Ground state tunneling due to a distribution of tunnel splittings in Mn_{12}-acetate

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We report on detailed measurements of the magnetization of a single crystal of Mn_{12}-acetate in a swept magnetic field for a set of closely spaced temperatures. 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 argue that this enigma implies there is a distribution of tunnel splittings, so that the (normalized) magnetization determines the fraction of distributed molecules that tunnel instead of the tunneling probability of an identical set of molecules. [DOI: 10.1063/1.1456423]

The high-spin molecular nanomagnet Mn_{12}-acetate, $([Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O)$, is composed of weakly interacting magnetic clusters of 12 Mn atoms, tightly coupled to give a ground-state spin $S=10$, regularly arranged on a tetragonal body-centered lattice. Strong uniaxial anisotropy yields a set of energy levels corresponding to different projections $m=\pm 10, \pm 9, \ldots, 0$ of the total spin along the easy c axis of the crystal. Below the blocking temperature, $T_B \approx 3$ K, steep steps are observed[1,2] in the M vs H curves due to enhanced relaxation of the magnetization whenever levels on opposite sides of the anisotropy barrier coincide in energy. Tunneling proceeds at values of longitudinal magnetic fields:

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

where the anisotropy $D=0.548(3)$ K, the fourth-order longitudinal anisotropy $A=1.173(4)\times 10^{-3}$ K, and g_z is estimated to be 1.94(1).[3,4] The tunneling occurs from level m' in the metastable well to level m in the stable potential well, and $N=|m+m'|$ is the Nth family of level crossings. The second term inside the bracket is smaller than the first so that steps N occur at approximately equally spaced intervals of magnetic field, $D/(g_z\mu_B)\approx 0.42$ T. Structure is observed within each step due to the presence of the fourth-order longitudinal anisotropy, A, allowing identification of the energy levels that are responsible for the tunneling observed at different temperatures, magnetic fields, and sweep rates.

The magnetization of small single crystals of Mn_{12}-acetate was determined by methods described elsewhere.[5] For different temperatures between 0.24 and 0.88 K for a fixed sweep rate of $dH_z/dt=1.88\times 10^{-3}$ T/s, Fig. 1 shows the first derivative, $\partial M/\partial H$, of the magnetization M with respect to the externally applied magnetic field H.[6] The maxima occur at magnetic fields corresponding to faster magnetic relaxation due to tunneling when levels cross on opposite sides of the anisotropy barrier. In the temperature range of these measurements, maxima are observed for $N=|m+m'|=5$ through 9. Considerable structure associated with different pairs (m,m') is clearly seen within each step N, with a transfer of "spectral weight" to lower values of m' deeper in the well as the temperature is reduced. A single feature corresponding to thermally assisted tunneling remains distinct from the ground state: it shifts gradually to the right towards a higher field as the temperature is reduced, becomes a shoulder as shown in Fig. 1 on the low-field side of the ground-state peak, and ultimately merges with it. For sufficiently low temperatures, the curves do not depend on temperature and the tunneling takes place from the lowest, ground state of the metastable well.

The progression can be examined in detail in Fig. 2,

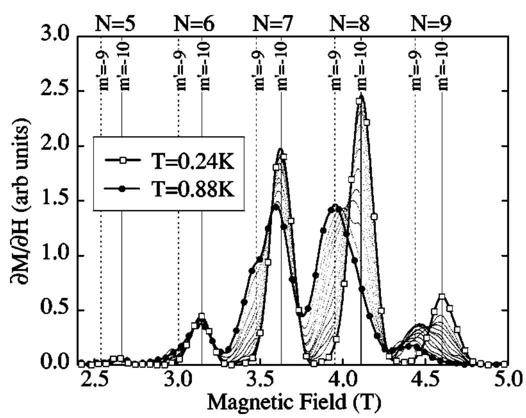

FIG. 1. The derivative $\partial M/\partial H$ vs H for a set of closely spaced temperatures. Selected data points are shown for 0.88 K and 0.24 K only. The remaining curves (unlabeled) correspond to intermediate temperatures $0.88>T>0.24$ K. Two distinct features are seen at intermediate temperatures for resonances $N=7,8$, and 9.

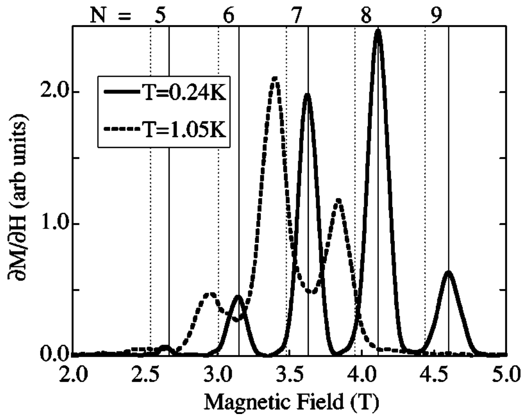

FIG. 2. The derivative $\partial M/\partial H$ vs H at two different temperatures. Vertical lines are drawn for each resonance N corresponding to the magnetic field for tunneling from the first excited state $m'=-9$ (dotted line at the lower field) and from the ground state $m'=-10$ (solid line at the higher field).

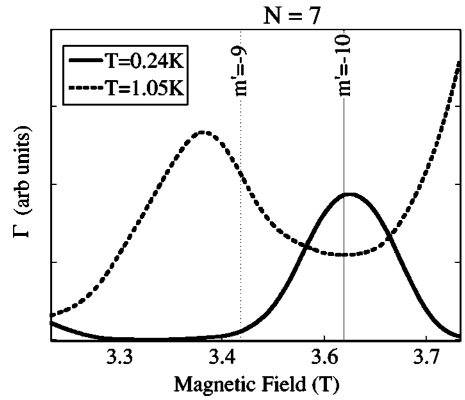

FIG. 3. The normalized tunneling rate $\Gamma=\partial M/\partial H/(M_{sat}-M)$ vs magnetic field at $T=0.24$ K and $T=1.05$ K for the $N=7$ transition.

where data are shown at 0.24 and 1.05 K. 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, the tunneling occurs neither from the ground state nor from the first excited state. Instead, the three maxima associated with the $N=6,7,8$ resonances are probably due to a superposition of tunneling involving thermal activation to higher states in the well ($m'=-8$, -7,...). At 0.24 K, all tunneling occurs from the ground state in the field range of these measurements.

We now arrive at the enigma referred to in the abstract. Examination of resonance $N=7$ at the two temperatures illustrated in Fig. 2 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 tunneling at 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 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 resolution to 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. 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 $(M_{sat}-M)$. Defined this way, the normalized tunneling rate, $\Gamma=\partial M/\partial H/(M_{sat}-M)$, removes the history dependence of the peak heights in $\partial M/\partial H$.

According to the Landau–Zener[7] theory of tunneling in a swept field, the tunneling probability depends only on the tunnel splitting and 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 1.05 K is significantly smaller[8] than it is at 0.24 K. Since the sweep rate is the same for both temperatures, we must conclude that Mn_{12}-acetate molecules have a distribution of tunnel splittings.

This scenario implies that the interpretation of the magnetization data is different from what has usually been assumed. For a set of identical molecules, the probability of tunneling from the ground state of the metastable well is given by the Landau–Zener formula $P_N=1-\exp(-\pi\Delta_N^2/2v_N)$,[7] where Δ_N is the tunnel splitting for the Nth ground-state resonance and v_N is the energy sweep rate defined by $v_N=(g_z\mu_B\hbar/k_B^2)(2S-N)dH_z/dt$. For a distribution of tunnel splittings, $\Delta_{N,i}$ (where i represents the ith molecule) the probability that a spin tunnel from the ground state of the metastable well must be averaged over all the molecules, $\langle P_{N,i}\rangle=(1/n_{gr})\Sigma_i 1-\exp(-\pi\Delta_{N,i}^2/2v_N)$, where n_{gr} is the total number of molecules in the ground state of the metastable well. If the distribution is sufficiently broad, then $\langle P_{N,i}\rangle$ is best examined on a log scale, where an exponential looks like a step function, so that $\exp(-\pi\Delta_{N,i}^2/2v_N)\approx\Theta(1-\pi\Delta_{N,i}^2/2v_N)$. This means that for a fixed field sweep rate, dH_z/dt, those molecules that have tunnel splittings obeying $\pi\Delta_{N,i}^2\geqslant 2v_N$ will tunnel from the ground state of the metastable well for each resonance N. Thus, with a sufficiently broad distribution of tunnel splittings, the normalized magnetization at each plateau represents the *fraction* of molecules that have large enough splittings to have tunneled, rather than determining the probability of tunneling of a set of identical clusters.[9] Thus, at any particular resonance, N, some fraction of molecular clusters have tunnel splittings that allow them to relax with a probability near 1, 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 $N=7$ as shown in Fig. 3, molecules that belong to the ''fast''-tunneling portion of the distribution relax; if the temperature is sufficiently 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 sufficiently broad distribution of tunnel splittings provides a natural explanation for the fact that ground-state tunneling is absent or substantially reduced in some circumstances even though a substantial amount of out-of-equilibrium magnetization remains in the system.

To summarize, we have shown 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 have presented experimental evidence that shows that the normalized tunneling rate, Γ, from the ground state depends on temperature, contrary to expectations for a set of identical magnetic centers. The enigma of the ''missing'' ground-state tunneling can be resolved if one assumes instead that there is a sufficiently broad distribution of tunnel splittings. In this case, the normalized magnetization should be viewed as a measure of the distribution of tunnel splittings rather than of the tunneling probability of identical magnetic clusters.

ACKNOWLEDGMENTS

The authors thank D. Garanin, E. Chudnovsky, and Jonathan Friedman for the numerous discussions that made this analysis possible. 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 the support of the German-Israeli Foundation for Scientific Research and Development.

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[8] 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.

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