PHYSICAL REVIEW B VOLUME 55, NUMBER 9 1 MARCH 1997-I

Evidence for resonant tunneling of magnetization in Mn_{12} acetate complex

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(Received 8 August 1996; revised manuscript received 4 November 1996)

We have measured the dc magnetization at low temperatures of tetragonal crystals of Mn_{12} acetate complex $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$, a material composed of a large (Avogadro's) number of identical magnetic molecules, each of spin 10. Exchange coupling between Mn ions within each molecule is very strong, while the interaction between molecules is negligible. A large, uniaxial anisotropy (~60 K) gives rise to a doubly degenerate ground state corresponding to spin projections of ± 10 along the easy axis (c axis); hysteretic behavior is found below a blocking temperature $T_b \sim 3$ K. Based on measurements of oriented crystallites at temperatures between 1.7 and 3.2 K, we report strong evidence for resonant tunneling of the magnetization: periodic steps in the hysteresis loop, and periodic marked increases in the magnetic relaxation rate at the magnetic fields corresponding to these steps. A total of seven increases in the relaxation rate were found within the temperature range of our experiments with a period of 0.46 T; we suggest that many more such steps would be found at lower temperatures. We attribute these observations to thermally assisted resonant tunneling of the magnetization and propose a detailed model to account for our results. [S0163-1829(97)00709-1]

BACKGROUND

The possibility of quantum tunneling of magnetization was first suggested in 1959 by Bean and Livingston,[1] has been revisited periodically,[2] and has recently become a subject of great interest. Guided by the concept of macroscopic quantum tunneling introduced by Caldeira and Leggett,[3] important theoretical progress was made in the late 1980's.[4–6]

Experimental evidence for tunneling has been reported by Awschalom and co-workers,[7] who have observed a resonance in the susceptibility of horse-spleen ferritin at very low temperatures; they attribute this to quantum coherent tunneling of the magnetization vector between two degenerate orientations in a double well potential. These results have received much attention and have elicited considerable debate.[8]

A great deal of effort has been devoted to obtaining experimental evidence of quantum tunneling of magnetization from measurements of magnetic relaxation. In many materials[9] the magnetic viscosity levels off to a constant, temperature-independent value below some crossover temperature, contrary to what one expects from classical (thermal) processes. This has been attributed to quantum-mechanical reversal of the magnetization. The occurrence of this phenomenon in a wide variety of systems strongly supports this interpretation, although relaxation measurements often do not lend themselves to rigorous comparison with theory.[10] The magnetic relaxation observed in most materials represents a statistical average over a large number of events broadly distributed in energy and time scale due to random factors such as particle size, making quantitative comparison with theory difficult; a notable exception is single-crystal orthoferrite $TbFeO_3$, where exponential magnetic relaxation indicates a single energy barrier throughout the material.[11]

It is thus very desirable for relaxation measurements (and imperative for experiments on resonant absorption) to obtain samples containing magnetic clusters that are closely monodispersed. In this paper we present results on such a material, $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$, often referred to as Mn_{12} acetate, or simply Mn_{12}. Unlike most ensembles of magnetic clusters, the magnetic subunits of such a molecular crystal have unique, chemically determined properties: a macroscopic sample of Mn_{12} is composed of a large (Avogadro's) number of identical particles with the same magnetic properties and identical characteristic energies. Another important feature of this system is that while the spin of each cluster, $S=10$, is large for a molecular system, it is small relative to most superparamagnetic systems. This small spin value together with the system's large magnetocrystalline anisotropy yields an appreciable energy separation between spin levels, allowing the observation of a novel physical effect: resonant spin tunneling between matching levels on opposite sides of a potential barrier. By virtue of these features, the relaxation measurements described below provide very strong evidence for spin tunneling in Mn_{12}.

Mn_{12} acetate has been the focus of a great deal of experimental[12–21] and theoretical[22–24] activity since it was first synthesized by Lis[25] in 1980. It contains four Mn^{4+} ($S=\frac{3}{2}$) ions in a central tetrahedron surrounded by eight Mn^{3+} ($S=2$) ions, as shown in the inset to Fig. 1. The Mn ions are coupled by superexchange through oxygen bridges; high-field and ac susceptometry experiments indicate an $S=10$ ground state,[16,17,20] suggesting a simple picture of the magnetic order with all the outer spins pointing up and the four

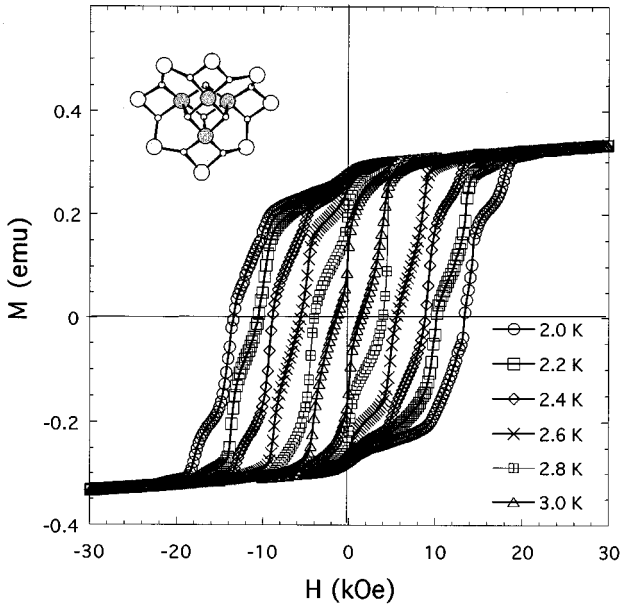

FIG. 1. Hysteresis loops at six temperatures of a Mn_{12} acetate sample oriented in paraffin. Inset: schematic diagram of $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$, taken from Ref. 18. Only the Mn^{4+} (large shaded circles), Mn^{3+} (large open circles), and oxygen (small circles) ions are shown.

inner ones pointing down.[16,18,22] These magnetic clusters crystallize into a tetragonal lattice, and magnetic interactions between them are thought to be negligible since the distance between Mn ions in neighboring molecules is at least 7 Å (Refs. 18 and 25) and the Curie temperature ≈ 0.05 K.[13–15,20] Experiments indicate a large magnetocrystalline anisotropy[12–21] and superparamagnetic behavior.[12–18,20,21] Hysteresis is observed[13,18,19,21] below a blocking temperature of about 3 K and ac susceptibility data as well as dc magnetic relaxation data have indicated a single characteristic relaxation time[13,15,18,20,21] that obeys an Arrhenius law down to 2.1 K, $\tau = \tau_0 e^{\Delta E/k_B T}$. Possible evidence for quantum tunneling at low temperatures has been cited by a number of authors.[12–15,19]

In this paper, we present details of experimental results[26,27] that provide strong evidence of resonant tunneling of the spin in Mn_{12} acetate complex. We base our conclusions on the observation of periodic steps in the hysteresis loop and periodic marked increases in the magnetic relaxation rate at the magnetic fields corresponding to these steps. We report increases in the relaxation rate that are periodic in magnetic induction, with a period of 0.46 T. Seven maxima have been found within the temperature range of our experiments (down to 1.7 K) and we suggest that experiments to lower temperatures will demonstrate that there are a total of $2S+1=21$ such steps. We attribute our observations to thermally assisted resonant tunneling in a double well potential[12,15] and propose a detailed model that quantitatively accounts for the effects. Our experimental results have recently been confirmed in measurements of a single crystal.[28]

SAMPLES AND EXPERIMENTAL PROCEDURE

Mn_{12} acetate was prepared following the published procedure of Lis.[25] Agreement between a measured x-ray powder

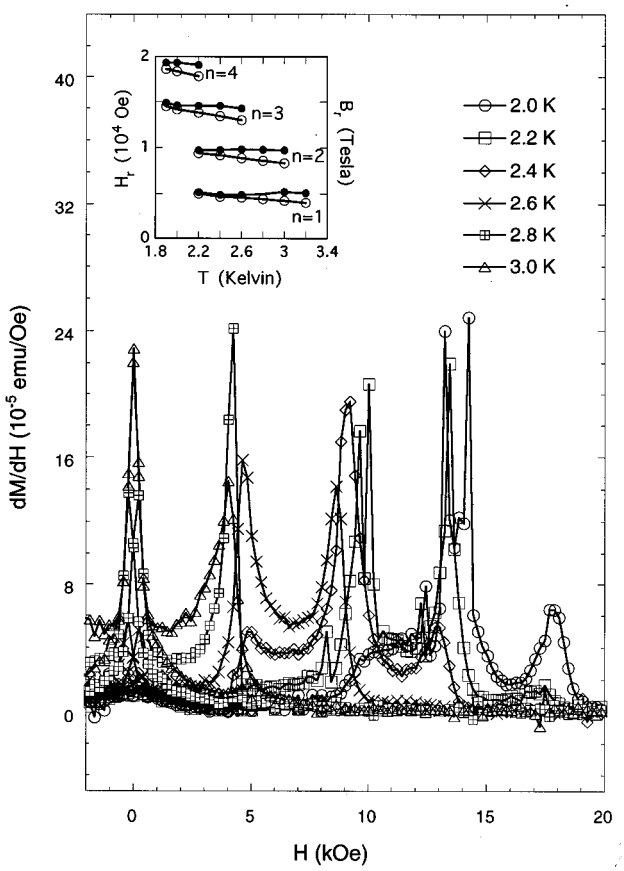

FIG. 2. The slope, dM/dH, of the curves of Fig. 1 as a function of magnetic field H. The inset shows the external magnetic field H (open symbols) and internal magnetic induction $B = H + 4\pi M$ (closed symbols) at which the maxima occur, plotted as a function of temperature.

pattern and one calculated from the published single-crystal data[25] confirmed the compound's identity; impurities are estimated to be less than 5%. The first specimens, in the form of small elongated crystallites, were oriented in a large magnetic field as described in Ref. 26.

The dc magnetization was measured between 1.7 and 15 K using commercial magnetometers equipped with a 55-kOe magnet. Measurements were taken for samples mounted with their easy axes at various angles with respect to the field. We estimate that the angle between the easy axis and the field direction was determined to within $\pm 5\%$.

EXPERIMENTAL RESULTS

The experimental data are shown in Figs. 1–5. For a sample oriented in paraffin, Fig. 1 shows hysteresis loops at six temperatures between 2 and 3 K as a function of magnetic field taken with the field applied along the easy axis of the sample. As expected, the area enclosed within the hysteresis loops is found to increase as the temperature is reduced. We call attention to the unexpected steps that are clearly evident. As one proceeds around the loop, steps occur as the magnetic field is increased from zero, no noticeable steps occur when the field is reduced back to zero, steps occur once more as the field is raised in the opposite direction, and so on. In short, steps are seen when the field in-

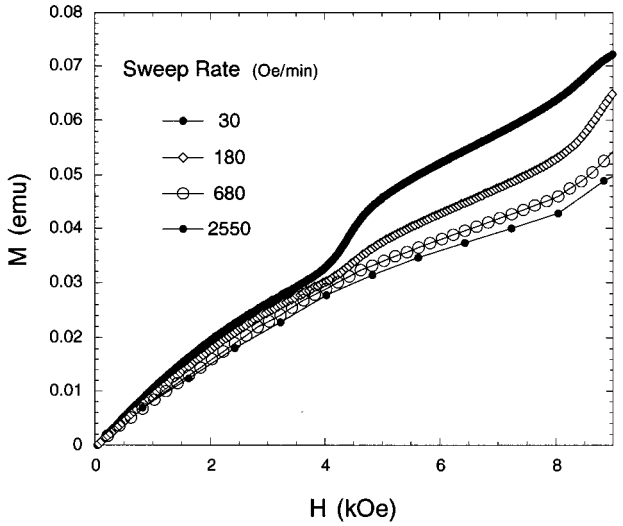

FIG. 3. First magnetization (i.e., initial magnetization after cooling the sample in zero field) of Mn_{12} acetate as a function of magnetic field for different sweep rates, as labeled, at 2.4 K. (Sample oriented in Stycast 1266).

creases in either direction, and they are absent when the field is decreased. Samples of oriented powder frozen in toluene as well as single crystals exhibited similar, but sharper steps. Powdered control samples that were not oriented during preparation showed smooth hysteresis loops with no steps (except for a ''pinched'' shape near zero field), a clear indication that the steps are associated with the orientational ordering.

Close examination of the data of Fig. 1 reveals that, despite the apparent complexity, the steps occur at specific values of magnetic field that are approximately independent of the temperature. This is clearly demonstrated in Fig. 2, where we plot the derivative dM/dH as a function of field H. As shown in the inset to Fig. 2, a careful analysis shows that the external field H for each step does shift slightly with temperature, and it is instead the magnetic induction internal

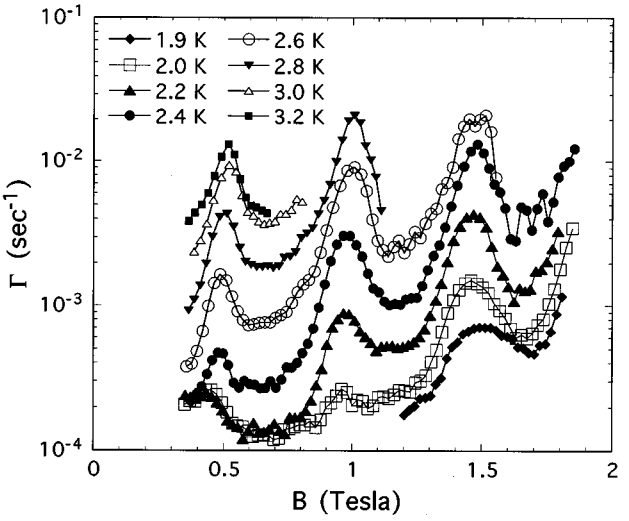

FIG. 4. For a sample oriented in Araldite, the decay rate Γ as a function of internal field B. Here Γ is deduced from Eq. (1) and the slopes (dM/dH) of the measured hysteresis loops.

to the sample, $B=H+4\pi M$, that remains fixed. This is not unreasonable, since the local mean field at each molecular site is B. The steps (or maxima) occur at equal intervals of magnetic induction of approximately 0.46 T. We have observed seven such maxima (including the one at zero field) and additional ones are expected at lower temperatures.

Figure 1 indicates interesting changes that occur with temperature: as temperature is lowered, new steps arise out of the saturation curve while others that are clearly observable at higher temperatures become less pronounced. These ''frozen'' steps can be recovered when the magnetic field is swept more slowly, as can be seen in Fig. 3, where first-magnetization data at 2.4 K is shown at several different sweep rates.

The periodic steps in the hysteresis loop, which are accompanied by dips in the blocking temperature at the same magnetic fields,[26] imply that the relaxation rate is significantly faster whenever the magnetic induction is an integer multiple of 0.46 T. This was confirmed through direct measurements of the relaxation at various fields and temperatures.[27] Here we further illustrate the periodic nature of the decay rate in the following way. If one assumes that for a given fixed field, the magnetization approaches its equilibrium value $M_{eq}(H)$ exponentially, i.e., $M(H,t)=M_{eq}(H)\{1-\exp(-\Gamma t)\}$, one can write

$$dM/dt=(dM/dH)(dH/dt)=\Gamma\{M_{eq}(H)-M(H,t)\}. \qquad (1)$$

Using the measured value $M(H,t)$ of the magnetization, the measured equilibrium magnetization $M_{eq}(H)$, and the known fixed sweep rate $dH/dt=10$ Oe/s, one can estimate the decay rate Γ at each temperature from the derivative (dM/dH) of the hysteresis loops. The resulting Γ plotted in Fig. 4 shows clear, periodic maxima in the relaxation rate as a function of magnetic induction B.

Studies of the magnetization were also made for several fixed angles between the easy axis of magnetization of an oriented sample and the external magnetic field H. The magnetization is shown in Fig. 5(a) as a function of the internal field B for angles 30°, 45°, and 60°. These curves, as well as their derivatives dM/dB plotted as a function of B in Fig. 5(b), indicate that the fields at which enhanced relaxation occurs depends on angle. On the other hand, Fig. 5(c) shows clearly that the maxima in dM/dB always occur at specific values of longitudinal component of the induction $B\cos\theta$. It is important to note that our control sample, composed of crystallites that are randomly oriented with respect to the field direction, has a continuous distribution of longitudinal fields $B\cos\theta$ giving rise to a distribution of resonant fields and smooth hysteresis loops, consistent with our observations. In orientationally disordered samples the steps are smeared out, making them unobservable.

Our experimental findings for orientationally ordered samples of Mn_{12} acetate complex can be summarized as follows. (1) Steps are observed in the hysteresis loop with increasing field at equal intervals of 0.46 T; no steps occur as the field is decreased. (2) The magnetic relaxation rate exhibits maxima at these fields. (3) New steps appear at higher fields as the temperature is reduced while steps at lower fields become less apparent. These ''frozen'' steps can be

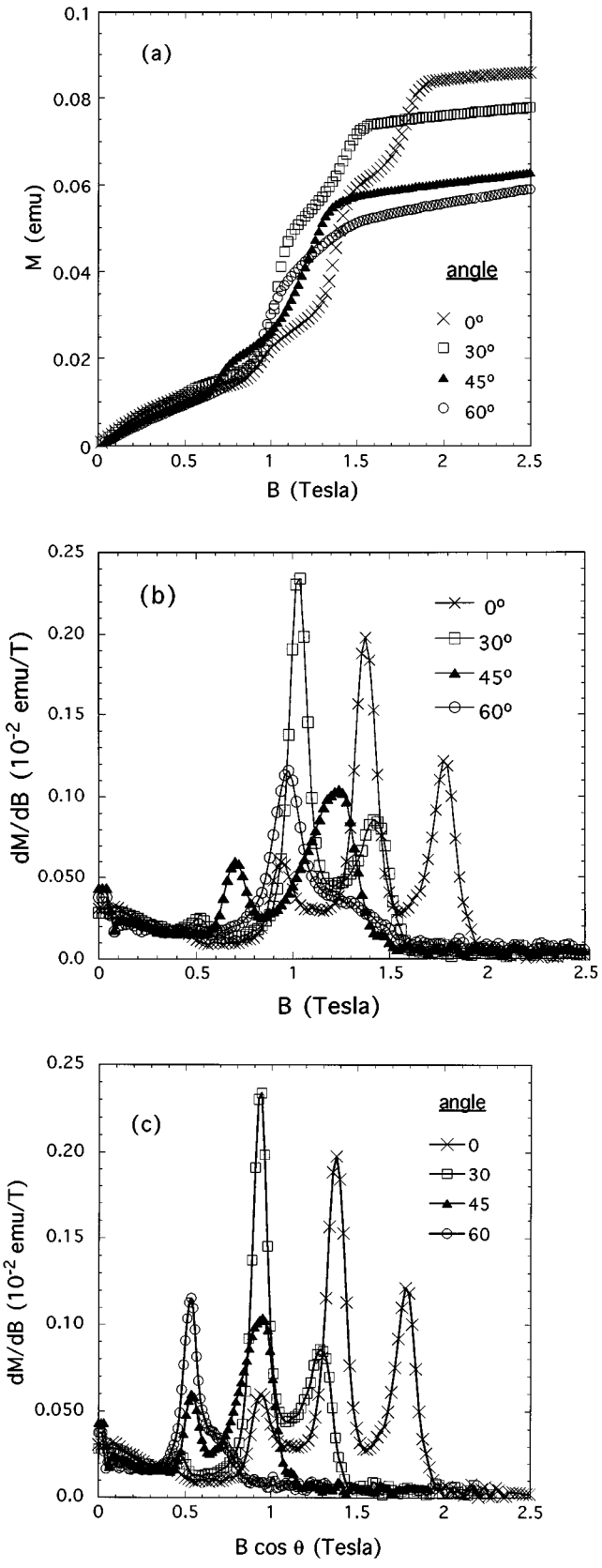

FIG. 5. (a) Magnetization as a function of the magnetic induction B for different angles θ=30°, 45°, and 60° between the external magnetic field and the easy axis of the sample. (b) The derivative dM/dB of the curves shown in (a), plotted as a function of B. (c) The derivative dM/dB of the curves shown in (a), plotted as a function of $B\cos\theta$. (Samples oriented in Araldite).

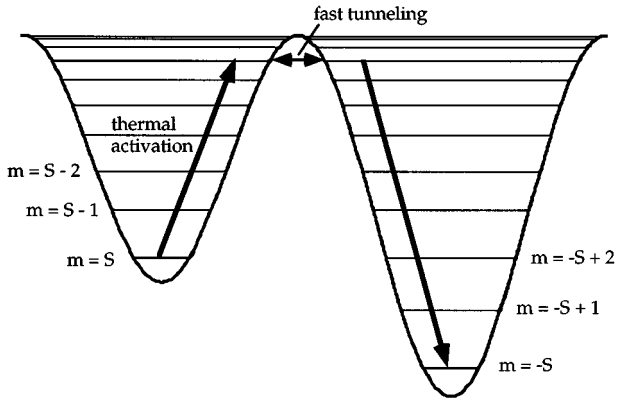

FIG. 6. Schematic diagram illustrating the proposed thermally assisted resonant tunneling process (after Ref. 15). On resonance, the system is thermally activated within the metastable left well to an excited state near the top of the energy barrier, where it rapidly tunnels to the right well.

recovered by reducing the field sweep rate. (4) Studies for several orientations of the magnetic field with respect to the easy axis of the sample demonstrate that these effects are periodic with *longitudinal* field, that is, the component of the field parallel to the easy axis of the sample.

PROPOSED MODEL

We attribute our observations to thermally assisted resonant tunneling between quantum spin states in Mn_{12}. We will discuss in detail a simple model that is consistent with all of the data described above.

Strong uniaxial magnetic anisotropy determines that each molecule of Mn_{12} has a doubly degenerate spin ground state in zero field. An anisotropy barrier separates these ground states, which correspond to the spin being parallel ($m=S$) or antiparallel ($m=-S$) to the c (easy) axis; a magnetic field breaks the symmetry making one state a true ground state. This is shown in Fig. 6, where the energy levels correspond to different projections of the spin along the easy axis. We propose that tunneling from the metastable left-hand well is induced when its energy levels coincide with energy levels in the right-hand well. In this picture, each step in the magnetization corresponds to such a resonance. Furthermore, following the suggestion of Novak and Sessoli,[15] we believe that the relaxation process is thermally assisted, with the tunneling primarily occurring between high-lying excited states where the tunneling rate is fastest. Figure 6 illustrates this process: the system is thermally activated to a fast-tunneling level near the top of the barrier, tunnels across and then spontaneously decays into the ground state in the right well. On resonance, this process then produces an effective reduction in the energy barrier. In contrast, for magnetic fields that do not correspond to resonant tunneling, the expected classical relaxation rate is determined by thermal transitions over the full barrier $U(H)=U(B)[1-B/B_c]^2$ with $B_c\approx 10$ T.

The simplest Hamiltonian for this system is

$$H=-DS_z^2-g\mu_B\mathbf{S}\cdot\mathbf{B}, \tag{2}$$

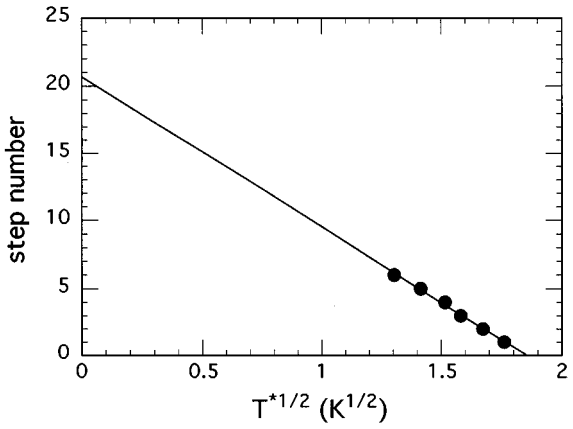

FIG. 7. Step number plotted as a function $(T^*)^{1/2}$. Here T^* is the temperature at which a step first appears, and is assumed to be proportional to the barrier height.

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. A simple calculation reveals that the field at which the state $|S,m\rangle$ (in the left well) coincides in energy with the state $|S,-m+n\rangle$ (in the right well), is

$$B_{m,-m+n}=-\frac{Dn}{g\mu_B}. \tag{3}$$

Thus, steps occur at even intervals of field, as observed. It is important to note that this result, Eq. (3), is independent of m, implying that all levels in the left well come into resonance with levels in the right well at the same values of magnetic field. In other words, within this model, whenever the field is tuned to a step, each state in the left well coincides with a state in the right well. Given that a step occurs every 0.46 T, Eq. (3) yields $D/g=0.21$ cm^{-1}, consistent with the published values of $D\sim0.5$ cm^{-1} and $g\sim1.9$ obtained from high-field and electron spin resonance (ESR) experiments.[16,17] As a further check, we estimate that the anisotropy barrier at zero field is $g(D/g)S^2\sim(1.9)(0.21$ cm$^{-1})$ $(100)=41$ cm$^{-1}=59$ K, consistent with values of $\approx$61–69 K deduced from other measurements.[12–15,18,20,21] For an $S=10$ system, there should be $2S+1=21$ steps ($n=0$ to 20), the last corresponding to the elimination of the barrier. One can estimate the total number of steps expected from the data of Fig. 1 by noting the temperature at which a step first appears. This temperature, T^*, is a rough measure of the barrier height and should decrease as $\approx(B-B_c)^2$. Since the step number n is proportional to B, one expects $T^*\approx(n-n_c)^2$. Figure 7 shows the step number plotted as a function $(T^*)^{1/2}$. The linear fit extrapolates to $n_c\approx20.6$ at zero temperature, consistent with 21 steps (counting $n=0$). Measurements at lower temperatures are needed to observe the higher-numbered steps; we estimate that step No. 19 should become apparent at around 10 mK and 8.74 T.

Since the Hamiltonian, Eq. (2), commutes with S_z, this simple form does not allow any tunneling at all. Tunneling must derive from off-diagonal terms in the Hamiltonian. Magnetic tunneling is most often attributed to the presence of a transverse component in the magnetocrystalline anisotropy tensor. Time-reversal symmetry requires that such an anisotropy must appear as an even power of the spin operator: $H'\sim aS_x^{2n}+bS_y^{2p}$, where n and p are integers. Mn_{12} has tetragonal symmetry, so that the lowest order transverse term is $H'=k(S_x^4+S_y^4)$, which can be rewritten as $H'=k/8(S_+^4+S_-^4)+$(terms that produce no transitions), where S_+ and S_- are the usual spin raising and lowering operators.[23,24] This form only allows transitions that obey the selection rule $\Delta m=\pm4q$ (integer q). This would, in turn, prohibit every other step: for whenever the system is tuned to an odd numbered step (e.g., $n=1$), the levels in resonance are always matched even/odd and odd/even (e.g., $10/-9$, $9/-8$, $8/-7$,...), yielding a forbidden, odd Δm for all matched levels.

TABLE I. Tunneling rates for different m values calculated from Eq. (4), taken from Ref. 31, with $s=10$, and $B_{\text{trans}}=0.01$ T and $D=0.41$ cm^{-1}.

m	Tunneling rate (Hz)
1	3.2×10^{8}
2	1.1×10^{5}
3	3.5×10^{0}
4	2.3×10^{-5}
5	4.7×10^{-11}
6	3.7×10^{-17}
7	1.2×10^{-23}
8	1.7×10^{-30}
9	1.1×10^{-37}
10	2.11×10^{-45}

On the other hand, the data indicate that all steps are observed and none are forbidden.[29] A possible source of tunneling, one that does not prohibit any steps, could be a small transverse magnetic field, perhaps of dipolar or hyperfine[24,30] origin. A transverse field would give rise to a perturbative term, $H'=-g\mu_BB_{\text{trans}}S_x=-g\mu_BB_{\text{trans}}(\frac{1}{2})(S_++S_-)$, which allows all transitions $\Delta m=\pm1q$, prohibiting no steps.

The tunneling rate of a large uniaxial spin in the presence of a transverse magnetic field has been calculated by Garanin[31] in zero longitudinal field at $T=0$. The tunnel splitting E_m of two degenerate states with spin projections $\pm m$ is given by

$$\Delta E_m=\frac{2D}{[(2m-1)!]^2}\frac{(S+m)!}{(S-m)!}\left(\frac{h}{2D}\right)^{2m} \tag{4}$$

with $h=g\mu_BB_{\text{trans}}$. Using an estimated 0.01 T for the transverse field and the value of D determined from our experiments, Eq. (4) yields the tunneling rates listed in Table I. The tunneling rates are very broadly distributed, with the rates of adjacent level crossings differing by several orders of magnitude. These results imply that tunneling from the ground states and first few excited states is negligible, while the tunneling between states near the top of the wells is so rapid that they are equivalent to a short. We contend that tunneling is strongly dominated by one or two levels near the top of the well, and the time rate of decay is determined by the time

required to repopulate these levels. Hence, on resonance the effective energy barrier is reduced: the system no longer needs to be thermally activated to the top of the barrier, but only to a fast-tunneling level at a somewhat lower energy, as illustrated in Fig. 6. The dips[26] found in the blocking temperature can be interpreted as drops in the effective energy barrier, consistent with this picture. If this model is correct in detail, the decay rate may not be sensitive to the precise value of transverse field, being instead determined by the time required for thermal activation to the level that dominates the tunneling. One might expect abrupt changes in the relaxation rate at particular values of the transverse field, when the dominant tunneling process crosses over from one level to another.

The data of Fig. 1 indicate that temperature plays an important role in the relaxation process. Steps in the hysteresis loop at small fields are quite pronounced at 2.9 K, and gradually fade as the temperature is lowered. This is consistent with tunneling from excited states near the top of the potential well. As the temperature is decreased, the levels near the top of the metastable well become depopulated and the transition rate decreases.

Friedman and Chudnovsky[32] have calculated the effect of a transverse magnetic field on the values of longitudinal field for which the level crossings occur. Their results indicate that for any value of $B_{\rm trans}$ the change in the resonance condition, Eq. (3), for the longitudinal field $B_{\rm long}$ at which a resonance occurs, is exactly zero up to fourth order in perturbation theory, and no appreciable change in the ''resonant'' longitudinal field is expected. This is borne out by the data shown in Fig. 5: while the transverse magnetic field $B \sin\theta$ changes as the easy axis of the sample is tilted with respect to the direction of the magnetic field, the values of the longitudinal field $B \cos\theta$ at which the resonances occur remains fixed.

An alternative model of the relaxation process in this system has been proposed by Burin, Prokof'ev, and Stamp[33,34] in which the relaxation proceeds via flip-flop transitions induced by dipolar coupling between Mn_{12} clusters. As discussed above, the energy levels on the two sides of the barrier coincide when the field is tuned to resonance. These authors suggest that the decay of the magnetization in the right-hand well generates energy quanta that precisely match the energies needed to raise a neighboring spin to excited levels in the left-hand metastable well, thus promoting relaxation at resonant values of the external field. This process involves the exchange of virtual photons since it is mediated by dipolar interactions. We note that the Curie-Weiss temperature, a measure of the dipolar interaction strength, is about 0.05 K for Mn_{12}, and one might thus expect interactions between spins to be negligible compared to spin-phonon couplings at measuring temperatures of 2 or 3 K. On the other hand, the anomalously small Arrhenius prefactor[13,14,18,20] found experimentally may indicate that spin-phonon relaxation times are uncharacteristically slow in this system, making it possible for dipolar interactions to be the dominant process. Measurements in similar materials in which the magnetic clusters are further apart could provide a test of this model.

SUMMARY AND CONCLUSIONS

The proposed model of field-tuned, thermally assisted resonant tunneling out of a metastable spin state is consistent with the experimental observations: (1) Resonant tunneling causes the transition rate to increase at values of the magnetic field that yield energy level crossings in the two wells. (2) When the field is reduced from saturation, no steps are seen because the spin is already in the lower-energy potential well. When the field is reduced to near zero or reversed, the populated spin states becomes metastable allowing resonant transitions and the corresponding steps. (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.

The fact that none of the transitions appear to be forbidden suggests that the tunneling does not originate from the magnetocrystalline anisotropy, but rather from some transverse field that may be hyperfine or dipolar in origin. Based on the calculation of Garanin[31] for the tunneling in such a double well potential (in zero longitudinal field at $T=0$), we further suggest that the tunneling is dominated by very few (perhaps one) pair of matched levels near the top of the barrier. Studies as a function of externally applied transverse magnetic field are currently underway to test this model.

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[35,36] and $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$, a paramagnetic molecular ring of Fe^{3+} ions that order antiferromagnetically.[37] These steps are found in a regime where the magnetization is reversible and mark the points when the field induces the total spin to change between discrete values. In contrast, for Mn_{12} there are no stable, stationary magnetization values other than equilibrium, and the system will always relax toward its equilibrium value; however, it does so most rapidly at periodic values of magnetic field that correspond to level crossings. Furthermore, treating our observed steps as due to total-spin transitions yields an unphysically low exchange constant of less than 1 K for Mn_{12}.

More similar to the present work are steps that have been observed in dilute paramagnetic systems, where the steps mark transitions between states within the same spin manifold.[38–40] The essential difference between all of these systems and Mn_{12} is that they all have a positive anisotropy parameter D and so have no magnetic metastability, no hysteresis and no possibility of tunneling. Steps have been found in other hysteretic systems,[41,42] but these occur at irregular fields that depend on the details of the measurement, such as the field sweep rate or temperature, and are attributed to the motion of domain walls.

In summary, we report the observation of periodic steps in the hysteresis loop, and periodic maxima in the relaxation rate of oriented crystallites of Mn_{12} acetate complex. These effects are strong evidence for thermally assisted resonant tunneling of the magnetization between different quantum spin states in this high-spin molecular magnet. Our data bear an interesting resemblance to the macroscopic resonant tunneling recently reported between energy levels in different fluxoid wells of a weakly damped superconducting quantum interference device.[43] We attribute our observation of quantum-mechanical effects on a macroscopic scale to the presence of a large (Avogadro's) number of identical molecules with their easy axes all oriented in the same direction.

Thomas *et al.*[28] have recently observed similar steps in the magnetization of Mn_{12} which they, as well as Stamp[44] and Chudnovsky,[45] attribute to resonant spin-tunneling in a double well potential.

ACKNOWLEDGMENTS

We are greatly indebted to Eugene Chudnovsky for numerous discussions, and for his continued participation and interest in this work. We thank J. Maciejewski for her participation in fabricating the samples. We thank A. L. Burin and Snezana Bogdanovic for many useful discussions, and Dariusz Przybylski for assistance in preparing some control samples. The work at City College was supported by the U.S. Air Force of Scientific Research under Grant No. F49620-92-J-0190.

*On leave from the University of Zaragoza.

[1] C. P. Bean and J. D. Livingston, J. Appl. Phys. **30**, 120S (1959).

[2] See, for example, T. Egami, Phys. Status Solidi A **20**, 157 (1973); B. Barbara, G. Fillion, D. Gignoux, and R. Lemaire, Solid State Commun. **10**, 1149 (1973); O. Bostanjoglo and H. P. Gemund, Phys. Status Solidi A **17**, 115 (1973); **48**, 41 (1978); J. A. Baldwin, Jr., F. Milstein, R. C. Wong, and J. L. West, J. Appl. Phys. **48**, 2612 (1977); W. Riehemann and E. Nembach, J. Appl. Phys. **55**, 1081 (1984); **57**, 476 (1986).

[3] A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. **46**, 211 (1981); Ann. Phys. (N.Y.) **149**, 374 (1983).

[4] E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. **60**, 661 (1988); Phys. Rev. B **37**, 9455 (1988).

[5] M. Enz and R. Schilling, J. Phys. C **19**, 1765 (1986).

[6] J. L. van Hemmen and A. Süto, Europhys. Lett. **1**, 481 (1986); Physica B **141**, 37 (1986).

[7] D. D. Awschalom, D. P. DiVincenzo, and J. F. Smyth, Science **258**, 414 (1992); S. Gider, D. D. Awschalom, T. Douglas, S. Mann, and M. Chaprala, Science **268**, 77 (1995), and references therein.

[8] J. Tejada, Science **272**, 424 (1996); A. Garg, *ibid*. **272**, 424 (1996); S. Gider, D. D. Awschalom, D. P. DiVincenzo, and D. Loss, *ibid*. **272**, 425 (1996).

[9] See, for example, J. Tejada, X. X. Zhang, and E. M. Chudnovsky, Phys. Rev. B **47**, 14 977 (1993); J. Tejada and X. X. Zhang, J. Appl. Phys. **73**, 6709 (1995); J. Tejada and X. X. Zhang, J. Magn. Magn. Mater. **140–144**, 1815 (1995); C. Paulsen, L. C. Sampaio, B. Barbara, R. Tucoulou-Tachoueres, D. Fruchard, A. Marchand, J. L. Tholence, and M. Uehara, Europhys. Lett. **19**, 643 (1992); J. I. Arnaudas, A. del Moral, D. de la Fuente, and P. A. J. de Groot, Phys Rev. B **47**, 11 924 (1993); M. M. Ibrahim, S. Darwish, and M. S. Seehra, *ibid*. **51**, 2955 (1995).

[10] See, for example, L. Gunther, in *Quantum Tunneling of Magnetization*, edited by L. Gunther and B. Barbara (Kluwer, Dordrecht, 1995), p. 413.

[11] X. X. Zhang, J. Tejada, A. Roig, O. Nikolov, and E. Molins, J. Magn. Magn. Mater. **137**, L235 (1994); J. Tejada, X. X. Zhang, A. Roig, O. Nikolov, and E. Molins, Europhys Lett. **30**, 227 (1995).

[12] B. Barbara, W. Wernsdorfer, L. C. Sampaio, J. G. Park, C. Paulsen, M. A. Novak, R. Ferré, D. Mailly, R. Sessoli, A. Caneschi, K. Hasselbach, A. Benoit, and L. Thomas, J. Magn. Magn. Mater. **140–144**, 1825 (1995).

[13] C. Paulsen and J.-G. Park, in *Quantum Tunneling of Magnetization* (Ref. 10), p. 189.

[14] C. Paulsen, J.-G. Park, B. Barbara, R. Sessoli, and A. Caneschi, J. Magn. Magn. Mater. **140–144**, 379 (1995).

[15] M. A. Novak and R. Sessoli, in *Quantum Tunneling of Magnetization* (Ref. 10), p. 171.

[16] A. Caneschi, D. Gatteschi, R. Sessoli, A. L. Barra, L. C. Brunel, and M. Guillot, J. Am. Chem. Soc. **113**, 5873 (1991).

[17] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. **115**, 1804 (1993).

[18] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature **365**, 141 (1993).

[19] C. Paulsen, J.-G. Park, B. Barbara, R. Sessoli, and A. Caneschi, J. Magn. Magn. Mater. **140–144**, 1891 (1995).

[20] M. A. Novak, R. Sessoli, A. Caneschi, and D. Gatteschi, J. Magn. Magn. Mater. **146**, 211 (1995).

[21] R. Sessoli, Mol. Cryst. Liq. Cryst. **274**, 145 (1995).

[22] J. Villain, F. Hartmann-Boutron, R. Sessoli, and A. Rettori, Europhys. Lett. **27**, 159 (1994).

[23] P. Politi, A. Rettori, F. Hartmann-Boutron, and J. Villain, Phys. Rev. Lett. **75**, 537 (1995).

[24] F. Hartmann-Boutron, P. Politi, and J. Villain, Int. J. Mod. Phys. **10**, 2577 (1996).

[25] T. Lis, Acta Cryst. B **36**, 2042 (1980).

[26] J. R. Friedman, M. P. Sarachik, J. Tejada, J. Maciejewski, and R. Ziolo, J. Appl. Phys. **79**, 6031 (1996); J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[27] J. M. Hernandez, X. X. Zhang, F. Luis, J. Bartolome, J. Tejada, and R. Ziolo, Europhys. Lett. **35**, 301 (1996).

[28] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature **383**, 145 (1996).

[29] Recent pulsed-field experiments performed at near 1.5 K indicate the presence of at least 12 steps, more than half the steps predicted by the model [S. Foner (private communication)]. This observation eliminates the possibility that half the steps are missing.

[30] N. V. Prokof'ev and P. C. E. Stamp, J. Low Temp. Phys. **104**, 143 (1996).

[31] D. A. Garanin, J. Phys. A **24**, L61 (1991).

[32] J. R. Friedman and E. Chudnovsky (private communication).

[33] A. L. Burin, N. V. Prokof'ev, and P. C. E. Stamp, Phys. Rev. Lett. **76**, 3040 (1996).

[34] A. L. Burin (private communication).
[35] S. Foner, Y. Shapira, D. Heiman, P. Becla, R. Kershaw, K. Dwight, and A. Wold, Phys. Rev. B **39**, 11 793 (1989).
[36] Y. Shapira, J. Appl. Phys. **67**, 5090 (1990).
[37] K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, and S. J. Lippard, J. Am. Chem. Soc. **116**, 823 (1994).
[38] J. J. Smit, L. J. de Jongh, D. de Klerk, R. L. Carlin, and C. J. Conner, Physica **86–88B**, 1147 (1977); J. J. Smit, H. J. van Wijk, L. J. de Jongh, and R. L. Carlin, Chem. Phys. Lett. **62**, 158 (1979).
[39] F. Varret, Y. Allain, and A. Miedan-Gros, Solid State Commun. **14**, 17 (1974).
[40] V. Bindilatti, A. N. Anisimov, N. F. Oliveira, Y. Shapira, M. Goiran, F. Yang, S. Isber, M. Averous, and M. Demianiuk, Phys. Rev. **50**, 16 464 (1994); S. Isber, M. Averous, Y. Shapira, V. Bindilatti, A. N. Anisimov, N. F. Oliveira, V. M. Orera, and M. Demianiuk, *ibid*. **51**, 15 211 (1995).
[41] M. Uehara, B. Barbara, B. Dieny, and P. C. E. Stamp, Phys. Lett. **114A**, 23 (1986).
[42] A. Paduan-Filho, C. C. Becerra, V. B. Barbeta, Y. Shapira, J. Campo, and F. Palicio, J. Magn. Magn. Mater. **140–144**, 1925 (1995).
[43] R. Rouse, S. Han, and J. E. Lukens, Phys. Rev. Lett. **75**, 1614 (1995).
[44] P. C. E. Stamp, Nature **383**, 125 (1996).
[45] E. Chudnovsky, Science **274**, 938 (1996).