\overline{T}_b$ is a very useful concept and its location does not necessarily agree with T_p, the temperature where the ZFC susceptibility peaks. Second, the magnetic viscosity coefficient S has significant nonlinearity in its temperature dependence, beginning with a temperature-independent region at lower temperatures due to quantum tunneling and an apparent critical behavior around $\overline{T}_b$. This result of the apparent critical behavior is a new result not reported in any system yet primarily because the reported measurements have been limited to the lower temperatures. It is hoped that this paper will encourage theoretical developments and the measurements of S around $\overline{T}_b$ in other systems.

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