Ground-state tunneling in Mn_{12}-acetate

K. M. Mertes, Yoko Suzuki, and M. P. Sarachik
Physics Department, City College of the City University of New York, New York, New York 10031

Y. Paltiel, H. Shtrikman, and E. Zeldov
Department of Condensed Mater Physics, The Weizmann Institute of Science, Rehovot 76100, Israel

E. M. Rumberger and D. N. Hendrickson
Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, California 92093

G. Christou
Department of Chemistry, University of Florida, Gainesville, Florida 32611

(Received 10 August 2001; revised manuscript received 1 October 2001; published 14 May 2002)

We report Hall sensor measurements of the magnetic relaxation of Mn_{12}-acetate as a function of magnetic field applied along the easy axis of magnetization for a series of closely spaced temperatures between 0.24 K and 1.9 K. The occasional absence (or suppression) of ground-state tunneling under conditions where one would expect it to be readily observable is attributed to the presence of a broad distribution of tunnel splittings.

DOI: 10.1103/PhysRevB.65.212401 PACS number(s): 75.45.+j,75.50.Xx

Crystals of the high-spin molecular nanomagnet Mn_{12}-acetate ($[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$) exhibit dramatic quantum mechanical phenomena on a macroscopic scale and have been the focus of intense interest in recent years. The material consists of weakly interacting nominally identical spin-10 Mn_{12} clusters[1] regularly arranged on a tetragonal lattice. Measurements[2,3] below the blocking temperature of 3 K have revealed a series of steep steps in the curves of M versus H at roughly equal intervals of magnetic field due to enhanced relaxation of the magnetization whenever levels corresponding to spin projections $m=\pm 10,\pm 9,\ldots,0$ on opposite sides of the anisotropy barrier coincide in energy. Different ''steps'' dominate at different temperatures, indicating that the tunneling is thermally assisted.

Mn_{12}-acetate can be modeled by the effective spin Hamiltonian

$$\mathcal{H}=-DS_z^2-g_z\mu_B H_z S_z-AS_z^4+\cdots, \tag{1}$$

where the anisotropy constant $D=0.548(3)$ K, the second term is the Zeeman energy, and the third term $A=1.173(4)\times 10^{-3}$ K is the next higher-order term in longitudinal anisotropy[4–7]; additional small terms that do not commute with the Hamiltonian and which drive the tunneling (such as transverse internal magnetic fields, transverse anisotropy) are not explicitly shown. Tunneling occurs from level m' in the metastable well to level m in the stable potential well at fields:

$$H_z=N\frac{D}{g_z\mu_B}\left[1+\frac{A}{D}(m^2+m'^2)\right], \tag{2}$$

where $N=|m+m'|$ is the step number and the level matching condition is $m=-m'-N$. The second term in the bracket is smaller than the first so that steps N occur at approximately equally spaced intervals of magnetic field of ≈ 0.48 T. Structure within each step due to the presence of the fourth-order term AS_z^4 (the levels do not cross simultaneously) allows identification of the energy levels that are responsible for the tunneling observed at different temperatures and magnetic fields. The process by which the magnetic moment relaxes toward equilibrium depends on temperature: over-the-barrier relaxation above the blocking temperature, $T_B\approx 3$ K, thermally assisted tunneling at lower temperatures, and pure ground-state tunneling for temperatures below ≈ 0.6 K.

In this paper we report detailed measurements of the magnetization of a single crystal of Mn_{12} in a swept magnetic field for a set of closely spaced temperatures. Confirming earlier reports,[8–10] there is an abrupt transfer of ''spectral weight'' to ground-state tunneling as the temperature is reduced. We show that under some circumstances relaxation that should proceed from the ground state appears to be missing under conditions where one would expect it to be present. We describe this enigma in detail and argue that it is due to the fact that, rather than being single valued, the tunnel splittings are broadly distributed and vary locally throughout the crystal.

The magnetization of small single crystals of Mn_{12} was determined from measurements of the local magnetic induction at the sample surface using 10×10 μm^2 Hall sensors composed of a two-dimensional electron gas (2DEG) in a GaAs/AlGaAs heterostructure.[11] The 2DEG was aligned parallel to the external magnetic field, and the Hall bar was used to detect the perpendicular component (only) of the magnetic field arising from the sample magnetization. The external magnetic field was swept at a constant rate of 1.88×10^{-3}T/s.

For different temperatures between 0.24 K and 1.05 K, Fig. 1 shows the first derivative $\partial M/\partial H$ of the magnetization M with respect to the externally applied magnetic field H.[12] The maxima occur at magnetic fields corresponding to faster magnetic relaxation due to level crossings on opposite sides of the anisotropy barrier. In the temperature range of these

 ©2002 The American Physical Society

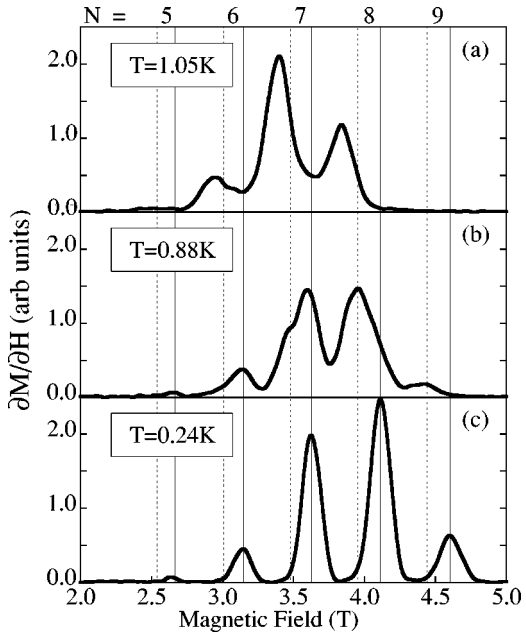

FIG. 1. The derivative of the magnetization with respect to field vs magnetic field at three different temperatures, as labeled. Pairs of vertical lines are drawn for each resonance N corresponding to the magnetic field for tunneling from the first excited state $m'=-9$ (dotted line at the lower field) and from the ground state $m'=-10$ (solid line at the higher field).

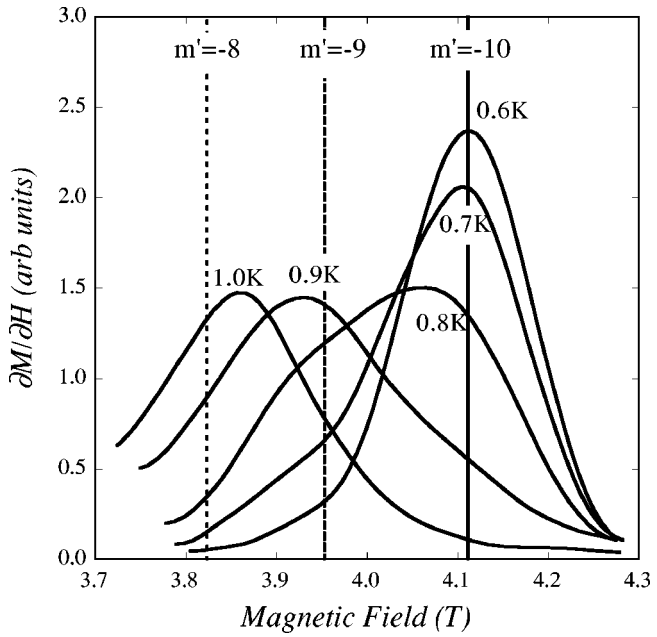

FIG. 2. The derivative of the magnetization with respect to field vs magnetic field for step $N=8$ at several different temperatures, as labeled. The three vertical lines correspond to magnetic fields for tunneling from $m'=-8$, $m'=-9$, and $m'=-10$. A single peak is observed at 1 K and 0.9 K which cannot be resolved into a set of Gaussians (or Lorentzians); it is apparently due to a superposition involving thermal activation to states ($m'=-9,-8,\ldots$).

measurements, maxima are observed for $N=|m+m'|=5$–9. For each resonance, $N=\ldots,5,6,7,8,\ldots$, the two vertical lines denote the magnetic fields corresponding to tunneling from the first excited state, $m'=-9$ (dotted line), and the lowest state, $m'=-10$ (solid line). At 1.05 K, shown in Fig. 1(a), the main source of the tunneling is neither the ground state nor the first excited state. Instead, the three maxima associated with the $N=6,7,8$ resonances are apparently due to a superposition of tunneling involving thermal activation to higher states in the well ($m'=-9,-8,-7,\ldots$); this is illustrated in Fig. 2 for step $N=8$, where magnetic fields for different m' sublevels are indicated and data are shown for several temperatures.

The tunneling at 0.88 K, shown in Fig. 1(b), takes place at magnetic fields corresponding to the ground state for steps $N=5$ and $N=6$; some magnetic relaxation begins to appear at the first excited state for $N=7$, and for $N=8$ and 9 there is tunneling mostly from $m'=-9$ while ground-state tunneling from $m'=-10$ is barely observed. At the lowest temperature of 0.24 K, all tunneling occurs from the ground state in the field range of these measurements, as shown in Fig. 1(c).

We now arrive at the enigma referred to in the introduction. Examination of resonance $N=7$ at the three temperatures illustrated in Fig. 1 shows that tunneling proceeds almost entirely from the excited levels at $T=1.05$ K with nearly no contribution from the ground state while the relaxation at $T=0.24$ K is entirely due to ground-state tunneling for $N=7$. The enigma is that ground-state tunneling appears to be absent at the higher temperature. Similar behavior is found at every step. One should bear in mind that although the population of the excited states is exponentially sensitive to temperature, $n=n_0e^{-E/kT}$, the population of the ground state, $n_{gr}=n_0[1-e^{-E/kT}]\approx n_0$, at any low temperature, $T<T_B$. The spin population of the lowest level in the metastable well is therefore essentially the same at 1.05 K, 0.88 K, and 0.24 K, and if tunneling occurs from the ground state at the lower temperatures, it should also be observable at 1.05 K. One could understand the absence of ground-state tunneling at step $N=7$ at 1.05 K if relaxation at lower fields had effectively depleted the out-of-equilibrium spin magnetization, so that the system has relaxed to near equilibrium. However, as the magnetic field sweeps beyond the field corresponding to ground-state tunneling at $N=7$ at 1.05 K, a sizable maximum develops at the next resonance $N=8$, indicating that an appreciable fraction of the spin magnetization is still out of equilibrium and is available to relax instead at the next set of level crossings at $N=8$.

The enigma is most simply revealed by the following analysis. The tunneling amplitude at a given field depends on how much out-of-equilibrium magnetization remains, which depends on how much magnetization has relaxed at earlier fields. For ground-state tunneling, the dependence on past history can be folded out of the problem by normalizing $\partial M/\partial H$ by the remaining out-of-equilibrium magnetization $(M_{sat}-M)$. Thus, we define the normalized tunneling rate $\Gamma=(\partial M/\partial H)/(M_{sat}-M)$ and plot this quantity as a function of magnetic field in Fig. 3.

According to Landau-Zener[13] theory as well as the density matrix formalism developed by Chudnovsky and Garanin[14] for tunneling in a swept magnetic field, the tunnel-

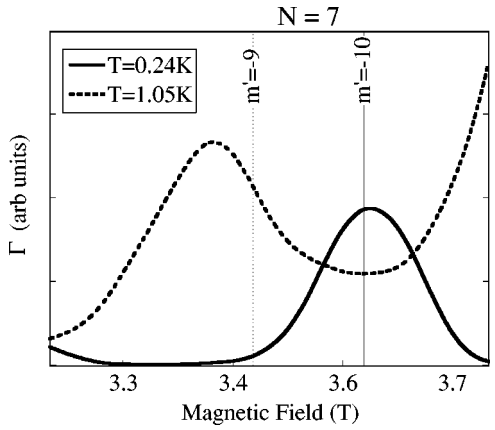

FIG. 3. The normalized tunneling rate $\Gamma=(\partial M/\partial H)/(M_{sat}-M)$ vs magnetic field at $T=0.24$ K and $T=1.05$ K for the $N=7$ transition.

ing probability depends only on the tunnel splitting and the sweep rate. Therefore, for a set of identical molecules, Γ at fields corresponding to transitions from the ground state should be independent of temperature. It is clear in Fig. 3 that this is not the case. The total normalized tunneling rate at the magnetic field corresponding to the ground state ($m'=-10$) is significantly smaller at 1.05 K (Ref. 15) than it is at 0.24 K.

The enigma discussed above can be understood if one assumes a broad distribution of tunnel splittings, so that the tunneling rates of the magnetic molecules vary from point to point with some relaxing very slowly and others relaxing rapidly. At any particular resonance (N,m'), some fraction of molecular clusters have tunnel splittings that allow them to relax with a reasonable probability, while other molecules with much smaller tunnel splittings have relaxation rates that are sufficiently slow that they cannot tunnel. In the example discussed above where ground-state tunneling is missing at $N=7$, molecules that belong to the ''fast''-tunneling portion of the distribution relax; if the temperature is high, they tunnel by thermal activation to excited spin states, $N=7$, $m'=-9,-8,\ldots$, depleting the magnetization of the ''fast''-tunneling magnetic clusters so that no magnetization remains that can relax from the ground state $N=7$, $m'=-10$. Meanwhile, the magnetic centers that have small tunnel splittings remain in the metastable potential well at step $N=7$ and tunnel instead at the next resonance $N=8$ (or higher) when the magnetic field is now larger and the potential barrier commensurately lower. In this way, a broad distribution of tunnel splittings and tunneling rates provides a natural explanation for the fact that ground-state tunneling is absent in some circumstances even though a substantial amount of out-of-equilibrium magnetization remains in the system.

Chudnovsky and Garanin[14,16] (CG) recently suggested theoretically that there is a broad distribution of tunnel splittings in Mn_{12}-acetate crystals, and experimental support for a distribution has been obtained from magnetization,[17,18] electron paramagnetic resonance[19] (EPR), and terahertz[20] experiments. Such a distribution could arise from a locally varying second-order transverse anisotropy due to the dislocations suggested by CG (Refs. 14 and 16) or from a distribution of longitudinal anisotropies D.

Mn_{12} molecules have recently been proposed as qubits for quantum computers.[21,22] Such qubits would have to be operated at millikelvin temperatures where the ground-state tunneling creates a quantum superposition of spin-up and spin-down states. The enigma of the ''missing'' ground-state tunneling provides support for the presence of tunnel splittings that vary from molecule to molecule in Mn_{12}-acetate. Such a broad distribution of tunnel splittings would necessitate the use of isolated individual magnetic molecules.

We thank D. A. Garanin, E. M. Chudvnosky, and J. R. Friedman for valuable discussions. Work at City College was supported by NSF Grant No. DMR-9704309 and at the University of California, San Diego, by NSF Grant Nos. CHE-0095031 and DMR-0103290. Support for G.C. was provided by NSF Grant No. CHE-0071334. E.Z. acknowledges support of the German-Israeli Foundation for Scientific Research and Development.

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

[2] J.R. Friedman, M.P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[3] J.M. Hernandez, X.X. Zhang, F. Luis, J. Bartolome, J. Tejada, and R. Ziolo, Europhys. Lett. **35**, 301 (1996); L. Thomas, F. Lionti, R. Ballou, R. Sessoli, D. Gatteschi, and B. Barbara, Nature (London) **383**, 145 (1996).

[4] Y. Zhong, M.P. Sarachik, J.R. Friedman, R.A. Robinson, T.M. Kelley, H. Nakotte, A.C. Christianson, F. Trouw, S.M.J. Aubin, and D.N. Hendrickson, J. Appl. Phys. **85**, 5636 (1999).

[5] M. Hennion, L. Pardi, I. Mirebeau, E. Suard, R. Sessoli, and A. Caneschi, Phys. Rev. B **56**, 8819 (1997).

[6] I. Mirebeau, M. Hennion, H. Casalta, H. Andres, H.U. Güdel, A.V. Irodova, and A. Caneschi, Phys. Rev. Lett. **83**, 628 (1999).

[7] A.L. Barra, D. Gatteschi, and R. Sessoli, Phys. Rev. B **56**, 8192 (1997).

[8] A.D. Kent, Y. Zhong, L. Bokacheva, D. Ruiz, D.N. Hendrickson, and M.P. Sarachik, Europhys. Lett. **49**, 521 (2000).

[9] L. Bokacheva, A.D. Kent, and M.A. Walters, Phys. Rev. B **85**, 4803 (2000).

[10] K.M. Mertes, Y. Suzuki, M.P. Sarachik, Y. Paltiel, H. Shtrikman, E. Zeldov, E. Rumberger, D.N. Hendrickson, and G. Christou, Europhys. Lett. **55**, 874 (2001).

[11] For details see E. Zeldov, D. Majer, M. Konczykowski, V.B. Geshkenbein, V.M. Vinokur, and H. Shtrikman, Nature (London) **375**, 373 (1995).

[12] We use H instead of the total field $B=H+\alpha(4\pi M)$; the field due to the sample magnetization is on the order of 300 Oe.

[13] W. Wernsdorfer, C. Paulsen, and R. Sessoli, Phys. Rev. Lett. **84**,

5678 (2000); L.D. Landau, Phys. Z. Sowjetunion **2**, 46 (1932); C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932); S. Miyashita, J. Phys. Soc. Jpn. **64**, 3207 (1995); V.V. Dobrovitsky and A.K. Zvezdin, Europhys. Lett. **38**, 377 (1997); M.N. Leuenberger and D. Loss, Phys. Rev. B **61**, 12 200 (2000).

[14] E.M. Chudnovsky and D.A. Garanin, Phys. Rev. Lett. **87**, 187203 (2001).

[15] Since Γ at 1.05 K includes contributions from the tails of the maxima due to excited-state tunneling at $N=7$ and $N=8$, the tunneling from the $N=7$ ground state is even smaller.

[16] D.A. Garanin and E.M. Chudnovsky, Phys. Rev. B **65**, 094423 (2002).

[17] K.M. Mertes, Y. Suzuki, M.P. Sarachik, Y. Paltiel, H. Shtrikman, E. Zeldov, E.M. Rumberger, D.N. Hendrickson, and G. Christou, Phys. Rev. Lett. **87**, 227205 (2001).

[18] J.M. Hernandez, F. Torres, J. Tejada, and E. Molins, cond-mat/0110515 (unpublished); F. Torres, J.M. Hernandez, E. Molins, A. Garcia-Santiago, and J. Tejada, cond-mat/0110538 (unpublished).

[19] K. Park, M.A. Novotny, N.S. Dalal, S. Hill, and P.A. Rikvold, Phys. Rev. B **65**, 014426 (2002).

[20] B. Parks, J. Loomis, E. Rumberger, D.N. Hendrickson, and G. Christou, Phys. Rev. B **64**, 184426 (2001).

[21] M.N. Leuenberger and D. Loss, Nature (London) **410**, 789 (2001).

[22] J. Tejada, E.M. Chudnovsky, E. del Barco, J.M. Hernandez, and T.P. Spiller, Nanotechnology **12**, 181 (2001).