Specific heat and magnetic relaxation of the quantum nanomagnet $Mn_{12}Ac$

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We present specific-heat and ac-susceptibility measurements providing more evidence that magnetic quantum tunneling occurs in $Mn_{12}Ac$ spin clusters. The total anisotropy energy barrier determined by fitting an Arrhenius law to the magnetic relaxation time is underestimated when compared to the specific-heat data. The expected magnetic contribution using a quadratic spin Hamiltonian needs higher-order terms to improve the agreement with the experiments, as recently done for electron-paramagnetic-resonance spectra. In addition, another interesting effect was observed in the specific-heat measurements when a dc magnetic field is applied. The extra magnetic contribution due to Zeeman splitting is suppressed below the expected superparamagnetic blocking temperature in the time scale of the measurements. [S0163-1829(98)06109-8]

Superparamagnetic relaxation is a well-known phenomenon in the study of ultrafine magnetic particles since the pioneering work of Néel[1] associated with the study of rock magnetism. Since then, technological applications in magnetic recording and other areas such as biomagnetism and ferrofluids kept the interest high. Despite several decades of research, a complete understanding of the dynamics of such systems is still lacking. Recently, much evidence of a low-temperature saturation of the magnetic relaxation attributed to macroscopic quantum tunneling[2–8] focused more attention on the subject. One of the problems encountered in this area is the lack of experimental systems whose particle sizes are exactly known and monodisperse. Many of those drawbacks are overcome by the molecular cluster

$$[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}]\cdot 2CH_3\text{—}COOH\cdot 4H_2O,$$

$Mn_{12}Ac$, whose magnetization was found to undergo slow relaxation like superparamagnets at low temperatures.[9] These magnetic clusters, embedded in large molecules, have well isolated $S=10$ spins at low temperatures and a high anisotropy of crystalline origin responsible for the slow relaxation of the magnetization observed below 4 K. The strict monodispersion together with the negligible dipolar interaction puts this kind of molecular crystals in a unique position to clarify several questions in this field.

The molecular crystals have a tetragonal symmetry of spatial group I4 with unit cell parameters $a=17.3$ Å and $c=12.39$ Å and a molecular weight of 2060.[10] The clusters have crystal-imposed $S4$ symmetry, with eight Mn^{+3} ions ($S=2$) and four Mn^{+4} ions ($S=3/2$) coupled due to the superexchange interaction mediated by oxygen bridges. Below 20 K a ferrimagnetic structure with $S=10$, corresponding to all Mn^{+3} spins up and all Mn^{+4} spins down, is stabilized. The high uniaxial crystalline anisotropy splits the levels in 10 doublets plus one singlet, with $m_s=\pm 10$ lowest in energy. This corresponds to an Ising-type anisotropy with the easy axis of magnetization parallel to the crystallographic c axis. At the simplest level the effective spin Hamiltonian in zero field for axial symmetry may be written as

$$\mathcal{H}=DS_z^2. \tag{1}$$

The zero-field splitting parameter D has been determined by electron-paramagnetic-resonance (EPR) spectroscopy[11,12] to be $D/k_b=-0.86$ K, corresponding to a total anisotropy energy barrier $\Delta E/k_B=86$ K. At very low temperatures, each cluster of this system can be considered as blocked in one of the two ''macroscopic'' degenerated states $|m_s=\pm 10\rangle$. Classically, the switching between those states occurs only by a thermal activation process over the barrier. The magnetic relaxation time was found to follow an Arrhenius law:[11]

$$\tau=\tau_0 e^{\Delta E/k_B T}, \tag{2}$$

with $\Delta E/k_B=61$ K and the prefactor $\tau_0=2.1\times 10^{-7}$ s. ac-susceptibility measurements[13] done in powder samples showed a single relaxation time, evidenced by semicircular Argand diagrams, following Eq. (2), with $\Delta E/k_B=64$ K and $\tau_0=2.4\times 10^{-7}$ s.[14] Below 2 K, the relaxation time deviates from the Arrhenius law, becoming temperature independent[15] and being attributed to quantum tunneling of magnetization. An unusual field dependence of the relaxation in ac-susceptibility experiments with an increase of τ for small fields[14] has led the authors to propose a model based on thermally activated quantum tunneling. More recently, results in magnetization and susceptibility measurements under a field[16,17] showed steps in the magnetization and maxima in the susceptibility at regular field intervals, where the energy levels determined by Eq. (1) would cross due to Zeeman splitting, a process called field-tuned thermally assisted quantum tunneling. So far, most of the studies were done by magnetic measurements. We will present hereinafter specific-heat measurements in order to check the magnetic contribution due to the energy levels given by Eq. (1) and ac-susceptibility relaxation measurements performed on single crystals that give further confirmation to the quantum tunneling hypothesis.

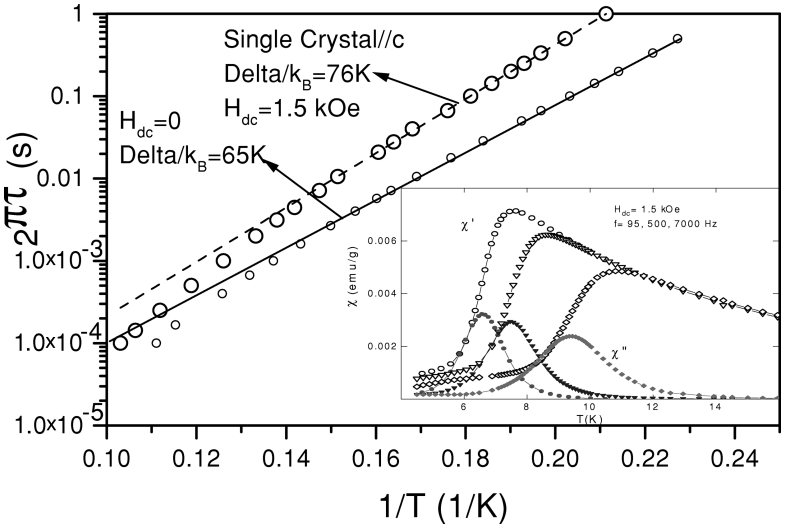

FIG. 1. Arrhenius plot for the relaxation time of a $Mn_{12}Ac$ single crystal in a zero field. The fit gives $\Delta E/k_B = 65$ K and shows a deviation at higher temperature. The inset shows a typical Ac susceptibility from which the relaxation time is obtained for three different frequencies.

Single crystals of $Mn_{12}Ac$ were grown following the procedure reported in the literature.[10] Five crystals with an elongated prism shape weighing around 2 mg each were glued in a small glass plate with the long axis parallel to each other. The uncertainty in the parallelism of the c axis among the crystals was estimated to be less than 5°. The ac-susceptibility measurements were made in a commercial susceptometer in the frequency range 1 Hz–10 kHz. The temperature dependence of the relaxation data was obtained from the maxima of the imaginary part of the susceptibility, as described in detail previously for powder sample measurements.[14] The present single-crystal results, shown in Fig. 1, give a more accurate estimate of the total effective energy barrier, $\Delta E/k_B = (65 \pm 2)$ K for a zero field, $\Delta E/k_B = (76 \pm 2)$ K for 1.5 kOe, and $\tau_0 = 2.8 \times 10^{-8}$ s for both cases. In the high-temperature region (high-frequency runs) a small deviation is observed. If a small range of temperature in the high-temperature (and frequency) range is considered, the fit gives a higher effective energy barrier and a smaller value for the parameter τ_0.

The specific-heat measurements were done using the semiadiabatic heat pulse method in a homemade calorimeter from 1.3 K up to 20 K. The data were collected using a heat pulse for typically 2 min and monitoring the temperature drift for 6 min before and after the heat pulse with an automated data acquisition system. The measurements were done with (0.4889 ± 0.0005) g of a fresh, coarse, $Mn_{12}Ac$ powder sample mixed with (0.5140 ± 0.0005) g of copper powder and (0.0848 ± 0.0005) g of Apiezon N grease. The mixture was pressed to provide a better thermal coupling within the calorimeter. The heat capacities of the calorimeter, copper powder, and grease were subtracted at the end of process. The accuracy in the net heat capacity of the sample is indicated by selected error bars in Fig. 2. The reproducibility from one run to another was of the order of 1%.

The total specific heat measured (c_{total}) at a zero field, shown in the inset of Fig. 2, presents no anomaly resulting from interactions between the clusters (as previously found).[13] Three different contributions to c_{total} should be present: lattice (c_l), hyperfine (c_h), and Schottky (c_{Sch}),

$$c_{total} = c_l + c_h + c_{Sch}. \tag{3}$$

The hyperfine contribution is assumed to be negligible in the temperature range measured. The lack of existence of a diamagnetic compound with the same crystalline structure makes it more difficult to separate the magnetic from the lattice contribution, so the only way to analyze the data is to compare the results with calculation of the magnetic

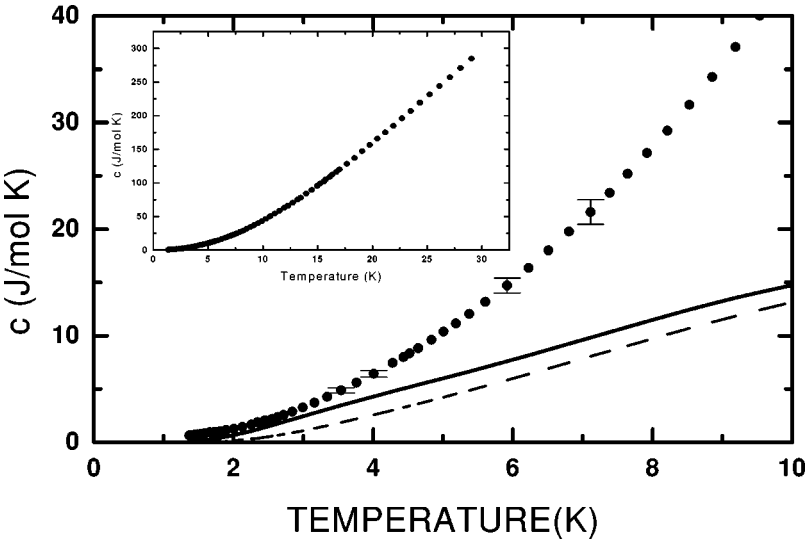

FIG. 2. Specific heat of $Mn_{12}Ac$ powder in a zero field (●). The calculated Schottky contribution is shown for $\Delta E/k_B = 65$ K (solid line) and $\Delta E/k_b = 86$ K (broken line). The inset is the specific heat in the whole temperature range measured. The accuracy in the net heat capacity of the sample is indicated by selected error bars.

Schottky contribution from the energy levels given by Eq. (2). It is thus possible to see whether or not the values attributed to the anisotropy energy barrier are reasonable by what is left for the lattice contribution. The Schottky contribution is easily calculated by differentiating the averaged energy over all accessible states:

$$\langle E\rangle = \frac{R\sum_{r=S}\sum_{i=-m_s}^{m_s}\epsilon_{i,r}(S,m_s)\exp(-\epsilon_{i,r}/T)}{\sum_{r=S}\sum_{i=-m_s}^{m_s}\exp(-\epsilon_{i,r}/T)}. \quad (4)$$

In this equation $\epsilon_{i,r}$ is the energy of the ith level for the rth multiplet and $R=8.314\ 57\ \mathrm{JK}^{-1}$. The sum can be carried from $S=10$ to other multiplets ($S=9,8,\ \ldots$), higher in energy but being at least 40 K above $S=10$ their contribution becomes small for smaller S at low temperatures. We thus calculated the Schottky contribution considering only $S=10$ and 9, with the energy level obtained from

$$\epsilon_{i,r}(S,m_s)=D(S^2-m_s^2)+\delta, \quad (5)$$

where

$$\delta=\begin{cases}0 & \text{for } S=10\\ 40\ \mathrm{K} & \text{for } S=9.\end{cases} \quad (6)$$

Using the known zero-field splitting parameter from EPR, $D=-0.86$ K (where $D=-\Delta E/100$), we calculated the lattice contribution by subtracting the Schottky contribution shown in Fig. 2. The same procedure was done by setting $\Delta E/k_B=65$ K, which is equivalent to $D=-0.65$ K, the expected energy barrier from the relaxation measurements. Here it can be seen that below 3 K, another very small and broad contribution with an apparent maximum below 2 K appears, and is currently under investigation. In Fig. 3 we plotted $c_{total}-c_{Sch}$ in the traditional c/T versus T^2 plot. Clearly the results using $\Delta E/k_B=65$ K are eliminated as they would imply an unphysical negative linear term ($c/T<0$ as $T\to 0$). The data calculated with $\Delta E/k_B=86$ K exhibit better behavior, but imply a very big linear term. This higher value for the energy barrier can also be seen if one looks carefully at the Arrhenius plot in Fig. 1, where a clear curvature deviating from the straight line is observed. We can define an effective energy barrier from the slope of $\ln\tau$ versus $1/T$. At the highest temperatures (near 9 K), the slope is about 95 K and may still increase with T. In this temperature range the quantum effects should not play a significant role relative to thermal activation and the real value of the total energy barrier should be equal to the effective one.

The discrepancy between the anisotropy energy barrier observed at low temperature from magnetic dynamics and that estimated by specific-heat measurements can be explained by using the recently proposed thermally activated quantum tunneling process.[14] The specific-heat results depend on the real energy level spacing, while the ac-susceptibility relaxation depends on the effective energy barrier, which is affected by quantum tunneling between the $+m_s$ and $-m_s$ states. As the temperature is lowered, the pure thermal activated spin reversal process becomes less probable, with more contribution due to quantum tunneling. This also explains qualitatively the observed departure from the Arrhenius behavior as a change of the effective energy barrier with temperature.

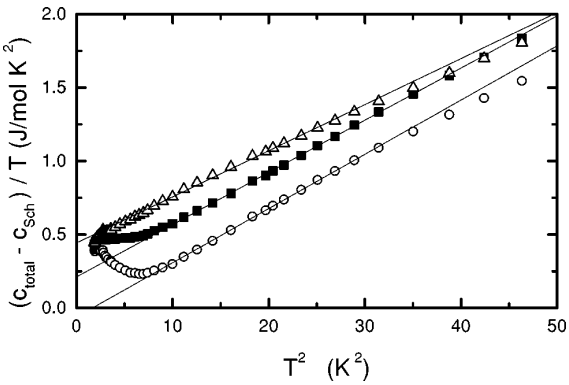

FIG. 3. $c_{total}-c_{Sch}$ in the c/T versus T^2 plot. The specific heat data obtained from Eq. (2) are shown using $\Delta E/k_B=65$ K, (○) and $\Delta E/k_B=86$ K (△). Full squares are data obtained using the present Hamiltonian.

Recently, a more refined Hamiltonian has been proposed in order to explain the high-field EPR spectra[18] by including higher-order terms:

$$\mathcal{H}=DS_z^2+AS_z^4+B(S_+^4+S_-^4). \quad (7)$$

The parameters for this Hamiltonian are $D=-0.56$ K, $A=1.11\times10^{-3}$ K, and $B=2.9\times10^{-5}$ K, equivalent to a total anisotropy energy barrier of 67.2 K. We thus made the same calculation for the Schottky magnetic anomaly using the energy levels deduced from Eq. (7). The results are also plotted in Fig. 3 with the fit in the region where a linear behavior could be found, obtaining a value for Debye temperature $\theta_D=(38\pm4)$ K. It is clear from this plot that the lattice and other contributions exhibit a better behavior using the present Hamiltonian (7), although an extra contribution below 3 K still remains to be explained.

We now consider the effect of an external magnetic field. The symmetry and degeneracy of the m_s states are broken, leading to an extra field-dependent Schottky anomaly of the Zeeman split states. Although the system cannot be considered to be in equilibrium, one may consider it to be in quasiequilibrium and count only the states that are accessible in the measuring time. Recall that at 3 K the average time for spin reversal is of order of 300 s [using Eq. (2)].

This system may be regarded as two sets of spins with the same energy-level spacing, one with the $+m_s$ or down states and the other with the $-m_s$ or up states, separated by the anisotropy barrier. In a zero applied field, each of the $+m_s$ states may be thermally excited to a higher $+m_s$ or $-m_s$ state, but with different probabilities if they pass over or tunnel through the energy barrier. At low enough temperature, when the time scale to switch to the other side of the barrier is much longer than the typical measuring time, the two sets of energy levels become independent from each other, i.e., in the time scale of the experiment, the number of accessible states is reduced to about one-half. This reduction should not change the specific heat in a zero field. Even in the presence of a magnetic field, as long as the two sets of levels continue being independent of each other and maintain the level spacing, the specific heat should remain the same.

We made measurements in a field of 0.30 T using a superconducting solenoid in the persistent mode. No differences between field cooling or zero field cooling were detected within the experimental accuracy, so most runs were done by cooling the sample in the field from 4.5 K. Figure 4 shows the specific-heat data in the applied field as well as in

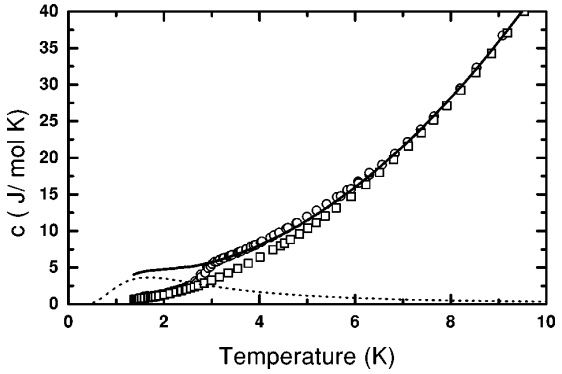

FIG. 4. Specific heat of $Mn_{12}Ac$ powder in 0.3 T (○). The expected specific heat is shown for a 0.3-T field (solid line). The zero-field curve is shown as squares and the Schottky contribution due to Zeeman splitting is shown by a dotted line.

the zero field. A clear bump around 3 K is observed in this case.

This is the first time, to our knowledge, that this kind of behavior has been observed in the specific heat of superparamagnetic samples. The excess contribution due to the field is mostly suppressed at temperatures below about 3 K, which corresponds to the blocking temperature for the experimental time window. At the lowest temperature (about 1.5 K), the relaxation time by thermal activation [Eq. (2)] would be about 10^9 yr. Even considering the possible quantum tunneling between the $m_s = \pm 10$ states, the relaxation time is of order of 10^7 s (Ref. 15) and still much longer than the time scale of our measurements. Therefore, we consider each cluster spin blocked on either side of the barrier. In the presence of a small field the magnetization should not relax during the course of the measurements, so the specific heat will depend on the energy-level spacing between the lowest states, which are almost the same on both sides of the barrier, so the specific-heat data are the same as in the zero-field case. As the temperature increases, the overall relaxation time decreases and when it becomes comparable to the experimental time the spins are progressively unblocked. The field-shifted states of both sides become accessible and the specific heat has higher values than in the zero field.

Very recently Fominaya *et al.* made heat-capacity measurements in single crystals of $Mn_{12}Ac$ as a function of sweeping magnetic fields at different fixed temperatures using a very sensitive nanocalorimeter.[19] They were able to detect heat pulses due to resonant tunneling when the field was integral multiples of 0.4 T, where the energy-level crossing occurs using the second-order Hamiltonian (2). They could also see the different behavior above and below the blocking temperature on the time scale of 0.1 s. In their analysis no quantitative comparison of the data with theoretical models was done. Their measurements were not done in equilibrium due to the field sweep; also with the ac heat-capacity technique used, an absolute value for the specific heat is difficult to extract accurately.

We note here that the specific-heat behavior we found could only be observed in this sample due to the fact that it is a set of identical superparamagnetic particles having the same relaxation time. We have made an estimate of the specific heat in a field by adding a Zeeman term to the Hamiltonian (1), using a powder average over all directions and only the lowest-energy levels; the result is presented in Fig. 4 as the dotted line. The sum (full line) of this contribution and the zero-field results agrees well with the data above the blocking temperature.

In conclusion, we have presented clear evidence from specific-heat measurements that the anisotropy energy barrier $\Delta E/k_B = 65$ K, deduced from an Arrhenius fit to ac-susceptibility relaxation results, is significantly smaller than the real value considering the Hamiltonian to be DS_z^2. Even the value deduced from early EPR measurements (86 K) does not agree with a well behaved lattice contribution to the specific heat. Much better behavior is obtained by using the recently proposed Hamiltonian with higher-order terms. The lower value observed by ac susceptibility can be considered as an effective anisotropy barrier combining thermally activated quantum tunneling plus pure thermal activation over the barrier. Finally, we have seen superparamagnetic relaxation effects in specific-heat measurements. The blocking of the relaxation process could be seen by a decrease of the specific heat under the field, below the blocking temperature due to a reduction of the accessibility between the two sets of opposite magnetization states in the time scale of the measurements.

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