Low-temperature magnetic hysteresis in Mn$_{12}$ acetate single crystals

A. D. Kent$^1$(*), Yicheng Zhong$^2$, L. Bokacheva$^1$, D. Ruiz$^3$, D. N. Hendrickson$^3$ and M. P. Sarachik$^2$

1 Department of Physics, New York University
4 Washington Place, New York, NY 10003 USA
2 Physics Department, City College of the City University of New York
New York, NY 10031 USA
3 Department of Chemistry and Biochemistry, University of California at San Diego
La Jolla, CA 92037 USA

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Abstract. – Precise magnetic-hysteresis measurements of small single crystals of Mn$_{12}$ acetate of spin 10 have been conducted down to 0.4 K using a high-sensitivity Hall magnetometer. At higher temperature ($> 1.6$ K) step-like changes in magnetization are observed at regularly spaced magnetic-field intervals, as previously reported. However, on lowering the temperature the steps in magnetization shift to higher magnetic fields, initially gradually. These results are consistent with the presence of a higher-order uniaxial magnetic anisotropy (fourth order in $S_z$), first observed by EPR spectroscopy, and thermally assisted tunnelling with tunnelling relaxation occurring from levels of progressively lower energy as the temperature is reduced. At lower temperature an abrupt shift in step positions is found. We suggest that this shift may be the first evidence of an abrupt, or first-order, transition between thermally assisted and pure quantum tunnelling, suggested by recent theory.

Introduction. – The high-spin ($S = 10$) molecular magnets Mn$_{12}$ acetate and Fe$_8$ have become prototypes for the study of the transition from classical superparamagnetism to quantum tunnelling of mesoscopic spins. Much of the recent interest in these materials has been stimulated by the observation of a remarkably regular series of steps and plateaus in the magnetic-hysteresis loops of Mn$_{12}$ at low temperature (below a blocking temperature of 3 K), first in oriented powders [1] and shortly thereafter in single crystals [2]. These results indicate that the relaxation rate of the magnetization toward equilibrium is greatly enhanced at well-defined intervals of magnetic field. These observations have been interpreted within a simple effective spin Hamiltonian for these molecules and a model of thermally assisted tunnelling of the magnetization, suggested in ref. [3]. This model describes a regime intermediate between thermal activation over the anisotropy barrier (superparamagnetism) and pure quantum tunnelling ($T = 0$) in which both thermal activation and quantum tunnelling are important to the magnetization reversal.

(* ) E-mail: andy.kent@nyu.edu

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Mn\textsubscript{12} has subsequently been studied extensively and by a variety of techniques. Notably, both EPR [4] and inelastic neutron spectroscopy [5–7] have been used to independently determine the parameters for the spin Hamiltonian of Mn\textsubscript{12}. These have shown that higher-order terms in the Hamiltonian—not considered in the analysis thus far of magnetic-hysteresis data—are necessary to fit the spectra. Surprisingly few experiments have been conducted at lower temperature in Mn\textsubscript{12} to study the transition to pure quantum tunnelling behaviour, in contrast to important studies of this type in Fe\textsubscript{8} [8, 9]. Some earlier experiments showed the appearance of “magnetic avalanches” at lower temperature, that is, rapid and uncontrolled magnetization switching to its saturation value, which precluded controlled low-temperature relaxation studies [10]. Later studies using cantilever magnetometry revealed several new higher-field magnetization steps at lower temperature, consistent with the model of thermally assisted tunnelling [11].

In this letter we present precise low-temperature high-field magnetic-hysteresis measurements on Mn\textsubscript{12} which reveal two important new aspects of the magnetization reversal. First, on lowering the temperature below 1.6 K, we find that steps in magnetization shift gradually to higher magnetic field, consistent with the presence of a second-order uniaxial magnetic anisotropy (i.e., a term proportional to $S_4^z$) determined by EPR spectroscopy [4] and, recently, by precise inelastic neutron scattering measurements [5, 6]. Second, at lower temperature an intriguing abrupt shift in step position is found. We suggest that this shift may be due to an abrupt transition between thermally assisted and pure quantum tunnelling in Mn\textsubscript{12} acetate, first predicted theoretically by Chudnovsky and Garanin [12]. We also discuss other possible origins of this observation.

**Background.** – Mn\textsubscript{12} acetate crystals have a tetragonal lattice ($a = 1.73$ nm and $b = 1.24$ nm) of molecules with 12 interacting mixed valent Mn ions with a net ground state spin of 10, $S = 10$ [13]. Thus each molecule has $2S + 1 = 21$ magnetic levels in its ground state, labeled by quantum number $m$ ($m = -10, -9, -8, ..., 10$). The molecules have a strong uniaxial magnetic-anisotropy energy, and to a good approximation the spin Hamiltonian can be written:

$$H = -DS_2^z - BS_4^z - g_z\mu_B H_z S_z + H'. \quad (1)$$

The parameters $D$ and $B$ have been determined first by EPR spectroscopy [4] and now very accurately by inelastic neutron spectroscopy [6] to be $D = 0.548(3)$ K, $B = 1.173(4) \times 10^{-3}$ K, and $g_z$ is estimated to be 1.94(1) [4]. Spin alignment is favored to be up ($m = 10$) or down ($m = -10$) along the $z$-axis. The energy barrier between up and down states is approximately 67 K. The third term is the Zeeman energy for fields applied parallel to the easy axis. $H'$ represents small terms which break the axial symmetry and, hence, produce tunneling. These are due to transverse fields (i.e., terms like $H_x S_x$), and higher-order magnetic anisotropies, the lowest-order form allowed by tetragonal symmetry being $(S_4^x + S_4^y)$. By itself, this last term would lead to a tunneling selection rule with $\Delta m = 4i$, with $i$ an integer. Since this is not found experimentally, it is likely that transverse fields due to hyperfine, dipolar fields ($\sim 0.1$ K) and/or an external applied field (such as due to a small misalignment between the applied field and the $z$-axis) are most important to mixing the $m$-levels and producing tunneling.

The steps observed in magnetic-hysteresis measurements, their temperature dependence and magnetization relaxation experiments provide strong evidence for thermally assisted tunneling. Within this model magnetization reversal occurs by tunneling from thermally excited magnetic sublevels (i.e., $m = 9, 8, 7, ..., -8, -9$) at magnetic fields at which these levels are in resonance with levels on the opposite side of the anisotropy barrier (inset fig. 1). From (1)
levels $m$ and $m'$ have the same energy when

$$H = nH_0 \left[ 1 + \frac{2B}{D} \left( \left( m - \frac{n}{2} \right)^2 + \frac{n^2}{4} \right) \right],$$

(2)

where $n = m + m'$ is the step index, $H_0 = D/g_z\mu_B = 0.42$ T is a field “quantum” and $m$ is the escape level from the metastable well. At these magnetic fields, the magnetization relaxation can occur on measurement time scales and give rise to the step-like changes in magnetization. Otherwise, the relaxation rate is slower, leading to plateaus in the magnetic-hysteresis loop. The relaxation rate from any level is proportional to the product of the thermal occupation probability of that level and the probability for quantum tunnelling from the level, and thus should increase exponentially with temperature, as found in experiments above 2 K [13,14]. Since the tunnelling probability is intrinsically small for lower-lying levels (with large $\Delta m = m - m'$), larger magnetic fields are necessary at lower temperature to produce observable tunnelling relaxation, also, as seen in experiments.

Importantly, within this model, tunnelling relaxation occurs from small group of quasilevels in the metastable well — the escape levels, $m_{esc}$. This is because the tunnelling probability increases exponentially with energy $E$, as the effective barrier height becomes lower, while the thermal occupation probability decreases exponentially with energy, $\exp[-E/kT]$. Note also from eq. (2) that for a given step index $n$ the fields at which steps occur depend on the escape levels. Larger fields are necessary to bring lower-lying levels, i.e., larger $m$ levels, into resonance (as, generally, $m > n/2$), so that a shift in step position to higher fields signals tunnelling from states deeper in the metastable potential well (i.e., larger $m_{esc}$). Finally, dipolar interactions between clusters, interactions with nuclear spins [15] and spin-phonon interactions are essential to a quantitative and microscopic understanding of the relaxation [16,17], such as the observation of non-exponential relaxation [8,18] and both the linewidth and form of the relaxation peaks [19].

**Experiment.** — The magnetization of small single crystals of Mn$_{12}$-acetate in the form of a parallelepiped ($50 \times 50 \times 300$ $\mu$m$^3$) was measured using a high-sensitivity micro-Hall effect.
Fig. 2 – Derivative of the magnetization with respect to applied field vs. field at temperatures from 2.4 K to 0.4 K. Data are acquired from \( M = 0 \) at constant field ramp rate of 0.1 T/min. The small peaks at low temperature and fields \( (H/H_0 < 3) \) are due to a small magnetic impurity phase in the crystal, discussed in ref. [20]. Data near the \( n = 5 \) peak at 0.4 K is multiplied by 10 and offset so that it is visible on the plot.

magnetometer [21]. Like a micro-superconducting quantum interference device (\( \mu \)-SQUID) [22], this magnetometer measures a magnetic field induced by the crystal’s magnetization. The measurements are done in a rf-shielded automated high-field helium 3 system, in which careful attention has been paid to reducing electrical noise and to thermalizing the sample. Temperature is measured both at the cold stage of the cryostat and with a small resistance thermometer mounted within a few mm of the sample. These measurements are always within 50 mK of one another. Figure 1 shows a typical portion of a hysteresis curve measured at 0.4 K starting from a demagnetized state, \( M = 0 \), and measured at a ramp rate of 0.1 T/min, with the field along the easy axis (within a few degrees). Prominent step-like changes in magnetization are observed at fields between 3 and 5 T.

Figure 2 shows the derivative of the magnetization curves \( dM/dH \) vs. applied field at different temperatures. Peaks in \( dM/dH \) correspond to maxima in the magnetization relaxation rate at that applied field, sample magnetization and measurement temperature. Examining the data from high to low temperature; first, above 1.6 K the data are in good accord with previous experiments [1, 2], Peaks appear at approximately equally spaced field intervals (\( \sim 0.45 \) T) and their amplitude is a strong function of the temperature. As the temperature is reduced, higher numbered maxima in \( dM/dH \) appear, while lower field peaks decrease in amplitude, again, consistent with the model of thermally assisted tunnelling. Second, on lowering the temperature peaks shift continuously to higher fields. For instance, peak \( n = 5 \), at 2.2 K is at 2.20 T and by 1.4 K has shifted to 2.33 T. Third, and most intriguing, at lower temperature \( (T < 1.2 \text{ K}) \) peaks in \( dM/dH \) shift dramatically in position as a function of
Fig. 3 – Relaxation peak positions, $H_{\text{int}} = H + 4\pi M$ [23], normalized to $H_0$, the field quantum, vs. temperature. The solid line shows the approximate temperature below which peak positions are temperature independent.

Fig. 4 – Energy level diagram vs. field for Mn$_{12}$-acetate obtained by diagonalizing the Hamiltonian (eq. (1)). Energy is measured relative to the lowest-lying state in the metastable well. The levels important to the low-temperature relaxation are indicated. The abrupt shifts in the magnetization steps with decreasing temperature are consistent with the escape levels changing as illustrated by the dashed arrows from $m = 8$ to $m = 10$.

temperature. This is well illustrated by the behaviour of the $n = 7$ peak as the temperature is reduced. This peak first appears at 1.6 K at $H = 3.10$ T, grows in amplitude and shifts to significantly higher fields on lowering the temperature and, at 1.0 K, abruptly develops a high-field shoulder. On slightly lowering the temperature to 0.9 K, “spectral” weight is transferred into this shoulder and at the lowest temperature the peak remains fixed in position. This peak has shifted to 3.53 T, by a full field quantum $H_0$, in this temperature interval. Shifts in peak position of this order are seen for all the steps observed at low temperature ($5 \leq n \leq 9$). Finally, note that at 0.6 K and lower temperature, the maxima remain fixed in field and approximately constant in amplitude.

The dependence of the d$M$/d$H$ peak positions on temperature are summarized in fig. 3. Here the peak positions, in internal field ($H_{\text{int}} = H + 4\pi M$) divided by the field quantum, $H_0$, are plotted vs. temperature. Note that peaks initially shift gradually to higher magnetic fields as the temperature is lowered. Between 0.6 K and 1.2 K the peak positions shift abruptly, with higher step indices changing position at lower temperature. The solid vertical line demarcates the approximate temperature at which these sudden shifts in step position occur. Below this line the step positions are independent of temperature.

Discussion. – These experiments are the first to show that the steps in magnetization of Mn$_{12}$ are not always at regular magnetic-field intervals and that steps shift to higher magnetic fields as the temperature is lowered. The data are consistent with the presence of a second-order (fourth power) uniaxial term in the magnetic anisotropy of Mn$_{12}$ (eq. (1)) and indicate that lower-lying magnetic sublevels dominate the tunnelling relaxation as the temperature is reduced (eq. (2)).

We can clearly distinguish the physical behaviour in two different temperature regimes. At higher temperature (above the solid line in fig. 3) the step positions shift gradually with temperature. This is the regime of thermally assisted tunnelling, where the magnetic escape is from thermally excited magnetic levels. We associate shifts in step positions with incremental
changes in these levels, such as from \( m \) to \( m + 1 \), as the temperature is reduced and/or changes in the relative importance of a few levels, which contribute “in parallel” to the magnetization relaxation at a given temperature. Figure 4 shows the energy levels vs. field for the Mn\(_{12}\) spin Hamiltonian (eq. (1)). The vertical solid lines indicate the level coincidences important to the magnetic relaxation in this temperature and field range. For example, for \( n = 6 \), the step positions we find are consistent with transitions from \( m = 8 \) to \( m' = -2 \) and \( m = 7 \), to \( m' = -1 \).

The second regime is at low temperature (below the solid line in fig. 3) in which the position of peaks in \( \frac{dM}{dH} \) are independent of temperature. This is consistent with magnetization relaxation being of a pure quantum nature, i.e. tunnelling escape occurring from the lowest level in the metastable well, \( m = 10 \). At 0.6 K and below, the amplitude of the peaks are also temperature independent; this is additional evidence for a quantum regime in Mn\(_{12}\), as it indicates that the relaxation of the magnetization in our measurement time window has become temperature independent.

The most striking feature of these data is the abrupt shift in step position, observed at the boundary between these temperature regimes. This shift suggests that different levels become important to the tunnelling relaxation in a narrow temperature interval. The shift in peak positions of fig. 3 is consistent with the change in levels responsible for tunnelling illustrated by the dashed arrows in fig. 4 — \( m_{\text{esc}} \) changes by 2 in an interval of 0.1 to 0.2 K. The abrupt nature of this transition is evident directly from the magnetic-hysteresis data in fig. 2. For example, that the shoulder which develops for the \( n = 7 \) peak at 1.0 K (fig. 2) indicates that metastable levels \( m = 8 \) (\( m' = -1 \)) and \( m = 10 \) (\( m' = -3 \)), both contribute to the magnetic relaxation at this temperature but at different easy axis magnetic fields.

We now speculate as to the origin of the abrupt in shift step position with temperature. The most interesting possibility is that the abrupt shift in peak position we observe is evidence for a first-order transition between thermally assisted and pure quantum tunnelling, as suggested in ref. [12]. In this theory it is shown that for a small uniaxial magnetic particle the energy of the quasilevels in the metastable magnetic well which dominate the magnetic escape need not be a smooth function of temperature. Larkin and Ovchinnikov called the smooth transition from classical thermal activation to pure quantum tunnelling a second-order transition [24], regarding the energy of escape as analogous to an order parameter in a phase transition problem. For small transverse fields, Chudnovsky and Garanin find that the transition can be first-order with certain energy levels in the metastable well being skipped entirely as the temperature is varied. They considered both a large uniaxial spin in a quasiclassical approximation [12] as well as small spins (\( S \sim 10–100 \)) with a discrete level spectrum [25,26], as in Mn\(_{12}\).

There may, of course, be other explanations for the observed shift in relaxation peaks with temperature. A tacit assumption we make is that peaks in \( \frac{dM}{dH} \) correspond to maxima in the relaxation rate at a given field (including the internal field). Then the maximum shift in relaxation rate maxima due to the internal fields is about \( 4\pi M \approx 0.06 \) T, which is smaller than the changes that we observe (\( \approx 0.4 \) T). However, it may not be possible to account for the internal fields in this average way. For instance, the distribution of internal fields throughout the crystal likely changes in a complex manner during our field sweep experiments.

It is also possible that sample heating plays a role. For example, if the sample were not in thermal equilibrium with the thermometers during the measurements and actually at a higher temperature, this would explain the temperature-independent behaviour observed below 0.6 K. Sample heating may also play another role. Relaxation of the magnetization leads to strong dissipation, which leads to sample heating which, in turn, leads to enhanced magnetization relaxation. This positive feedback is at the origin of the magnetic avalanches.
reported in ref. [10]. Perhaps, this positive feedback could produce the shoulder-like structures we observe on certain \( \frac{dM}{dH} \) peaks in fig. 2 (0.9 and 1.0 K). We estimate that the maximum heat generated in these experiments is \( H(\frac{dM}{dt}) = H(\frac{dM}{dH})(\frac{dH}{dt}) = 1 \) nW, which is of the same order as the heat dissipated in our Hall magnetometer (2 nW). Nonetheless, we have sometimes observed magnetic avalanches at higher sweep rates (0.4 T/min) — so we cannot completely rule out this possibility. Finally, while the peak shifts we observe are abrupt, the transition could still be continuous but occur over a narrow temperature interval. Further detailed experimentation and modeling are likely to clarify this situation.

In summary, we have presented new data which suggest the transition between thermally assisted and pure quantum tunneling in \( \text{Mn}_{12} \) may be abrupt, or first order. Importantly, these results show that magnetization relaxation and magnetic-hysteresis measurements may be used to do a new type of spectroscopy of the levels important to magnetic escape in \( \text{Mn}_{12} \). Further experiments and modeling will undoubtedly lead to a better fundamental understanding of this transition between thermally assisted and pure quantum tunneling.

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