EUROPHYSICS LETTERS 15 September 2001

Europhys. Lett., **55** (6), pp. 874–879 (2001)

Abrupt crossover between thermally activated relaxation and quantum tunneling in a molecular magnet

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(received 22 May 2001; accepted 27 June 2001)

PACS. 75.45.+j – Macroscopic quantum phenomena in magnetic systems.
PACS. 75.50.Xx – Molecular magnets.

Abstract. – 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. Detailed data taken at a series of closely spaced temperatures between 0.24 K and 1.4 K indicate an abrupt shift between thermally activated and ground-state tunneling over a narrow range of temperature.

Single-molecule magnets are organic materials which contain a large (Avogadro's) number of identical magnetic molecules; ($[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$), generally referred to as Mn_{12} acetate, is a particularly interesting 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 [1]. 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 [2,3] below the blocking temperature of 3 K have revealed a series of steep steps in the curves of M *vs.* 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 [4,5] to thermally assisted quantum tunneling of the spin magnetization.

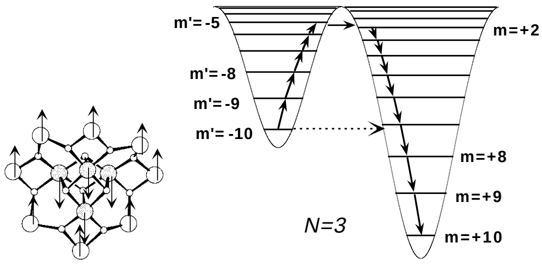

Fig. 1 – Double-well potential in the presence of a longitudinal magnetic field applied along the easy c-axis. Thermally assisted tunneling is indicated by straight-line arrows. The left side of the figure shows a schematic of the Mn_{12} molecule composed of four inner spin ($S = -3/2$) Mn^{4+} ions and eight outer spin ($S = +2$) Mn^{3+} ions with oxygen bridges, yielding a total spin $S = 10$ ground state at low temperatures.

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, tunneling proceeds from progressively lower energy levels deeper in the potential well.

Chudnovsky and Garanin [6, 7] have proposed that the crossover from thermally assisted tunneling (straight-line arrows in fig. 1) to pure ground-state tunneling (the dotted line) can occur either continuously ("second order" transition) or abruptly ("first order" transition) as the temperature is reduced. Experiments in Mn_{12} have yielded conflicting results on this question: data of Kent *et al.* [8] indicate there is an abrupt shift, while Chiorescu *et al.* [9] claim that the transition is smooth. In the present paper we report careful measurements for a series of very closely spaced temperatures that show in detail that there is indeed an abrupt transfer over a narrow range of temperatures to enhanced magnetic relaxation at the magnetic field corresponding to tunneling from the lowest state of the metastable well.

Identification of the levels that participate in tunneling is based on the following considerations. The spin Hamiltonian for Mn_{12} is given by

$$\mathcal{H} = -DS_z^2 - g_z\mu_{\mathrm{B}}H_zS_z - AS_z^4 + \dots, \tag{1}$$

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:

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

where $N = |m + m'|$ is the step number. Thus, a series of steps N_i occurs at approximately equally spaced intervals of magnetic field, $D/(g_z\mu_{\mathrm{B}}) \approx 0.42$ T; for a given step all pairs

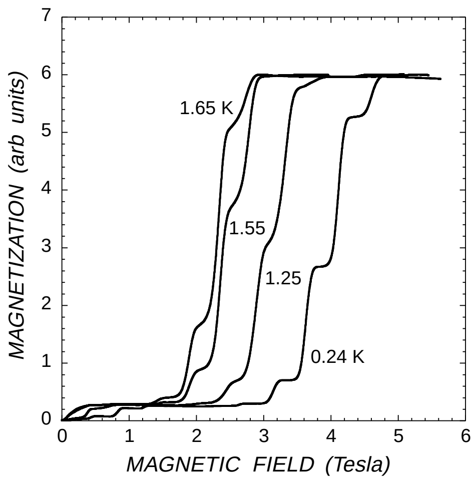

Fig. 2 – Magnetization *vs.* longitudinal magnetic field for a Mn_{12} sample starting from a demagnetized state, $M = 0$; data are shown at four different temperatures, as labeled. Note the steep segments, or steps, corresponding to faster magnetic relaxation at specific values of magnetic field.

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_z^4; 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 [10] and neutron scattering [11–13] experiments have yielded precise values of $A = 1.173(4) \times 10^{-3}$ K/mol and $D = 0.548(3)$ K,

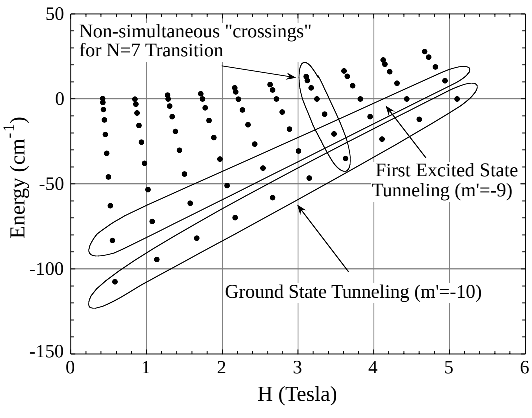

Fig. 3

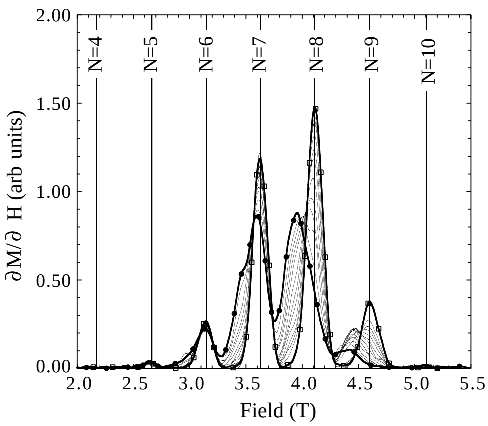

Fig. 4

Fig. 3 – Energy level diagram obtained for the spin Hamiltonian for Mn_{12}. The dots indicate magnetic fields where pairs of energy levels on opposite sides of the barrier cross, giving rise to enhanced magnetic relaxation via tunneling.

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 $N = |m' + m| = 5, 6, 7, 8$, and 9.

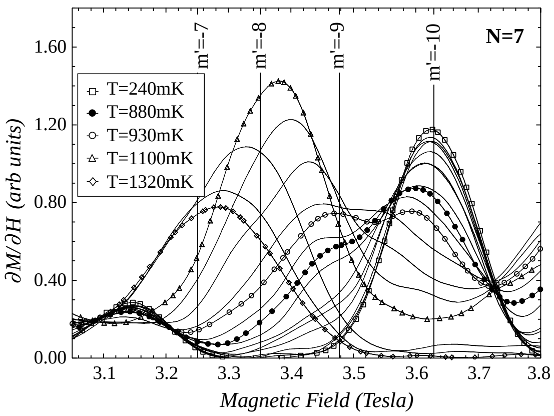

Fig. 5 – The first derivative of the magnetization with respect to magnetic field *vs.* magnetic field shown on an expanded scale for $N = |m' + m| = 7$. The vertical lines denote the magnetic fields corresponding to tunneling between different pairs of levels (m', m) on opposite sides of the potential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

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 10×10 μm^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([1]).

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([2]). 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

([1])A detailed description of the measurement techniques can be found in [14, 15].
([2])Throughout this paper, we have used H instead of the effective field $H_{\text{eff}} = H + \alpha(4\pi M)$; the field due to the sample magnetization is on the order of 300 Oe.

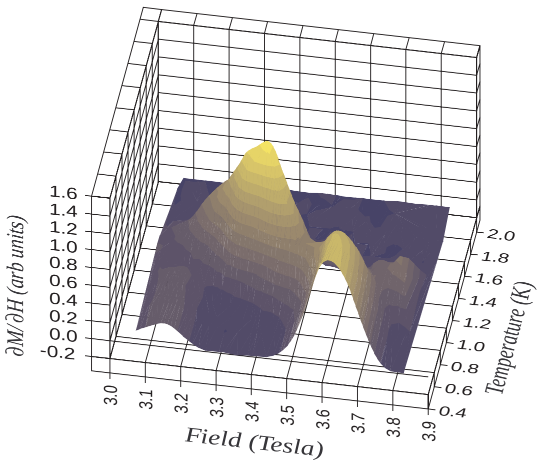

Fig. 6 – For step $N = |m' + m| = 7$, $\partial M/\partial H$ is shown as a function of magnetic field H and temperature T. Yellow shading denotes large $\partial M/\partial H$ while blue corresponds to smaller amplitudes.

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.

This is shown more explicity 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

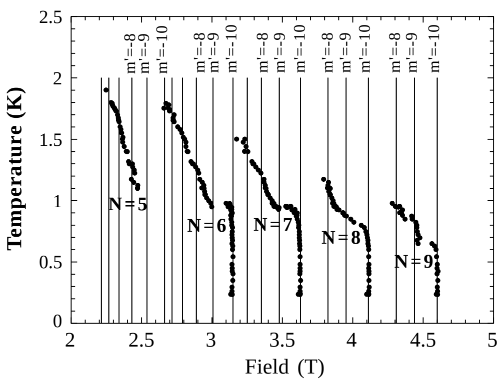

Fig. 7 – The magnetic field of the maxima in $\partial M/\partial H$ corresponding to enhanced magnetic relaxation plotted as a function of temperature. The fields corresponding to tunneling from different levels m' within each step N are indicated by vertical lines. With decreasing temperature, the 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.

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 show that there is an abrupt transfer from thermally assisted to ground-state tunneling as the temperature is reduced. Further detailed work is required to determine whether this rapid crossover is associated with the "first order" transition predicted theoretically [6, 7], or whether it is due to some other phenomenon.

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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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