

Heat Capacity Anomalies Induced by Magnetization Quantum Tunneling in a $\text{Mn}_{12}\text{O}_{12}$ -Acetate Single Crystal

F. Fominaya,¹ J. Villain,¹ P. Gandit,¹ J. Chaussy,¹ and A. Caneschi²

¹*CRTBT-CNRS, 25 avenue des Martyrs, 38042 Grenoble, France*

²*Department of Chemistry, University of Florence, Via Maragliano 77, 550144 Firenze, Italy*

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A particularly sensitive heat capacity measuring device has allowed us to measure the tunneling process of $\text{Mn}_{12}\text{O}_{12}$ -acetate single crystals (mass: 1 and 20 μg) from the irreversible tunneling process below the blocking temperature T_B to the reversible resonant tunneling process above T_B . Above the T_B (typically 3.5 K) we find specific heat anomalies at the magnetic field values that correspond to the crossing of spin up and spin down levels of different magnetic quantum numbers. Below T_B , heat relaxation pulses at the crossing of crystal field levels are observed for fields applied antiparallel to the initial magnetization. These measurements give a new scope to $\text{Mn}_{12}\text{O}_{12}$ -acetate investigations and show the great interest of nanocalorimetry for studies of big magnetic molecules. [S0031-9007(97)03794-0]

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Crystals of $\text{Mn}_{12}\text{O}_{12}$ -acetate clusters [1] are molecular spin systems that exhibit spectacular effects [2]. Twelve manganese ions (4 Mn^{3+} and 8 Mn^{4+}) are coupled by ferromagnetic exchange to a $S = 10$ macrospin. The $\text{Mn}_{12}\text{O}_{12}$ clusters are embedded in an organic matrix and show no exchange coupling from one cluster to another. The crystals are regular parallelepipeds with a strong magnetocrystalline anisotropy (~ 60 K) along the longitudinal axis. Once oriented, they present at low temperatures and zero magnetic field a very long relaxation time of the magnetization (two months at 2 K [3]). Recently, quantum tunneling of molecular spins through the anisotropy, at magnetic field values that correspond to the crossing of spin up and spin down levels of different magnetic quantum numbers, has been demonstrated [4–6].

The anisotropy lifts the $2S + 1$ degeneracy of the magnetic levels in zero field, creating a double well configuration [5] as sketched in Fig. 1. The manganese system is superparamagnetic and can be described by a Hamiltonian of the form [7]

$$\hat{H} = -DS_z^2 - g\mu_B S_z H + H^l, \quad (1)$$

where $D = 0.6$ K is the anisotropy energy per cluster, H the magnetic field applied parallel to the easy axis of magnetization, $g \simeq 2$ is the gyromagnetic factor, and S is the spin per cluster. H^l is a term that does not commute with S_z and is due to the demagnetizing field, dipole coupling, higher anisotropy terms, and/or hyperfine splitting. A great effort is underway to understand how it comes about [7,8].

Thermal measurements as a function of a magnetic field enlighten the interplay between the spin system and the lattice of the crystal, e.g., clarifying how the phonons influence the tunneling of the macrospins, therefore, giving a great deal of new information.

We have performed two kinds of measurements on $\text{Mn}_{12}\text{O}_{12}$ monocrystals, the heat capacity as a function

of an applied static magnetic field ($C[H]$) and the temperature as a function of a slowly scanned magnetic field ($T[H]$). The measure of very small single crystals promises a high quality of the sample and avoids the broadening found with powder samples due to the slightly different characteristics of every crystal. On the other side, it implies a great experimental difficulty. An experimental setup has been developed (described elsewhere [9]) that allows measuring samples as small as 1 μg . It roughly consists of a 3 μm thick silicon membrane with a planar thermometer and heater. The crystal is pasted on the membrane with Apiezon-N grease.

The specific heat measurements were conducted with the ac-steady state method [10]. A modulated power P is applied by the heater to the sample, so the sample temperature oscillates at a pulsation ω (working frequency range: 4 to 20 Hz) with an amplitude ΔT . In suitable conditions the heat capacity reads $C \simeq P/\Delta T\omega$. Absolute heat capacity $C[T]$ values corresponded within 20% with values measured on $\text{Mn}_{12}\text{O}_{12}$ powder [11].

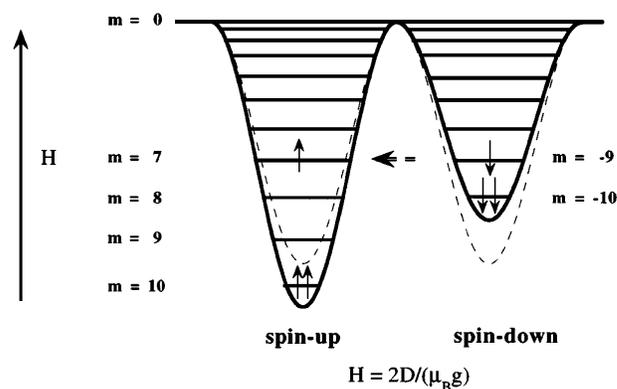


FIG. 1. Potential well of a $\text{Mn}_{12}\text{O}_{12}$ -acetate crystal at $H = 2D/g\mu_B$ and at zero field (dashed curve).

However, the real interest of the device is measuring C as a function of a magnetic field H . A sensitivity to heat capacity changes of $\Delta C/C \sim 10^{-4}$ was achieved.

Temperature measurements were performed by recording the thermometer's resistance (Niobium-nitride with $1/R \times dR/dT \approx 0.1 \text{ K}^{-1}$ at 4 K) versus magnetic field, without applying the modulated power P .

Three different samples were measured and the same qualitative results were found. The best measures were performed on the smaller crystals ($30 \times 60 \times 400 \mu\text{m}^3$ for $1 \mu\text{g}$ weight and $790 \times 180 \times 75 \mu\text{m}^3$ for $20 \mu\text{g}$). The external magnetic field was varied parallel to the easy axis of magnetization from -4 to 4 T, always starting from saturation. The heat capacity values were recorded after thermalization at every magnetic field step. Figure 2 shows a $C[H]$ measurement at different temperatures. Above 3.5 K a symmetric pattern of peaks appears at magnetic field values of ± 0.4 , ± 0.8 T and, in some cases, a residual peak at ± 1.2 T (Fig. 3). The shape of the anomalies changes with frequency and temperature; the height of the peaks increases as a function of the latter. The width of the anomalies does not depend on the amplitude of the temperature oscillation in the observed range of $30 \leq \Delta T \leq 500$ mK. The curve envelope changes exclusively with temperature. Above 5 K the peaks disappear into a broad maximum, which shifts to higher field values when the temperature is raised (Fig. 4).

Below 3.5 K no peaks appear and the envelope has a steeper fall, as can be seen for the 2.7 K curve of Fig. 2. On the other hand, if the thermalization time is too short, the curve is asymmetric and discontinuities at discrete values are observed when the field is applied antiparallel to the initial magnetization. The discontinuities strongly depend on the magnetic history of the sample and are clearly due to heat emissions. These heat pulses have been directly recorded with the thermometer (similar heat pulses due to avalanches of the magnetization have been observed by [3]), as it seemed more appropriate than heat capacity measurements: Figs. 5 and 6. Different scanning times of the magnetic field change the height and the width of the peaks. When the temperature is

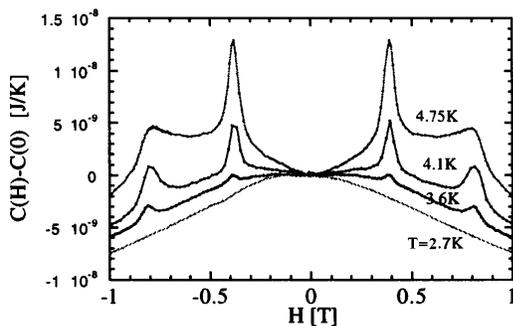


FIG. 2. Heat capacity of a $20 \mu\text{g}$ $\text{Mn}_{12}\text{O}_{12}$ -acetate monocrystal as a function of an applied magnetic field.

decreased, higher field peaks are enhanced and lower field peaks are diminished. The distance between pulses is always close to 0.4 T.

An interpretation of the results has to consider necessarily the relation between the measurement frequency ω and the magnetization's relaxation time τ . If τ is much longer than the period of measurement, i.e., if $\omega\tau \gg 1$, spins have no time to cross the anisotropy barrier and remain generally in the same potential well (see Fig. 1). In the following, this situation will be referred to as "unilateral regime." On the other hand, if $\omega\tau \ll 1$ the spin states in both wells are in thermal equilibrium so that the heat capacity measurement is an equilibrium measure of both wells. We call it "bilateral regime." Our typical measuring frequency was 10 Hz, the relaxation times of magnetization ranged from 10^6 s at 1.5 K to 0.1 ms at 7 K, so both cases, $\omega\tau \gg 1$ and $\omega\tau \ll 1$, were considered.

The internal energy of a magnetic system is given by

$$U = \frac{\sum_{n=1}^{N-1} \Delta_n \exp(-\beta \Delta_n)}{\sum_{n=0}^{N-1} \exp(-\beta \Delta_n)} \quad (2)$$

for a spin of modulus S : $N = 2S + 1$. In our case $S = 10$. $\beta = 1/T$, Δ_n is the energy difference, in kelvin, between the state n and the ground state $m = 10$. At low temperatures ($T < 3.5$ K), when the magnetization of the sample is saturated, only the $m = 9$ and $m = 10$ states of the spin up well, i.e., the lowest energy states, are significantly populated. If the magnetic field is augmented, the splitting of the states increases and thus the heat capacity decreases. In this case Eq. (2) gives

$$C = \frac{dU}{dT} \approx k_B \beta^2 \frac{\Delta_1^2 \exp(-\beta \Delta_1)}{[1 + \exp(-\beta \Delta_1)]^2}, \quad (3)$$

where $\Delta_1 = E_{m=10} - E_{m=9} \approx 12$ K. The dependence on the magnetic field H is introduced by substituting $\Delta_n(H) = \Delta_n^0 + \tilde{H}$, where $\Delta_n^0 = \Delta_n(H = 0)$ and $\tilde{H} = 2g\mu_B H$ ($\mu_0 H$: magnetic field in tesla). We get

$$C \approx k_B \beta^2 \frac{(\Delta_1^0 + \tilde{H})^2 \exp[-\beta(\Delta_1^0 + \tilde{H})]}{\{1 + \exp[-\beta(\Delta_1^0 + \tilde{H})]\}^2}. \quad (4)$$

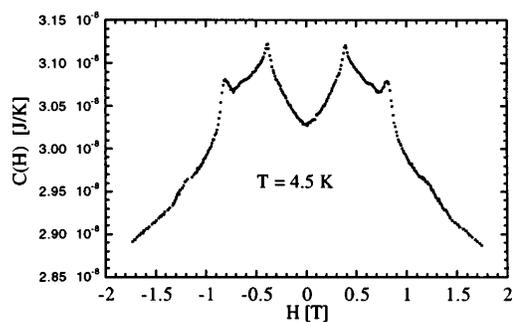


FIG. 3. Heat capacity $C[H]$ of a $1 \mu\text{g}$ $\text{Mn}_{12}\text{O}_{12}$ -acetate monocrystal. Addenda (mainly the grease) are estimated to be ~ 20 nJ/K.

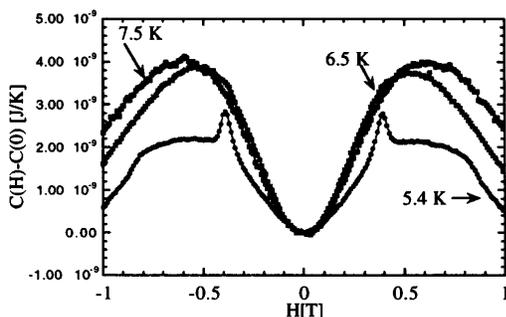


FIG. 4. Heat capacity $C[H]$ of a $1 \mu\text{g}$ $\text{Mn}_{12}\text{O}_{12}$ -acetate single crystal in the bilateral regime.

This equation accounts qualitatively for the behavior of the low temperature heat capacity measurement of Fig. 2 ($T = 2.7$ K). On the other hand, when the magnetic field is swept without permitting the system to reach equilibrium, discontinuities appear in the curve. The discontinuities are due to heat emissions that appear when the relaxation time of magnetization strongly decreases at positive magnetic field values $H_n = nD/g\mu_B \sim 0.4n$ T, and they can be interpreted as a spin tunneling when magnetic levels cross together (Figs. 5 and 6). Once a spin tunnels to the spin up well, it relaxes to the ground state under heat emission, so the process is irreversible. This explains the fact that the peaks only appear for a field applied antiparallel to the initial magnetization and that their shape strongly depends on the sweeping velocity. The relaxation times of the spins roughly follow an Arrhenius law [12] $\tau = \tau_0 \exp(T_0/T)$, where $\tau_0 = 10^{-7}$ s and $T_0 = 61$ K. With decreasing temperature, the relaxation times of the lower field peaks (0.4 T, 0.8 T) become too long, so not enough spins flip to produce a heat pulse and gradually the peaks disappear, favoring the creation of new ones at higher fields where τ is still small enough (Fig. 6).

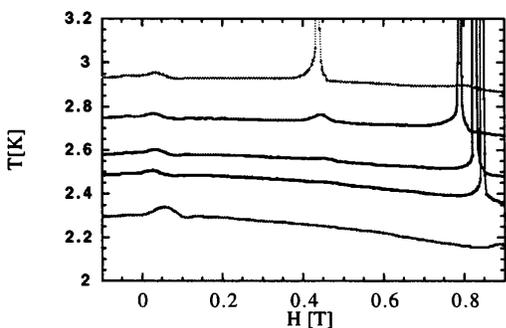


FIG. 5. Heat emissions of a $20 \mu\text{g}$ $\text{Mn}_{12}\text{O}_{12}$ -acetate monocrystal as a function of a swept magnetic field (17 mT/s). The shift of the 0.8 T peaks to higher fields with decreasing temperature could be due to higher order anisotropy (see [16]) or to the influence of magnetization on the local field of the sample $B = H + 4\pi M$.

At temperatures above 6 K the spins are spread on both wells and occupy excited states m with a probability that is proportional to the Boltzmann factor: $p_{\pm m} \propto \exp(-\beta E_{\pm m})$. The relaxation times are so short, $\tau < 1$ ms, that thermal equilibrium is established within the measuring period $1/\omega$. Excitations happen not only between states of the same well but also from one well to the other. Both wells contribute to the magnetic heat capacity, thus it is greater than in the unilateral case. The observed broad maximum (Fig. 4) can be understood by simply considering the two most populated states $m = \pm 10$: At zero field they are degenerated, so there is no magnetic contribution to the heat capacity, at high fields the gap between both states is very large and only few excitations occur. At an intermediate value $\tilde{H} \approx k_B T$, a large number of excitations occur and $C[H]$ has a maximum. Of course, to get the real temperature value of the maximum, all states must be considered.

The range from 3.8 to 5 K is characterized by large heat capacity anomalies at multiples of $0.4 \text{ T} \sim D/g\mu_B$. The characteristic relaxation times do not clearly belong to either the unilateral or bilateral regimes. The anomalies are probably due to a change from a rather unilateral regime to a bilateral one at the discrete magnetic field values where reversible tunneling reduces the relaxation time τ . Lioni *et al.* [13] have found at 5 K, $\tau = 0.012$ s at zero field and $\tau = 0.007$ s at $H = 0.4$ T. For a typically working frequency of $\omega = 16 \times 2\pi$ Hz the system is, for $H = 0.4$ T, rather in the bilateral regime ($\omega\tau = 0.7 < 1$) and for other field values, where no tunneling occurs, in the unilateral ($\omega\tau = 1.2 > 1$). The heat capacity difference between both regimes, i.e., the

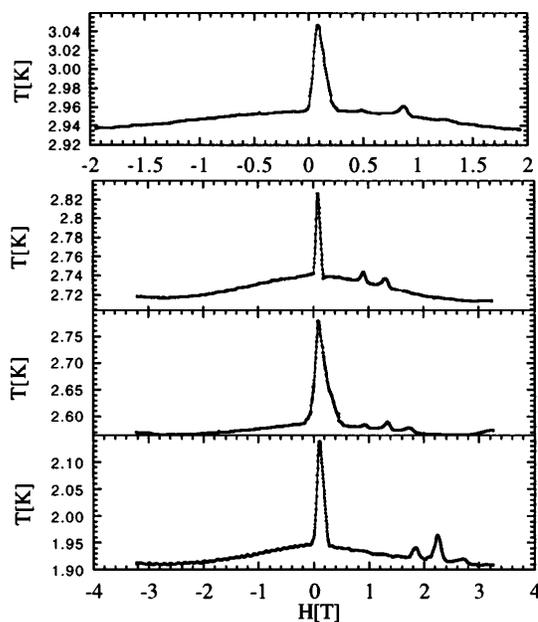


FIG. 6. Heat emissions of the $1 \mu\text{g}$ $\text{Mn}_{12}\text{O}_{12}$ -acetate crystal as a function of a swept magnetic field (5 mT/s).

height of the peaks, can be estimated using Eq. (2). Let us consider only the lowest levels $m = \pm(S - 1)$ and $m = \pm S = \pm 10$.

In the unilateral regime at $H = D/g\mu_B \sim 0.4$ T the heat capacity is given by Eq. (4). In the bilateral regime the $m = -S$ level must also be taken into account:

$$C_{\text{bil}} \approx k_B \beta^2 \frac{\sum_{n=1}^2 (\delta_n)^2 \exp(-\beta \delta_n)}{\left[\sum_{n=0}^2 \exp(-\beta \delta_n) \right]^2}, \quad (5)$$

where $\delta_1 = E_{10} - E_9$ and $\delta_2 = E_{10} - E_{-10} = 2s\tilde{H} = 12$ K. Thus $\delta_2 = \delta_1$ and $C_{\text{bil}} \approx 2C_{\text{uni}}$. Notice that at zero field $C_{\text{bil}} = C_{\text{uni}}$. That is why no anomaly appears at $H = 0$, although it is the most important level crossing.

An estimate of the magnetic heat capacity of the 20 μg crystal at a temperature of 4.8 K yields $2C_{\text{uni}} \sim C_{\text{bil}} \sim 2 \times 10^{-8}$ J/K, the order of magnitude measured in Fig. 2 (1.3×10^{-8} J/K). From formulas (2) to (4) it can be seen that the magnetic contribution to the heat capacity of the sample becomes actually of the same order of magnitude as the phonon contribution when the temperature is much below the Debye temperature (35 K according to [11]) but not too small with respect to the first excited level (12 K) of the spin Hamiltonian [Eq. (1)].

Nanocalorimetry has proved to be a powerful tool that permits us to measure mesoscopic effects of single magnetic crystals as small as 10^{-4} mm³. The tunneling process of Mn₁₂O₁₂ crystals, below and above the blocking temperature, has been measured. The magnetic specific heat of Mn₁₂O₁₂ exhibits a variety of broad and narrow peaks as a function of external field and temperature that can be explained in terms of a quantum tunneling of magnetization through the anisotropy barrier. We have presented a qualitative analysis in which the basic parameters are the uniaxial anisotropy constant D and the relaxation time τ of the magnetization. Our results are in qualitative agreement with magnetic measurements of τ [6,14,15]. Moreover, a more quantitative analysis of the specific heat data will provide a test of the theoretical model, e.g., delivering information about the presence or

absence of higher order anisotropy terms (in S_z^4 , etc.) in the spin Hamiltonian [Eq. (1)].

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