Macroscopic Quantum Tunneling in Magnetic Proteins

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We report low-temperature measurements of the frequency-dependent magnetic noise and magnetic susceptibility of nanometer-scale antiferromagnetic horse-spleen ferritin particles, using an integrated dc SQUID microsusceptometer. A sharply defined resonance near 1 MHz develops below $T \sim 0.2$ K. The behavior of this resonance as a function of temperature, applied magnetic field, and particle concentration indicates that it results from macroscopic quantum tunneling of the Néel vector of the antiferromagnets.

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Several years ago it was suggested that in sufficiently tiny magnets macroscopic quantum tunneling (MQT) of the magnetic moment from one easy axis to an equivalent one might be experimentally observable [1]. Calculations of this effect for ferromagnetic [1(a)] particles predict the occurrence at low temperatures of a resonance in the frequency-dependent magnetic susceptibility $\chi(\omega)$. In a recent paper [2], we described attempts to realize this exciting possibility in arrays of nanometer-scale ferromagnets produced by a scanning-tunneling-microscope deposition technique. A resonance was observed in $\chi(\omega)$, but its behavior as a function of temperature, particle size, and magnetic field showed that the phenomenon was not consistent with magnetic MQT [2]. However, new theoretical estimates [3] indicate that conditions for the observation of these macroscopic tunneling phenomena should be more favorable in *antiferromagnetic* particles.

In this paper we report measurements of both the magnetic noise $S(\omega)$ and $\chi(\omega)$ on horse-spleen ferritin, a naturally occurring, antiferromagnetic, iron storage protein. These proteins contain a 7.5-nm-diam magnetic core with ~ 4500 spins, and so have a volume more than 100 times smaller than the previously studied ferromagnets. Owing to their biological significance, the ferritin particles have been investigated intensively and are quite well characterized. Although they are basically antiferromagnetic, they have a small uncompensated moment which allows one to probe their dynamics by measuring $S(\omega)$ and $\chi(\omega)$. We have studied solutions of these particles with three different concentrations, observing in the more dilute solutions a well-defined resonance below roughly 200 mK in both $S(\omega)$ and the imaginary part, $\chi''(\omega)$, of $\chi(\omega)$. We find that the frequency of this resonance is 2000 times higher than in the previous study [2]. Moreover, in marked contrast to the earlier measurements, the behavior as a function of temperature and magnetic field is consistent with theoretical expectations for the occurrence of MQT in antiferromagnets.

Horse-spleen ferritin [4] has been structurally characterized by dark-field TEM [5] and x-ray [6] and electron diffraction [7], and chemically analyzed by iron-coupled plasma atomic emission spectrometry [8]. The results reveal a 7.5-nm-diam crystal core of ferrihydrite (with approximate formula $9Fe_2O_3 \cdot 9H_2O$) [9], which is a close relative of the antiferromagnetic mineral hematite (αFe_2O_3). The crystalline core contains $N_{spin} \simeq 4500$ Fe^{3+} ions and is surrounded by a 2-nm-thick spherical protein shell. This scale is smaller than the width of a domain wall, and Mössbauer spectroscopy measurements [10,11] show that the particles are in fact superparamagnetic (i.e., single domain Néel order is well established in each particle, but its direction fluctuates in time) below the Néel ordering temperature of $T_N \sim 240$ K. Different samples having reduced magnetic particle densities are formed by systematically diluting a concentrated protein solution with diamagnetic apoferritin [12].

A fully integrated thin-film dc SQUID susceptometer serves as the sensor for the high-frequency magnetic noise and magnetic susceptibility experiments [13]. In order to reduce the effects of stray magnetic fields, two remotely located series Josephson junctions are connected in a low-inductance fashion to a microfabricated gradiometer detector. This pickup loop structure consists of two square counterwound Nb pickup loops 15.0 μm on a side over a superconducting ground plane, one of which contains a measured sample of magnetic proteins. In addition, a center-tapped field coil which takes a single square turn around each pickup loop is used to apply an ac magnetic field (10^{-5} G) for susceptibility measurements as well as to apply static dc fields. The single chip experiment and associated electronics are attached to the mixing chamber of a dilution refrigerator and cooled to $T \sim 20$ mK. In addition, the susceptometer assembly is electronically and magnetically shielded within an rf-tight superconducting chamber, and cooled within Mumetal cylinders to achieve a magnetic flux noise of $< 10^{-7}\phi_0/\sqrt{\mathrm{Hz}}$.

Figure 1 shows the observed resonance at frequency $\nu_{res} \equiv \omega_{res}/2\pi \sim 940$ kHz in both $S(\omega)$ and $\chi''(\omega)$ for a 1000:1 diluted solution containing $\sim 38\,000$ of the magnetic protein particles at 29.7 mK. (Similar results are obtained for 10000:1 dilutions.) Only a single resonance

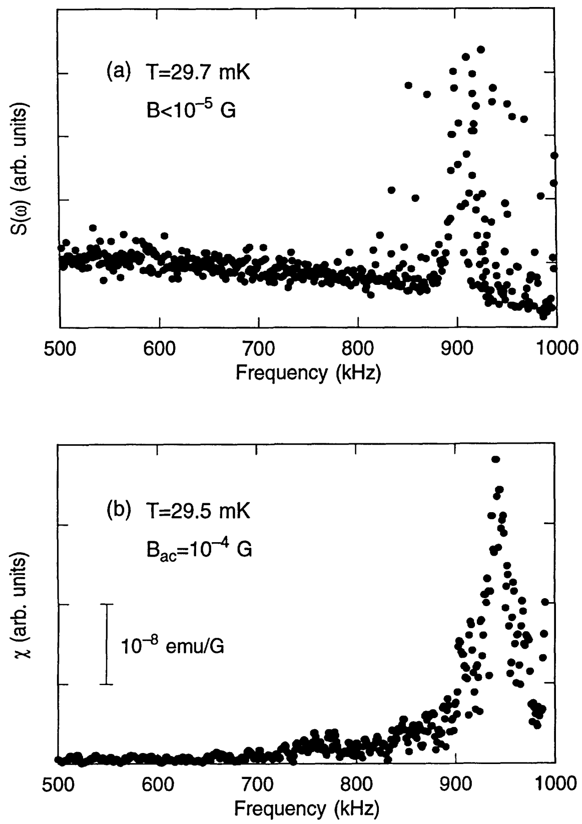

FIG. 1. (a) Magnetic noise spectrum of a 1000:1 diluted solution of magnetic proteins. (b) Frequency-dependent magnetic susceptibility of the same sample after cycling the temperature to $T=4$ K. The effect of flux motion is seen through the small shift in resonance frequency.

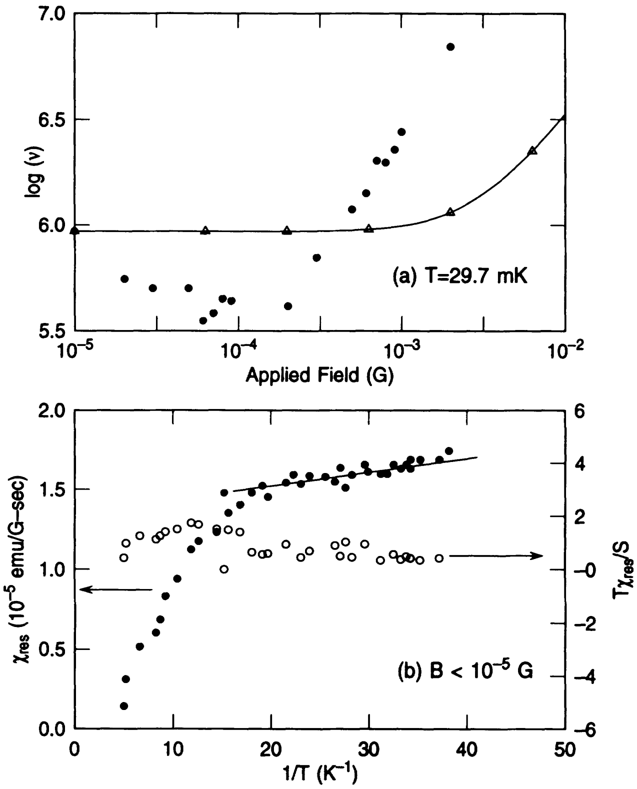

FIG. 2. (a) Dependence of the resonance frequency on applied dc magnetic field. The curve with the Δ symbols is the simple model of Eq. (4). (b) Temperature dependence of the resonance amplitude in near-zero field showing a linear dependence at low temperature. (There is little shift in frequency.) Also, the quantity $T\chi(\omega_{res})/S(\omega_{res})$, as a check of Eq. (1).

is observed up to the maximum measured frequency of 5 MHz. One expects the resonant frequencies for these two spectra to be identical since they are related by the fluctuation-dissipation theorem:

$$\chi''(\omega)=(1-e^{-\hbar\omega/k_BT})S(\omega)/2\hbar\simeq(\omega/2k_BT)S(\omega)\,. \quad (1)$$

[The second part of Eq. (1) is the high-temperature approximation, which is appropriate for the measurements reported here since $\hbar\omega_{res}/k_BT<10^{-3}$.] In fact, however, a slightly higher ω_{res} is obtained from χ'' than from S; this is due to the variation in residual magnetic fields from one run to another and/or an imbalance in the on-chip field coils. The resonant frequency is very sensitive to small fields [as is evident from Fig. 2(a)], and eventually may be fixed by cycling the temperature of the superconducting shield after initially cooling the sample. Equation (1) predicts that $T\chi''(\omega_{res})/S(\omega_{res})$ should be independent of temperature, and the data plotted in Fig. 2(b) show reasonable agreement with this prediction.

Figures 2(a) and 2(b) show the behavior of the resonance with applied magnetic field and temperature. Figure 2(a) shows that, in sharp contrast to the previous study [2], ω_{res} at low temperature is extremely sensitive to applied field; it decreases somewhat up to a field of about 5×10^{-4} G, above which it rises approximately linearly. Figure 2(b) shows the area under the χ'' resonance plotted against $1/T$. At $T^*\simeq200$ mK the resonant peak emerges out of the background, and by about 50 mK the area under the peak increases roughly linearly with $1/T$; ω_{res} is essentially independent of T below 200 mK.

Measurements of S and χ'' on an undiluted sample failed to show any resonant structure. We believe that this is a consequence of the appreciable interparticle interactions in the more concentrated material. Support for this interpretation is found in Fig. 3, which shows the low-frequency ($\nu=11$ Hz) magnetic susceptibility versus T for both dilute and concentrated solutions. The signal for the 1000:1 dilute case, as well as more dilute solutions, shows a reasonably good $1/T$ dependence, consistent with a Curie law and indicative of the absence of interparticle ordering: The individual particles act like essentially independent superparamagnets throughout the range of temperatures displayed. The data for the con-

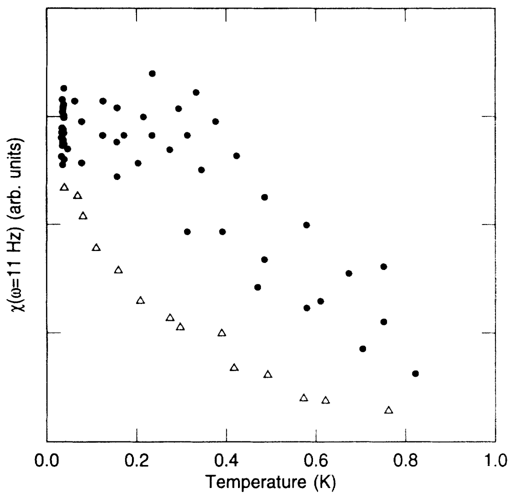

FIG. 3. Low-temperature dc magnetic susceptibility of the (●) concentrated ferritin and (△) 1000:1 diluted ferritin solutions.

centrated case are much noisier, being reminiscent of behavior in systems with strongly coupled particles or grains [14]; also, there seems to be some departure from Curie-law behavior at low temperature. These observations suggest substantial interparticle interaction and perhaps some local ordering at around 200 mK.

To judge whether the resonance phenomena in the dilute system are a consequence of magnetic tunneling, we now briefly review the theory of MQT in small magnets [3]. In the absence of dissipation, antiferromagnetic particles in the superparamagnetic regime are completely described by the operator describing the Néel order parameter $\mathbf{l}$. In the presence of magnetic anisotropies and/or an external field, the Hamiltonian $\mathcal{H}$ may have minima at two distinct orientations of the vector $\mathbf{l}$. Then the antiferromagnetic exchange interaction permits the vector $\mathbf{l}$ to tunnel quantum mechanically between the two local minimum-energy orientations. The effective Lagrangian which describes this tunneling is that of the nonlinear sigma model [15] familiar from the study of antiferromagnetic spin waves. If the two energy minima are equivalent, which occurs when the external field is negligibly small and the anisotropy has easy-axis (Ising) character, then the Néel vector performs a simple oscillation between them, and the magnetization correlation function takes the simple form [16]

$$S(\tau)\equiv\langle\mathbf{M}(t)\mathbf{M}(t+\tau)\rangle\simeq M_0^2\cos(\omega_{\rm res}\tau)\,, \qquad (2)$$

where $\omega_{\rm res}$ is the tunneling rate. Equation (2) predicts resonant behavior for the Fourier transform $S(\omega)\sim\delta(\omega\pm\omega_{\rm res})$, and hence, through the fluctuation-dissipation theorem (1), for $\chi''(\omega)$, as seen in the experiment. Here we follow Ref. [3] in assuming that if the particle has a small number of uncompensated excess spins and hence a magnetic moment M_0, the dynamics is determined by $\mathbf{l}$, and $\mathbf{M}$ simply follows $\mathbf{l}$ as a "slave" degree of freedom. A measurement of the excess magnetization of the ferritin particles in the superparamagnetic regime $1\ {\rm K}<T<240\ {\rm K}$ below the Néel temperature gives $M_0=217\mu_B$, where μ_B is the Bohr magneton. This is equivalent to ~43 spin-$\frac{5}{2}$ Fe^{3+} ions, a small fraction of the $N_{\rm spin}\sim4500$ spins in the particle, and roughly consistent with the expected number ($N_{\rm spin}^{1/3}$) of uncompensated surface spins on such a small particle [3]. Given the uncertainty of the detailed particle shape, these numbers are consistent with antiferromagnetic behavior in the bulk of the particle.

Assuming that the ferritin particles in the dilute solutions act independently, one can immediately apply this theory of MQT to predict their low-temperature behavior and compare with the data in Fig. 2. Combining Eq. (2) with Eq. (1) for $\hbar\omega\sim\hbar\omega_{\rm res}\ll k_BT$ gives

$$\chi''(\omega)\simeq(\pi N\omega M_0^2/2k_BT)\delta(\omega-\omega_{\rm res})\equiv\chi_{\rm res}\delta(\omega-\omega_{\rm res})\,. \qquad (3)$$

Here $N\simeq38\,000$ is the number of ferritin particles in the experiment. From the slope, $T\chi_{\rm res}\sim0.9\times10^{-7}$ emu K/G sec of Fig. 2(b) one can solve for M_0 in Eq. (3); taking the observed resonant frequency $\nu_{\rm res}\equiv\omega_{\rm res}/2\pi=9.4\times10^5$ Hz, one finds $M_0\simeq640\mu_B$, consistent within a factor of 3 of the high-temperature measurement, and hence with the conclusion that the number of uncompensated spins in the particle is small relative to $N_{\rm spin}$.

Taking the direct measurement of $M_0=217\mu_B$ to be the more reliable one, one can use the simple estimate [16] from two-level systems,

$$\nu_{\rm res}(B)\sim[\nu_{\rm res}(0)^2+(BM_0/h)^2]^{1/2}\,, \qquad (4)$$

to predict crudely the effect of external magnetic fields B on the resonant frequency. One can see from Fig. 2(a) that this matches the overall trend of the data.

Using $M_0=217\mu_B$, one can also check the assumption that the particles can be taken to be noninteracting in the 1000:1 diluted solution, where the typical interparticle distance r_0 is about 2000 Å. At these distances, the only significant interparticle interaction is dipolar: Each particle produces an effective field $\mathbf{B}_0\simeq\mathbf{M}_0/r^3$ on another particle a distance r away. Assuming that the moments of the various particles point in random directions, one estimates the typical net field experienced by any given particle as $B_{\rm eff}\simeq2M_0/r_0^3\simeq5.0\times10^{-4}$ G. While this is a small effective field, it has approximately the maximum value consistent with Eq. (4) and the measured value of the resonant frequency, $\nu_{\rm res}=9.4\times10^5$ Hz, given that $B_{\rm eff}M_0/h\simeq1.5\times10^5$ Hz. The same estimate for the undiluted solution, where $r_0\simeq200$ Å, yields $B_{\rm eff}\sim0.5$ G, which, according to Eq. (4), would raise $\nu_{\rm res}$ to $\sim10^9$ Hz, 2 orders of magnitude higher than the frequencies accessible in these experiments. We believe that this accounts for the absence of a resonance in the concentrated sample. The interaction energy in the dense solution $B_{\rm eff}M_0$ is equivalent to a temperature of roughly 7 mK. Near this temperature one would anticipate seeing significant interparticle ordering and a concomitant saturation of the low-frequency susceptibility for the concentrated system. As mentioned earlier, the effect of some local ordering may already be manifest in Fig. 3 below about 200 mK. This does not seem unreasonable, since we have seen evidence from electron microscope photographs for clustering of the particles, and hence for some stronger local interactions than we assumed in the estimate above.

By applying the theory of antiferromagnetic quantum tunneling in more detail, one can extract estimates of the anisotropy energy K and the transverse susceptibility $\chi_\perp$. As shown previously [3], $\omega_{\rm res}$ is given by $\omega_{\rm res} \simeq \omega_0 \exp[-(\chi_\perp K)^{1/2} V/\mu_B]$. Here V is the particle volume and ω_0 is a characteristic microscopic frequency of order 10^{10} sec^{-1}. The theory also provides an equation for T^*, the temperature [roughly 2 K in Fig. 2(b)] below which quantum tunneling through the anisotropy barrier dominates over thermal activation, and is given by $k_B T^* \simeq (\mu_B/2)(K/\chi_\perp)^{1/2}$. Solving for $\chi_\perp$ and K in these two equations, we find $K \simeq 1.9\times 10^3$ ergs/cm^3 and $\chi_\perp \simeq 5.2\times 10^{-5}$ emu/G cm^3. This value for $\chi_\perp$ is very characteristic of this class of antiferromagnetic materials [3]; the estimate for K is lower than is usually expected by a factor of 10 to 100.

Through their relations to other observable quantities one can check the self-consistency of these estimates. The transverse susceptibility is related to the Néel transition temperature by [3] $\chi_\perp \simeq \mu_B^2 N_{\rm spin}/k_B T_N V$. Using the above estimate for $\chi_\perp$ and taking $N_{\rm spin} = 4500$ one obtains $T_N \simeq 240$ K, in good agreement with the accepted Néel temperature. In Mössbauer spectroscopy [11] the blocking temperature T_B is the temperature at which the classical barrier crossing occurs within one Larmor precession time $\omega_L^{-1} \simeq 2.5\times 10^{-9}$ sec, and is related to the anisotropy by $\omega_L \sim \omega_0 \exp(-KV/2k_B T_B)$. Using the above estimate for K in this formula yields a blocking temperature $T_B \sim 0.5$ K. This is quite low in comparison with reported measurements of $T_B \sim 40$ K for horse-spleen ferritin, a consequence of our rather low value of anisotropy. On the other hand, there are indications that T_B is somewhat variable, and is reported as low as 10 K.

In summary, we show that the temperature, magnetic field, and concentration dependence of the resonance studied in these experiments at low temperature are qualitatively consistent with the theory of quantum tunneling in small antiferromagnets. Our confidence in ascribing the observed behavior to MQT is bolstered by the fact that the values of $\chi_\perp$ and of the Néel temperature T_N inferred from the data are so close to accepted values. The inferred values of the anisotropy K and the blocking temperature T_B are somewhat lower than those usually quoted, but not unreasonably so, given the uncertainties in these numbers.

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