Abrupt Transition between Thermally-Activated Relaxation and Quantum Tunneling in a Molecular Magnet.

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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. Data taken at a series of closely-spaced temperatures between 0.24 K and 1.4 K provide strong new evidence for an abrupt “first-order” transition between thermally-assisted relaxation and magnetic decay via quantum tunneling.

PACS numbers: 75.45.+j, 75.50.Xx

Single-molecule magnets are organic materials which contain a large (Avogadro’s) number of identical magnetic molecules; ([Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_{4}$]·2CH$_3$COOH·4H$_2$O), generally referred to as Mn$_{12}$ acetate, is a particularly simple and much-studied example of this class. The Mn$_{12}$ clusters are each composed of twelve Mn atoms (see Fig. 1) coupled by superexchange through oxygen bridges to give a sizable $S = 10$ spin magnetic moment that is stable at temperatures of the order of 10 K and below. These identical weakly-interacting magnetic clusters are regularly arranged on a tetragonal crystal. As illustrated by the double well potential of Fig. 1, shown there in the presence of a longitudinal field, strong uniaxial anisotropy (of the order of 65 K) yields doubly degenerate ground states in zero field and a set of excited levels corresponding to different projections $m_s = \pm 10, \pm 9, ..., 0$ 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. 2, 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. 2, different “steps” dominate at different temperatures, indicating that thermal processes play a central role. The steps in the magnetization curves have been attributed to thermally-assisted quantum tunneling of the spin magnetization.

Thermally-assisted tunneling is shown schematically for the third “step” or field-resonance by the sequence of straight-line arrows in Fig. 1: the magnetization is thermally activated to a level near the top of the metastable well (e. g. $m' = -5$), tunnels across the barrier (to $m = 2$), and decays to the ground state ($m = 10$) of the stable well. 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 the tunneling process 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.

![FIG. 1. Double-well potential in the presence of a longitudinal magnetic field applied along the easy c-axis. Thermally-assisted tunneling is indicated by straight-line arrows. The left side of the figure shows a schematic of the Mn$_{12}$ molecule composed of four inner spin ($S = -3/2$) Mn$^{4+}$ ions and eight outer spin ($S = +2$) Mn$^{3+}$ ions with oxygen bridges, yielding a total spin $S = 10$ ground state at low temperatures.](image-url)
Chudnovsky and Garanin [5] have recently proposed that as the temperature is reduced, the levels that dominate the tunneling can shift to lower energies either continuously (“second order” transition) or abruptly (“first order” transition), depending on the form of the potential. It may thus be possible to observe an abrupt transition from thermally assisted tunneling (straight-line arrows in Fig. 1) to pure quantum mechanical tunneling from the lowest state of the metastable well (denoted by the dotted line) as the temperature is reduced. Indeed, earlier magnetization experiments [6] have indicated that a rapid shift occurs to tunneling from the lowest state as the temperature is reduced.

In the present paper we report detailed measurements at a series of very closely spaced temperatures of the magnetization as a function of magnetic field applied along the easy axis of magnetization. We show that there is an abrupt transfer over a narrow range of temperature to enhanced magnetic relaxation at the magnetic field corresponding to tunneling from the lowest state of the metastable well. These results provide solid new evidence that there is an abrupt or “first order” transition between thermally-assisted and ground state tunneling in Mn$_{12}$. Identification of the levels that participate in tunneling is based on the following considerations. The spin Hamiltonian for Mn$_{12}$ is given by:

$$\mathcal{H} = -DS^2_z - g_z\mu_B H_z S_z - AS^4_z + \ldots$$  \hspace{1cm} (1)

where $D$ is the anisotropy, the second term is the Zeeman energy, and the third on the right-hand side represents the next higher-order term in longitudinal anisotropy; additional contributions (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 for magnetic fields:

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

where $N = |m + m'|$ is the step number. The second term in brackets is small compared to 1. Thus, a series of steps $N_i$ occurs at approximately equally spaced intervals of magnetic field, $D/(g_z\mu_B) \approx 0.42$ Tesla; for a given step all pairs of levels cross at roughly the same magnetic field. However, careful measurements show that there is structure within each step due to the presence of the term $AS^4_z$; as shown diagrammatically in Fig. 3, the levels do not cross simultaneously, an effect that is more pronounced for levels that are deeper in the well. EPR [7] and neutron scattering [8–10] experiments have yielded precise values of $A = 1.173(4) \times 10^{-3}$ K/mol and $D = 0.548(3)K$, and an estimate for $g_z$ of 1.94(1). Comparison of the measured magnetic fields with those calculated from Eq. (2) therefore provides an experimental tool that allows identification of the states that are predominantly responsible for the tunneling.

The magnetization of small single crystals of Mn$_{12}$-acetate was determined from measurements of the local magnetic induction at the sample surface using 10 $\times$ 10 $\mu$m$^2$ Hall sensors composed of a two-dimensional electron gas (2DEG) in a GaAs/AlGaAs heterostructure. The 2DEG was aligned parallel to the external magnetic field, and the Hall sensor was used to detect the perpendicular component (only) of the magnetic field arising from the sample magnetization [11].

Our results are shown in the next few figures. For different temperatures between 0.24 K and 0.88 K, Fig. 4...
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 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. The issue is whether this transfer occurs gradually or abruptly.

In order to address this question, we examine some of the data in greater detail. The derivative of the magnetization is shown on an expanded scale for step $N = 7$ in Figs. 5 and 6. Figure 5 shows $\partial M/\partial H$ as a function of magnetic field for different temperatures between 0.24 K and 1.32 K; the vertical lines indicate tunneling from levels corresponding to the different spin projections $m'$. Figure 6 shows the same data in the H-T plane, with $\partial M/\partial H$ shown in the third dimension by different shading, with lighter shade corresponding to larger amplitude. As the temperature is reduced, the maximum gradually moves to higher field and its amplitude changes. Figure 5 shows that there is structure at some temperatures that indicates the presence of more than one maximum, implying that more than one pair of levels is active; where a single maximum appears, it is probably the convolution of two or three maxima. It is noteworthy that the contribution from $m' = -9$ is minimal, or quite small, compared with other levels. In contrast, the contribution from $m' = -10$ becomes increasingly dominant as the temperature is lowered. There is an abrupt transfer of weight to tunneling from the lowest (ground) state of the metastable well.

FIG. 4. For a set of closely spaced temperatures, $\partial M/\partial H$ is shown as a function of magnetic field. The amplitude is a measure of the rate of magnetic relaxation. Note the substructure within each of the four maxima corresponding to steps $N = |m + m'| = 5, 6, 7, 8, 9$.

FIG. 5. The first derivative of the magnetization with respect to magnetic field versus magnetic field shown on an expanded scale for $N = |m' + m| = 7$. The vertical lines denote the magnetic fields corresponding to tunneling between different pairs of levels $(m', m)$ on opposite sides of the potential barrier: $(-7, 0), (-8, 1), (-9, 2), (-10, 3)$. Several intermediate temperatures were omitted from the legend for clarity.

FIG. 6. For step $N = |m' + m| = 7$, $\partial M/\partial H$ is shown as a function of magnetic field $H$ and temperature $T$. Yellow shading denotes large $\partial M/\partial H$ while blue corresponds to smaller amplitudes.
FIG. 7. The magnetic field of the maxima in $\partial M/\partial H$ corresponding to enhanced magnetic relaxation plotted as a function of temperature. The fields corresponding to tunneling from different levels $m'$ within each step $N$ are indicated by horizontal lines. With decreasing temperature, the maxima initially shift gradually upward in field, then exhibit an abrupt shift to tunneling from $m' = -10$ within a narrow temperature range, below which the field of the maximum remains constant.

This is shown more explicitly in Fig. 7. Here, the positions of the maxima are plotted as a function of temperature for all measured $N$. Within each step, the magnetic fields corresponding to tunneling from levels $m'$ in the metastable well are indicated by horizontal lines, as labeled. For each step, the position of the maximum shifts gradually and continuously to higher magnetic field as the temperature is decreased, and then moves abruptly to $m' = -10$ at some temperature below which the field of the maximum remains constant. Although no levels are skipped entirely for the conditions of our experiments, there is a sudden shift to tunneling at a magnetic field that is independent of the temperature, and the value of this magnetic field agrees quantitatively with the calculated position for tunneling from $m' = -10$.

To summarize, magnetization measurements in Mn$_{12}$ acetate taken at closely spaced intervals of temperature exhibit an abrupt shift over a narrow temperature range to rapid magnetic relaxation at a “resonant” magnetic field corresponding to tunneling from the lowest state of the metastable potential well; this resonant field is then independent of temperature as the temperature is reduced further. Our data provide solid evidence for an abrupt transition between thermally-assisted tunneling and pure quantum tunneling from the ground state.

Work at City College was supported by NSF grant DMR-9704309 and at the University of California, San Diego by NSF grant DMR-9729339. EZ acknowledges the support of the German-Israeli Foundation for Scientific Research and Development.

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[12] Throughout this paper, we have used $H$ instead of the effective field $H_{eff} = H + \alpha(4\pi M)$; the field due to the sample magnetization is on the order of 300 Oe.