On Ground State Tunneling in Mn$_{12}$-Acetate.

K. M. Mertes and M. P. Sarachik

Physics Department, City College of the City University of New York, New York, NY 10031

Y. Paltiel, H. Shtrikman, and E. Zeldov

Department of Condensed Matter 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, CA 92093

G. Christou

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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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. We map out a region in the $H - T$ plane where ground state tunneling is observed, a region where tunneling proceeds via thermally-assisted tunneling, and a crossover region where both participate in the relaxation. We observe the occasional absence of ground-state tunneling under conditions where one would expect it to be present, and suggest a resolution to the enigma.

Crystals of the high-spin molecular nanomagnet Mn$_{12}$-acetate ([Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$]-2CH$_3$COOH-4H$_2$O), exhibit dramatic quantum mechanical phenomena on a macroscopic scale, and have been the focus of intense interest and investigation in recent years. Mn$_{12}$ molecules have recently been proposed as qubits for quantum computers. 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 study of ground state tunneling in Mn$_{12}$ is, therefore, important for applications.

The magnetic core of the molecules consists of twelve Mn atoms strongly coupled by superexchange through oxygen bridges with a ground-state spin $S = 10$. These identical weakly-interacting magnetic clusters are regularly arranged on a tetragonal body-centered lattice. As illustrated by the double well potential shown in the inset to Fig. 1, 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. Measurements 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, as shown in Fig. 1, due to enhanced relaxation of the magnetization whenever levels on opposite sides of the anisotropy barrier coincide in energy. As demonstrated by the data of Fig. 1 different “steps” dominate at different temperatures, indicating that thermal processes play an important role. The steps in the magnetization curves have been attributed to thermally-assisted quantum tunneling of the spin magnetization.

![FIG. 1. Magnetization versus longitudinal magnetic field for a Mn$_{12}$ sample starting from a demagnetized state, $M = 0$; data are shown at four different temperatures, as labeled. Note the steep segments, or steps, corresponding to faster magnetic relaxation at specific values of magnetic field.](image-url)
Neutron scattering experiments \[1,2\] as well as EPR \[10\] measurements indicate that Mn$_{12}$-acetate can be modeled by the effective spin Hamiltonian:

\[
\mathcal{H} = -DS_z^2 - g_\parallel \mu_B H_z S_z - A S_z^4 + \ldots
\]

where $D = 0.548(3) \text{ K}$ is the anisotropy constant, the second term is the Zeeman energy, and the third term represents the next higher-order term in longitudinal anisotropy with $A = 1.175(4) \times 10^{-3} \text{ K}$; 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. Within this model, tunneling should occur from level $m'$ in the metastable well to level $m$ in the stable potential well for magnetic fields:

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

where $N = |m + m'|$ is the step number and the level matching condition is $m = -m' - N$. The second term inside the bracket is smaller than the first so that steps $N$ occur at approximately equally spaced intervals of magnetic field, $D/(g_\parallel \mu_B) \approx 0.42 \text{ Tesla}$. Careful measurements have revealed structure within each step due to the presence of the fourth-order term, $AS_z^4$; the levels do not cross simultaneously, an effect that is more pronounced for states that are deeper in the well. This allows identification of the energy levels that are responsible for the tunneling observed at different temperatures, magnetic fields and sweep rates.

The process by which the magnetic moment relaxes toward equilibrium depends on temperature: for temperatures above the blocking temperature, $T_B \approx 3 \text{ K}$, magnetic relaxation proceeds by over-the-barrier processes; at intermediate temperatures below $3 \text{ K}$, thermal activation to an excited state within the potential well is followed by tunneling across the barrier; for temperatures below approximately $1 \text{ K}$, tunneling in Mn$_{12}$ has been shown to proceed from the ground state only. Thermal activation becomes exponentially more difficult as one proceeds up the ladder to higher energy levels; on the other hand, the barrier is lower and more penetrable, so that tunneling becomes exponentially easier. Which level (or group of adjacent levels) dominates the tunneling is determined by competition between the two effects. As the temperature is reduced and thermal activation becomes more difficult, the states that are active in the tunneling move gradually to lower energies deeper in the potential well.

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. Our measurements provide a mapping in the $H - T$ plane of a region where only thermally-assisted tunneling occurs, a region where only ground state tunneling is observed, separated by a crossover region where both participate in the relaxation. We find that thermally assisted tunneling gives rise to a single broad feature that cannot be deconvoluted into a set of lines (either Gaussian or Lorentzian) associated with the different excited spin states in the potential well. Tunneling from the ground state gives rise to a separate Gaussian line. Interestingly, the maxima associated with thermally-assisted tunneling and ground state tunneling remain separate, while the contributions associated with the various excited states are unresolved, even though the field spacing between them is comparable. Confirming earlier reports \[11,13\] , there is an abrupt transfer of “spectral weight” to ground state tunneling as the temperature is reduced. We show further 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 offer a possible resolution to the puzzle.

![FIG. 2. For a set of closely spaced temperatures, the first derivative of the magnetization with respect to magnetic field is plotted as a function of magnetic field. The amplitude is a measure of the rate of magnetic relaxation. Selected data points are shown for $0.24 \text{ K}$ and $0.88 \text{ K}$ only. The remaining curves (unlabeled) correspond to intermediate temperatures $0.88 > T > 0.24 \text{ K}$. Note the substructure within each of the four maxima corresponding to steps $N = |m' + m| = 5, 6, 7, 8, \text{ and } 9$.](image-url)
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 $1.88 \times 10^{-3}$ T/s.

For different temperatures between 0.24 K and 0.88 K, Fig. 3 shows the first derivative, $\partial M/\partial H$, of the magnetization $M$ with respect to the externally applied magnetic field $H$. 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 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 higher values of $m'$ deeper in the well as the temperature is reduced. 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 tunneling appears in the form of two distinct features, one centered about the magnetic field corresponding to tunneling from the lowest state $m' = -10$ of the metastable well, and a second feature associated with thermally-assisted tunneling from all the higher energy levels, $m' = -9, -8, -7, ...$. We have been unable to separate this broad line into a superposition of Gaussians or Lorentzians centered at the magnetic fields corresponding to excited state level crossings. We note that the differences between the magnetic fields for the different level crossings within a given step are quite comparable. For example, for step $N = 7$, tunneling maxima associated with $m' = -10, -9, -8, -7, ...$ are expected at magnetic fields 3.629, 3.478, 3.352, 3.251... T, so that the differences $\Delta H$ are 0.151, 0.126, 0.101, ... T. If one can resolve ground-state tunneling, one should expect to resolve the excited state levels as well. Instead, a single feature corresponding to thermally assisted tunneling remains distinct from the ground state: it shifts gradually to the right toward higher field as the temperature is reduced, becomes a shoulder on the low-field side of the ground state peak, and ultimately merges with it.

The progression can be examined in detail in Fig. 3, where the derivative of the magnetization with respect to field is shown as a function of magnetic field for three different temperatures. For each resonance, $N = 5, 6, 7, 8, ...$, 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. 3 (a), 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 ($m' = -8, -7, ...$). The tunneling at 0.88 K, shown in Fig. 3 (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 only from $m' = -9$ while ground state tunneling from $m' = -10$ has disappeared. 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. 3 (c).

![FIG. 3. The derivative of the magnetization with respect to field versus 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).](image)

Based on extensive data taken for a closely-spaced set of temperatures, Fig. 3 shows a region of the $H-T$ plane where tunneling proceeds from the ground state only and a region where tunneling occurs from excited states only, separated by a crossover region where magnetic relaxation involves both ground state and thermally activated tunneling. The four points shown in the figure denote the crossover temperature and field where the two peaks in the $\partial M/\partial H$ curves have the same amplitude for a given step number, as illustrated in the inset for step $N = 7$. The line connecting the points in the main part of Fig. 3 denotes a boundary (of finite breadth) between thermal activation and ground state tunneling. A full mapping...
of the boundary will require data for a broader range of sweep rates (slower sweep rates for the high-temperature low-field region, and faster rates for the high-field low-temperature regime). Thus, the diagram of Fig. 3 shows that tunneling with no discernible contribution from the ground state, $N = 1$, at lower temperatures, ground state tunneling is observed for the lower-numbered resonances, with a shift to thermally-assisted tunneling occurring at higher magnetic fields.

![Diagram](image)

**FIG. 4.** Boundary in the $H-T$ plane separating a region where tunneling proceeds from the ground state only and a region where tunneling occurs from excited states only. For each value of $N$, the dotted line denotes the magnetic field for tunneling from the first excited state, $m' = -9$, and the solid line denotes the field for tunneling from the ground state, $m' = -10$. The four points denote the crossover temperature and 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 $N = 8$.

Chudnovsky and Garanin recently suggested that there is a broad distribution of tunnel splittings in Mn$_{12}$-acetate crystals. Within their model, this arises from a locally varying second-order transverse anisotropy which, although forbidden by tetragonal symmetry in the perfect crystal, is present in real crystals of Mn$_{12}$-acetate due to dislocations. The tunneling rate of the magnetic molecules varies from point to point, with some relaxing very rapidly and others quite slowly.

Regardless of the physical origin, a broad distribution of tunnel splittings provides a resolution to the enigma discussed above. 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, $N = 7, m' = -9, -8, ...$, 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.
neling is occasionally absent under conditions when one would expect it to be present was recently analyzed quantitatively by Garanin and Chudnovsky \[17\] in terms of a dimensionless parameter \(x(m', N, v, T)\) which depends on the resonance \(m'\), the step number \(N\), the magnetic field sweep rate \(v\), and the temperature \(T\). It was shown in Ref. \[17\] that for a broad distribution of tunnel splittings the \(m'\) resonance can be observed in a field-sweep experiment only if the condition \(x(m', N, v, T) < x((m' + 1), N, v, T)\) is satisfied. Otherwise, the molecules which would cross the barrier at the \(m'\) resonance have been depleted at the \((m' + 1)\) resonance. For a given \(m'\) and \(N\) this condition may or may not be satisfied depending on sweep rate \(v\) and the temperature \(T\). A detailed comparison with theory will be published elsewhere.

The enigma of the “missing” ground state tunneling provides support for the presence of tunnel splittings that vary from molecule to molecule in \(\text{Mn}_{12}\)-acetate. Ground state tunneling is strongly affected by such a wide distribution of tunnel rates within the crystal. Applications of molecular nanomagnets as qubits will therefore require the use of isolated individual magnetic molecules.

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