Quantum Tunneling of the Magnetization in an Iron Cluster Nanomagnet

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We have investigated the magnetic relaxation of clusters of eight iron ions characterized by a spin ground state of ten and an Ising anisotropy. Below 400 mK the relaxation rate is temperature independent suggesting that tunneling of the magnetic moment across its anisotropy energy barrier occurs. Using the anisotropy constants derived from EPR data, we can calculate both the crossover temperature T_c and the expected tunneling frequency $1/\tau$. The field dependence of the relaxation shows evidence of resonant tunneling. [S0031-9007(97)03302-4]

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Quantum tunneling of the magnetization (QTM) has become a focus of interest in physics and chemistry because it can provide a signature of quantum mechanical behavior in macroscopic systems [1–5]. A small mono domain ferromagnetic particle may be described by a single macroscopic degree of freedom, namely, its total spin. At low enough temperature, it has been predicted that this spin can tunnel through its magnetic anisotropy barrier. A variety of materials have been experimentally investigated in order to test this hypothesis, ranging from nanoscopic magnetic particles to ferritin [6–8]. Molecular clusters, which at low temperature behave like nanomagnets, are a particularly appealing class of materials for these investigations [9]. While conventional synthesis results in a distribution of size and orientation of the particles, the molecular approach has the advantage of providing ensembles of identical, iso-oriented nanomagnets.

Up to now the best example of a molecular nanomagnet showing QTM is a dodecanuclear manganese acetate complex referred to as Mn_{12ac}." The ground state of this cluster has a net spin of $S = 10$ [10]. Below 10 K the relaxation of the magnetization follows a thermally activated law,

$$\tau = \tau_0 \exp(\Delta E/k_B T), \qquad (1)$$

with an energy barrier $\Delta E/k_B \simeq 62$ K [11]. Below 2 K evidence for QTM has been reported [12,13] as well as thermally assisted QTM [14–16]. However, the mechanism of QTM is still under discussion because of the absence of the required transverse anisotropy, $K_\perp$. Without transverse anisotropy, S_z commutes with the Hamiltonian, the spin is in an eigenstate, and no tunneling will occur. Mn_{12ac} has tetragonal symmetry and only fourth order terms in the crystal field can provide the required low symmetry component [17,18].

In this Letter we report results of our experimental investigation on a new cluster made from eight iron ions, "Fe_8," which has no axial symmetry, and shows clear evidence of QTM at low temperature. The structure of this cluster [19], whose formula is $[(tacn)_6Fe_8O_2(OH)_{12}]^{8+}$, where tacn is the organic ligand triazacyclononane, is sketched in Fig. 1. The cluster has no strict symmetry elements and approximate D_2 symmetry. Magnetic measurements have shown that Fe_8 also has a spin ground state $S = 10$, which arises from competing antiferromagnetic interactions between the eight $S = 5/2$ iron spins as shown in the figure [20].

ac susceptibility experiments made down to 1.5 K as well as Mössbauer spectroscopy have shown that the relaxation of the magnetization of the cluster obeys a thermally activated law with an energy barrier of 22.2 K [21]. In addition, high frequency electron paramagnetic resonance (HF-EPR) measurements on polycrystalline powders provide an accurate estimate of the axial and in plane magnetic anisotropy by the evaluation of the axial and rhombic parameters of the zero field splitting. The spin Hamiltonian in zero field is given by $H = DS_z^2 + E(S_x^2 - S_y^2)$ which reflects the low symmetry responsible for the magnetic anisotropy. The EPR spectra

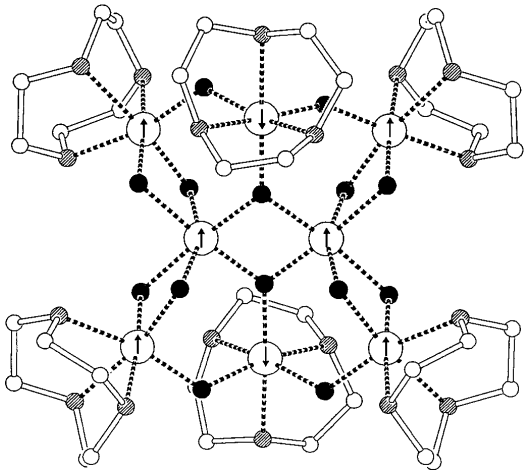

FIG. 1. View of the structure of Fe_8: the large open circles represent iron atoms, while full, hatched, and empty small ones stand, respectively, for O, N, and C. The spin structure of the $S = 10$ ground state is schematized by the arrows.

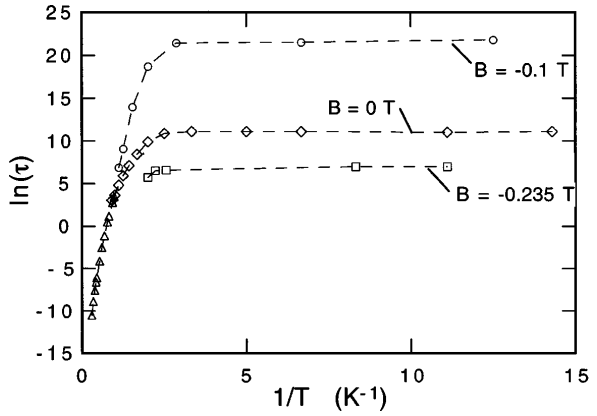

FIG. 2. $\ln(\tau)$ vs $1/T$: High temperature data follow thermal activation law with $\tau_0 = 3.4 \times 10^{-8}$ s and $E = 24.5$ K. Points below 400 mK show temperature independent QTM.

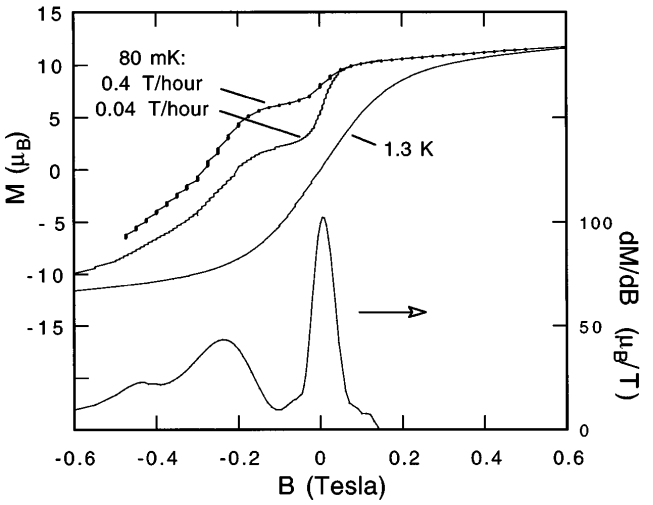

FIG. 3. M vs B: curve taken at 1.3 K shows no hysteresis. Below 400 mK curves are temperature independent, but depend on field ramp rate dB/dt as shown. dM/dB is shown for 0.04 T/h; peaks correspond to faster relaxation, verified by dc measurements.

were satisfactorily simulated with $D = -0.27$ K and $E = -0.046$ K [21].

We have now extended the ac susceptibility measurements to lower temperatures and frequencies. The ac experiments were made on a polycrystalline powder sample from 6 kHz down to 0.005 Hz using a low field low temperature SQUID magnetometer equipped with a miniature dilution refrigerator. The low frequency data give information on the relaxation down to 1 K. The relaxation times, τ, have been extracted from the imaginary part of the susceptibility by assuming that the temperature of the maximum corresponds to the blocking temperature, i.e., the temperature at which the relaxation time is equal to the time scale of the experiment $\tau = 1/\omega$. This is justified because the curves are well fit by considering a single relaxation time. The τ values are plotted as $\ln(\tau)$ vs $1/T$ in Fig. 2 which shows that the relaxation follows Eq. (1) with an energy barrier of 24.5 K and $\tau_0 = 3.4 \times 10^{-8}$ s. These results when combined with previously published data [21] indicate that thermal activation is more or less obeyed over a time scale of 10 decades. The unusually large value of τ_0 is similar to that which is observed in Mn_{12ac} and has been explained as arising from a multistep Orbach process [22].

In order to investigate the magnetic relaxation at lower temperature, dc measurements were performed using a high field low temperature SQUID magnetometer. Figure 3 shows magnetization versus field curves measured at 1.3 K and 80 mK after first saturating the sample in 8 T, where we find $M = 20\mu_B$ This is in agreement with $S = 10$ and $g = 2$ as seen in HF-EPR [21]. At zero field M is one half its saturation value as expected for our nonoriented powder sample, and indicates that after saturation, all clusters within each (randomly oriented) crystal are still perfectly aligned along the easy axes of the crystal. The low temperature curves were taken with two different ramp rates and show hysteresis and "steps" at well defined field values similar to those observed for Mn_{12ac}. For $T < 400$ mK the steps become temperature independent (at fixed ramping rate dB/dt). The hysteresis is due to the fact that the characteristic relaxation times are longer than the experimental ones; the steps occur at field values where the relaxation is enhanced.

dc relaxation experiments were made by first saturating the sample in a high field (>3.5 T), and then reducing the field to a predetermined value and measuring the decay of the magnetization over a period of hours and for up to one week. Some curves obtained at different temperatures are shown in Fig. 4. Above 1.1 K the relaxation is too fast to be measured by this technique, however, between 1.1 and 1 K there is an overlap with our very low frequency ac data. Below 400 mK and for a given measuring field, the relaxation curves taken at different temperatures completely superimpose, clearly showing that the relaxation is temperature independent as seen in Fig. 4.

A crossover from single exponential behavior to a more complex relaxation process is observed below 800 mK, where the magnetization curves can be well fit (over the relatively large time scales of our investigations) by a stretched exponential

$$M(t) = M(0)\exp[-(t/\tau)^{\beta}]. \quad (2)$$

The stretched exponential describes a relaxation rate that is faster at earlier times and which becomes progressively slower as the system evolves. It has often been used to describe the dynamics of disordered systems such as spin glasses [23]. However, it is also manifest in ordered systems, when the drive field responsible for the relaxation changes (reduces) as the system relaxes [24]. The average relaxation time is given by τ, and β is related

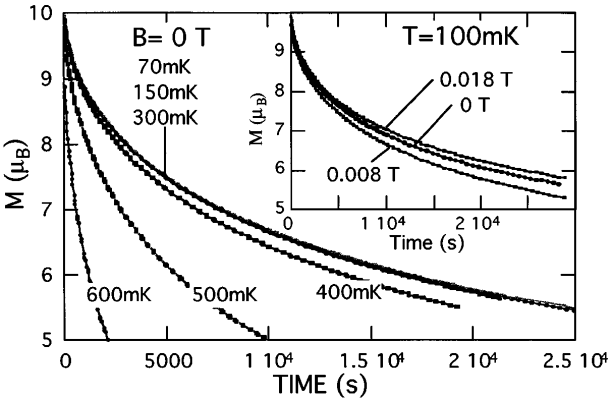

FIG. 4. Relaxation of the magnetization measured at $B = 0$ after first saturating in a field of 3.5 T. For $T < 400$ mK curves superimpose showing that the relaxation is independent of T. Inset shows subtle field dependence near resonance.

to the width of the distribution. We find that β increases from 0.4 below 400 mK to nearly 1 at 1 K. Most of our fits to Eq. (2) were made on relaxation curves in which the experimental time was long enough to see at least a 50% change in the overall magnetization. However, at some measuring fields this was not always feasible due to the very slow relaxation. For example, at $B = -0.1$ T, only a small portion of the curves could be measured, and, in this case, our data points come from extrapolations and may indicate a lower limit to τ.

The low temperature dc relaxation times are plotted in Fig. 2 for three different values of measuring fields. The main feature is the distinct deviation from the thermally activated law observed at high temperature to a regime where the relaxation becomes temperature independent below 400 mK. We suggest that this temperature corresponds to T_c, the crossover to the QTM regime.

All theories of QTM depend critically on a knowledge of the anisotropy constants. For example, calculations for the tunneling of large spins have been made in the semiclassical WKB approximation [1] giving

$$\tau = \tau_0 \exp(B) = \tau_0 \exp[S \ln(8K_{\parallel}/K_{\perp})], \qquad (3)$$

where S is the total spin, and $K_{\parallel}$ and $K_{\perp}$ are the parallel (easy axis) and perpendicular (easy plain) anisotropy, respectively. The attempt frequency, τ_0, also depends on the anisotropy. A crossover temperature T_c between the high temperature thermal activation and the temperature independent quantum tunneling regime is obtained by equating the Gamow exponent B to $\Delta E/k_B T_c$,

$$T_c = \Delta E/k_B[1/S \ln(8K_{\parallel}/K_{\perp})]. \qquad (4)$$

Since large single crystals of Fe_8 are not yet available, the axial and transverse anisotropy constants were evaluated by calculating the magnetization curves up to saturation for different orientations of the external field using the zero field splitting parameters D and E obtained from HF-EPR experiments previously reported [21]. From the area comprised between these curves we estimate the axial and the in plane anisotropy constant to be 1.82×10^6 erg/cm^3 and 6.27×10^5 erg/cm^3, respectively. Using these values, and for $B = 0$, we estimate $T_c \sim 0.7$ K, and $\tau \sim 10^4$ s, which are close to our experimental results.

Figure 2 shows that in zero applied field, the relaxation is more rapid, *by 4 orders of magnitude*, than at -0.1000 T, where *a priori* the height of the energy barrier has been reduced. In fact, the decay of the magnetization shows maxima (faster relaxation) at applied fields $B_a = +0.0080, -0.2350$, and -0.4500 T and minima (slower) at $B_a = -0.1200$ and -0.3500 T. This can also be seen by taking the derivative with respect to field (at fixed ramp dB/dt) of the low temperature hysteresis curves as shown in Fig. 3. The peaks correspond to enhanced relaxation.

This kind of field dependence, oscillations in an otherwise increasing decay rate, was first reported in Mn_{12ac} for both high temperature ac susceptibility measurements [14] and low temperature dc relaxation experiments [12,13] and was totally unexpected on the basis of classical theory of relaxation. Novak and Sessoli first interpreted these oscillations as evidence for resonant tunneling between degenerate states. In this picture, the tunneling amplitude is greatly enhanced when energy levels with M components of opposite sign, separated by the anisotropy barrier, have the same energy. This is the case, for example, when the internal field is zero and all pairs of levels $M_s = \pm 10$, ± 9, etc., are degenerate. However, when an external field is applied, although the energy barrier decreases, the levels shift and are no longer degenerate and the tunneling rate decreases. Upon a further increase of the field, the levels continue to shift until $M_s = +10$ and -9 become degenerate (and $M_s = +9$ and -8 and so on) and the relaxation is once again enhanced. At high temperature, enhancement at the resonance fields is aided by thermal activation. Recently these effects were clearly demonstrated as steps in the hysteresis cycles of Mn_{12ac} [15,16] where the authors also attribute the observed temperature dependence to "thermally activated" resonant tunneling.

We believe that resonant tunneling occurs in Fe_8, and, in fact, dominates the decay process in the quantum tunneling regime. It is observed in both the decay of the magnetization and in the hysteresis cycles in the thermal activation regime. More important, it is clearly observed below 400 mK where the effect is temperature independent and orders of magnitude larger than that observed in Mn_{12ac}.

In Fe_8 the maximum in the relaxation rate is observed at 0.008 T. We attribute this to the effect of internal fields, which also justify the observed stretched exponential relaxation. The internal fields are expected to be weak but different from zero. Besides the applied field, there are basically three contributions to the local field: the dipole field of neighboring clusters, the demagnetization field of

each small crystal, and the overall demagnetization field of the sample due to its form. (It must be stressed that all three fields change while the magnetization decays.) Starting from saturation, we have calculated the strength of the dipole field due to all neighbors within a radius of up to 100 Å and using an average demagnetization field for the particles and the demagnetization field due to the sample form and packing we estimate an internal field of approximately -0.010 T with a distribution width of some 0.020 T.

This field is too small to result in magnetic ordering at our lowest measured temperature; however, it does shift the peaks in the decay rate, and may play an important role in justifying the stretched exponential relaxation. As mentioned, the first resonant tunneling maximum should occur when the local field at a given cluster site is zero. Thus our first maximum should be in a field which compensates for this small negative internal field, as experimentally observed (inset of Fig. 4) [25]. At this field, a large population of clusters will be sitting in an internal field of zero, and thus will begin to relax at a much faster rate than clusters off resonance, and M decreases rather quickly. But after a certain time this population will be depleted and the relaxation continues, but at a slower off resonance rate.

In conclusion, Fe_8 is an excellent candidate for the study of quantum effects in nanomagnets. The anisotropy barrier is some 3 times smaller than Mn_{12ac}, which makes low temperature relaxation measurements experimentally feasible. The anisotropy constants have been derived from EPR data allowing for direct comparison to existing theories. Resonant tunneling occurs in Fe_8, and for the first time the effect has been clearly observed in the temperature independent QTM regime where the tunneling rate decreases by more than 4 orders of magnitude in an applied field of 0.1 T. A more quantitative interpretation of the data is still far from complete, and work is now in progress to obtain large crystals for experiments on oriented single crystals.

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[25] We point out that careful measurements also indicate a shift in the resonate field for Mn_{12}ac at an applied field of approximately -0.02 T. This reflects the smaller contribution from demagnetization fields and larger unit cell for these needle shaped crystals (to be published).