Macroscopic Measurement of Resonant Magnetization Tunneling in High-Spin Molecules

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We report the observation of steps at regular intervals of magnetic field in the hysteresis loop of a macroscopic sample of oriented $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ crystals. The magnetic relaxation rate increases substantially when the field is tuned to a step. We propose that these effects are manifestations of thermally assisted, field-tuned resonant tunneling between quantum spin states, and attribute the observation of quantum-mechanical phenomena on a macroscopic scale to tunneling in a large (Avogadro's) number of magnetically identical molecules. [S0031-9007(96)00131-7]

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Quantum effects are rarely observed through macroscopic measurements because statistical averaging over many states usually masks all evidence of discreteness. Notable exceptions include the dc and ac Josephson effects, the de Haas–van Alphen effect, and the quantum Hall effect. In this Letter, we report the observation of quantum-mechanical effects in the magnetization of a macroscopic sample: steps at regular intervals of magnetic field in the hysteresis loop of oriented $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ crystals. We interpret these steps as evidence for thermally assisted, field-tuned resonant tunneling between quantum spin states in a large number of identical high-spin molecules.

Quantum tunneling of magnetization has been the subject of much interest since it was considered theoretically in the 1980s [1–3]. Experimental work in this area has centered on magnetic relaxation measurements in a variety of systems [4–6] and resonance experiments in horsespleen ferritin [7]. The aim of these experiments has been to detect the coherent tunneling of a large number of spins (typically 1000 or more) coupled by a strong exchange interaction through a magnetocrystalline anisotropy barrier.

There have also been recent attempts [6,8–11] to identify tunneling in high-spin molecules, which lie in a magnetic regime that bridges the atomic and mesoscopic scales [12]. In contrast to most ensembles of small magnetic clusters, which are comprised of particles with various magnetic sizes and properties, a macroscopic sample of molecular magnets consists of a large number of chemically identical entities that are characterized by a unique set of parameters. This feature allows precise characterization of a sample and rigorous comparison with theory. $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ (often referred to as Mn_{12}) has been the subject of much experimental [6,8,9,11,13–17] and theoretical [18,19] work since it was first synthesized by Lis [20] in 1980. This molecule contains four Mn^{4+} ($S = 3/2$) ions in a central tetrahedron surrounded by eight Mn^{3+} ($S = 2$) ions, as shown at the top of Fig. 1. Oxygen bridges allow superexchange coupling among the Mn ions, and both high-field and ac susceptometry experiments indicate an $S = 10$ ground state [13,14,17], suggesting a simple picture of the magnetic order with all the spins of one valence pointing up and the remainder pointing down [13,15,18]. These molecules crystallize into a tetragonal lattice in which magnetic interactions between molecules are thought to be negligible since the distance between Mn ions in neighboring

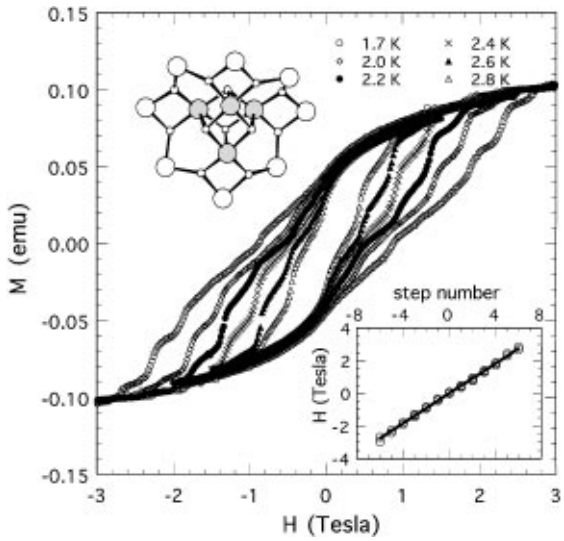

FIG. 1. Magnetization of Mn_{12} as a function of magnetic field at six different temperatures, as shown (field sweep rate of 67 mT/min). The inset shows the fields at which steps occur versus step number (with step 0 at zero field). The straight line is a least-squares fit, yielding a slope of 0.46 T per step. The structure of the Mn_{12} molecule (from Ref. [15]) is represented at the top. Only the Mn^{4+} (large shaded circles), Mn^{3+} (large open circles), and oxygen (small circles) ions are shown.

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molecules is at least 7 Å [15,20]. Experiments indicate a large magnetocrystalline anistropy [8,9,11,13–17] and superparamagneticlike behavior [8,9,11,13–15,17]. Hysteresis is observed [8,15,16] below a blocking temperature of about 3 K, and ac susceptibility data as well as dc magnetic relaxation data indicate a single characteristic relaxation time [8,11,15,17] that obeys an Arrhenius law, $\tau = \tau_0 e^{\Delta E/k_B T}$, down to 2.1 K; studies [6,9] down to 175 mK show deviations that have been interpreted as possible evidence of quantum tunneling of the spin in these high-spin molecules.

Some very recent work [6,8,9,11] has shown that the relaxation time depends nonmonotonically on applied field, exhibiting an anomalous dip near zero field and 0.3 T. The authors suggest that the effect is due to thermally assisted resonant tunneling between spin states. In this Letter we present data that provide clear, quantitative evidence that Mn_{12} exhibits resonant magnetization tunneling.

A fresh sample was prepared following the published procedure [20]. Agreement between a measured x-ray powder pattern and one calculated from the published single crystal data [20] confirmed the compound's identity; impurities are estimated to be less than 5%. Typical crystallite size is on the order of 10 μm long with an aspect ratio of about 10. Powdered material was mixed into Stycast 1266 and allowed to set in a magnetic field of 5.5 T at 300 K. This served to orient the crystallites with their easy axes (c axes) along the field direction; the orientation was confirmed visually under a microscope at 1000× magnification. A control sample was similarly prepared without an applied field. To ensure that the epoxy matrix plays no role, some of the measurements were repeated on a sample of Mn_{12} powder oriented and frozen in toluene. No corrections were made for the diamagnetic susceptibility of the epoxy, or for the diamagnetism of the nonmagnetic ligands in the molecule, which were both considered negligible. The dc magnetization was measured between 1.7 and 15 K in a Quantum Design MPMS-5 magnetometer equipped with a 5.5 T magnet.

Figure 1 shows the hysteresis loops taken with the magnetic field applied along the easy axis of the oriented sample at six temperatures between 1.7 and 2.8 K. Steps can be seen as the field is increased, while no noticeable steps occur when the field is reduced back to zero. The orientationally disordered control sample exhibited no steps. The inset of Fig. 1 shows that the steps occur only at specific values of magnetic field. Here the field at which a step occurs is plotted as a function of step number, with the one at zero field labeled 0. The linear fit indicates that there are steps at equal intervals of approximately 0.46 T. Seven steps, including 0, are observed, and we expect that more would be seen at lower temperatures. Not all steps are apparent at all temperatures: as temperature is lowered, new ones arise out of the saturation curve while others that are clearly observable at higher temperatures disappear. These "frozen" steps can be recovered when the magnetic field is swept more slowly.

After cooling the sample to 1.7 K in zero field, the magnetization was measured with increasing temperature in several applied fields, as shown in Fig. 2. The maximum in the curve, which corresponds to the blocking temperature T_B where the thermal energy becomes comparable to the barrier height, decreases as the measuring field is raised, as expected for a superparamagnetic system. However, the 0.9-T curve (marked with a bold line) shifts abruptly toward lower temperatures and actually crosses the 1.0- and 1.1-T curves. The blocking temperature is shown in the inset as a function of measuring field from 0.01 to 1.9 T. Superimposed on the overall decrease are several distinct dips, which occur at approximately the same fields as the steps in Fig. 1. Ignoring the dips, one obtains a zero-field blocking temperature of ~3.5 K. Using a measurement time of 100 sec and an Arrhenius prefactor, τ_0, of 2×10^{-7} sec [8,9,11,15,17], this corresponds to an energy barrier $\Delta E \approx 49$ cm^{-1}, in agreement with published results [8,9,13,14,17].

The periodic steps in the hysteresis loop, accompanied by dips in the blocking temperature at the same magnetic fields, as well as the crossing of the 0.9- and 1-T curves in Fig. 2, all imply that the relaxation rate is significantly faster at these fields. Evidence for this is shown in Fig. 3, where the difference between the magnetization and its asymptotic value, M_0, is plotted as a function of time on a semilogarithmic scale. Here the sample was cooled to 2.4 K in zero field and measured in a field of 0.9 or 0.95 T, as marked. While the asymptotic value of the magnetization is higher at the higher field, as expected, there is dramatically faster relaxation at 0.9 than at 0.95 T. The data exhibit exponential decay, $M = M_0(1 - e^{-(t-t_0)/\tau})$, as expected for a set of identical particles characterized by a single energy barrier. There is a faster-than-exponential decay during the initial

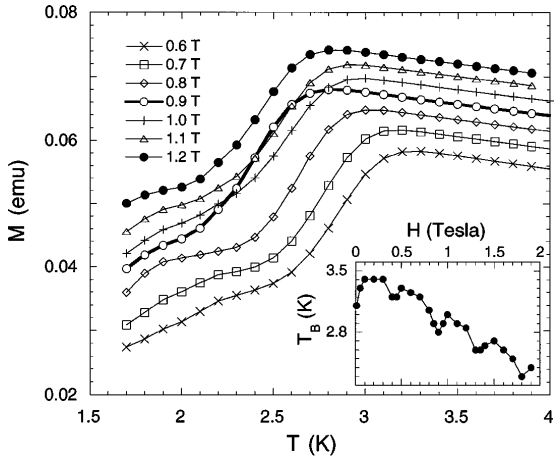

FIG. 2. Zero-field-cooled data for different measuring fields between 0.6 and 1.2 T. The data for 0.9 T (bold line) are anomalous, shifting abruptly towards lower temperatures. The inset shows the superparamagnetic blocking temperature, T_B, as a function of magnetic field. The anomalous dips occur at approximately the same fields as the steps in the hysteresis loops of Fig. 1.

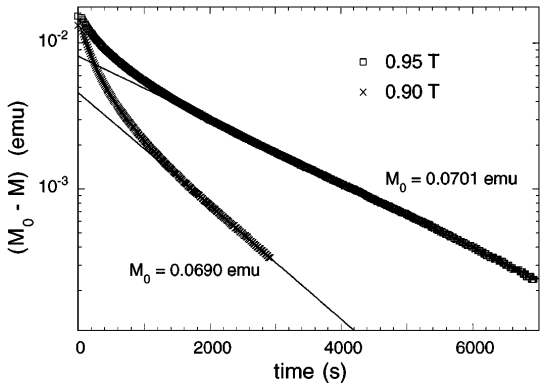

FIG. 3. The difference between the magnetization M and its asymptotic value, M_0, versus time on a semilogarithmic plot for a sample cooled to 2.4 K in zero field and then exposed to a field of 0.9 and 0.95 T. The straight lines are fits to an exponential function with the first ~2000 sec of data omitted. The values of M_0 were determined from the fit.

~2000 sec that is not understood. Fits to the data for $t > 2000$ sec yield time constants of 1048 and 2072 sec for 0.9 and 0.95 T, respectively. Similar increases in relaxation rate occur at all magnetic fields where steps in the magnetization are observed.

Our experimental findings for the orientationally ordered sample can be summarized as follows: (1) Steps are observed in the hysteresis loop with increasing field at equal intervals of field; no steps occur as the field is decreased. (2) The magnetic relaxation is more rapid when the magnetic field is in the neighborhood of such a step. (3) New steps appear at higher fields as the temperature is reduced while steps at lower fields become less apparent. (4) These frozen steps can be recovered by reducing the field sweep rate.

Following the suggestion of Barbara *et al.* [6] and of Novak and Sessoli [11], who found anomalous relaxation rates at $H = 0$ and 0.3 T in an unoriented sample, we attribute our observations to thermally assisted resonant tunneling between quantum spin states in Mn_{12}. In zero field, the spin of the molecule has two degenerate ground states separated by an anisotropy barrier, corresponding to spin parallel ($m = S$) or antiparallel ($m = -S$) to the c axis; a magnetic field breaks the symmetry making one state a true ground state. This is illustrated in Fig. 4, where the system is initially populated in the metastable $m = S$ ground state in the left-hand well. Tunneling across the barrier is induced when an applied field makes this state resonant with an excited level in the right-hand well; the tunneling is followed by rapid spontaneous decay from the excited state to the ground state. We propose that each step in the magnetization corresponds to such a resonance.

The simplest Hamiltonian for this system is

$$\mathcal{H} = -D\mathbf{S}_z^2 - g\mu_B\mathbf{S}\cdot\mathbf{H}, \qquad (1)$$

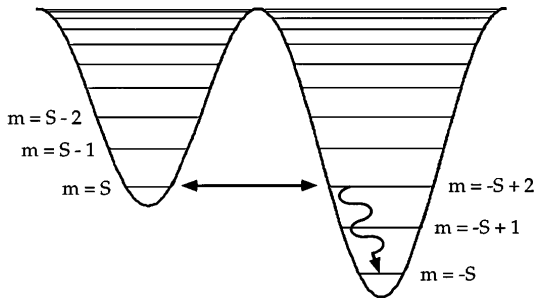

FIG. 4. Schematic diagram of the resonant tunneling model. Tunneling from the metastable state $m = S$ to an excited state $m = -S + n$ is followed by a rapid spontaneous decay into the ground state.

where D represents the anisotropy energy that breaks the zero-field Zeeman degeneracy. (We assume that the exchange interactions within the molecule are so large that it can be treated as a single spin-10 object). If the field is applied along the easy axis, the eigenstates of this Hamiltonian are $|S, m\rangle$, where S is the total spin and m is the corresponding magnetic quantum number. For clarity, we make $|S, S\rangle$ the initial state of the system. A simple calculation reveals that the field at which the state $|S, S\rangle$ coincides in energy with the state $|S, -S + n\rangle$, is

$$H_{S,-S+n} = -Dn/g\mu_B. \qquad (2)$$

Thus, steps occur at even intervals of field, as observed. Since the Hamiltonian, Eq. (1), commutes with S_z, the tunneling must arise from a perturbation, such as transverse anisotropy or a small off-axis component of the magnetic field. Interestingly, our model implies that whenever the field is tuned to a step, each state in the left well coincides with a state in the right well, setting up a multiple resonance. Given that a step occurs every 0.46 T, we find $D/g = 0.21\ \text{cm}^{-1}$, consistent with the published values of $D \sim 0.5\ \text{cm}^{-1}$ and $g \sim 1.9$ obtained from high-field and ESR experiments [13,14]. As a further check, we estimate that the anisotropy barrier at zero field is $g(D/g)S^2 \sim (1.9)(0.21\ \text{cm}^{-1})(100) = 41\ \text{cm}^{-1}$, consistent with the estimate of $49\ \text{cm}^{-1}$ obtained from the blocking temperature. For an $S = 10$ system, there should be 21 steps ($n = 0$ to 20), the last corresponding to the elimination of the barrier. Assuming that the blocking temperature on resonance scales as $T_B \sim (1 - H/H_c)^2 \sim (1 - n/n_c)^2$, we find a zero-temperature intercept of $n_c = 21.6$, indicating there are roughly the number of steps predicted by our model. Measurements at lower temperatures are needed to observe the higher-numbered steps; we estimate that step 19 should become apparent at around 10 mK and 8.74 T.

We find experimentally that the transition rate decreases rapidly as temperature is reduced, indicating that the resonant tunneling is thermally assisted. As noted above, our model predicts multiple level crossings at each resonant field, implying that all levels can tunnel simultaneously. Novak and Sessoli [11] have suggested that the

thermally populated excited states dominate the tunneling at zero field. As the temperature is decreased, the levels near the top of the metastable well become depopulated and the transition decreases.

The proposed model of field-tuned, thermally assisted resonant tunneling out of a metastable spin state is consistent with the experimental observations. (1) When the field is reduced from saturation, no steps are seen because the system is already in the true ground state. When the field is reduced to near zero or reversed, the state becomes metastable allowing resonant transitions and the corresponding steps. (2) Resonant tunneling causes the transition rate to increase when the field is tuned to a step. (3) The higher-numbered steps have progressively faster magnetic relaxation times because the anisotropy barrier is lowered by the applied field. Therefore, lower temperatures are needed to observe them. (4) The recovery of frozen steps as the field sweep rate is reduced can be understood qualitatively. If the field is swept too fast, not enough time is spent in the region of a step, and no appreciable relaxation occurs; the step is "frozen out." It will appear when the sweep rate is sufficiently slow that the time spent within the region of the step is comparable to its characteristic relaxation time.

To our knowledge, this is the first observation of magnetization steps at an ordered set of fields within a hysteresis loop. Similar steps, which occur, however, with both increasing and decreasing field, have been seen in some other systems. These include dilute magnetic semiconductors with antiferromagnetically coupled spin pairs [21,22] and $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$, a paramagnetic molecular ring of Fe^{3+} ions that order antiferromagnetically [23]. These steps are found in a regime where the magnetization is reversible and are thought to occur when the field induces the total spin to change between discrete values. We note that for the Mn_{12} such a model yields an unphysically low exchange constant of less than 1 K. Furthermore, the Mn_{12} has no stable, stationary magnetization values other than saturation. Steps have also been found in other hysteretic systems, notably $SmCo_{3.5}Cu_{1.5}$ [24], but these occur at irregular fields that depend on details of the measurement, such as the field sweep rate, and are attributed to avalanches triggered by domain wall depinning events.

In summary, we report quantum-mechanical effects on a macroscopic scale in the magnetization of oriented Mn_{12} crystals. We attribute this to thermally assisted, field-tuned resonant tunneling of magnetization between different quantum spin states, and suggest that its observation in a sample of macroscopic size derives from tunneling in a large (Avogadro's) number of identical high-spin molecules.

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