Time-dependent heat capacity of Mn_{12} clusters

M. Sales, J. M. Hernandez, and J. Tejada
Departament de Física Fonamental, Universitat de Barcelona, Diagonal 647, Pta. 3, 08028 Barcelona, Spain

J. L. Martínez
Instituto Ciencia Materiales de Madrid, CSIC Cantoblanco, Madrid E-28049, Spain

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In this paper we discuss both theoretical and experimental results on the time dependence of the heat capacity of oriented Mn_{12} magnetic clusters when a magnetic field is applied along their easy axis. Our calculations are based on the existence of two contributions. The first one is associated with the thermal populations of the 21 different S_z levels in the two potential wells of the magnetic uniaxial anisotropy and the second one is related to the transitions between the S_z levels. We compare our theoretical predictions with experimental data on the heat capacity for different resolution times at different fields and temperatures.
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I. INTRODUCTION

Magnetic clusters such as Mn_{12} and Fe_8 are systems that can be described by metastable wells. Early relaxation experiments suggested escape from the wells by tunneling through a barrier[1,2] and energy-level quantization within a well. Very recent dynamic hysteresis and magnetization relaxation dc and ac experiments demonstrate the existence of resonant tunneling between these quantized levels in the macroscopically distinct anisotropy wells.[3–8] Theoretical studies[9–13] agree with experimental results. It has also been theoretically calculated[9] and experimentally tested[14] that resonant spin tunneling between the levels in the two wells is greatly enhanced by increasing the transversal component of the magnetic field, the latter due to the increased degree of mixing between the unperturbed energy levels. Very recently there have also been published experimental reports and theoretical discussion on the heat capacity and thermal avalanches in these molecular clusters.[15–18] In the two papers of Forminaya *et al.*,[15,16] it was clearly demonstrated that the quantum transitions that take place between the levels in the two wells at the resonant fields, manifest themselves as peaks in the heat capacity and in the heat emission associated with the staircase decay occurring due to quantum transitions. Fernandez *et al.*[17] have published a theoretical explanation of the data by Forminaya *et al.* by using Pauli's master equation in order to obtain the frequency dependence of the specific heat. We have recently studied[18] the dependence of the magnetization process on a pulse magnetic field applied parallel to the easy axis. Our data show the occurrence of spin-phonon avalanches, which are responsible for the heat emission observed by Fominaya *et al.*[15]

The spin Hamiltonian of an isolated molecular cluster of Mn_{12}-acetate in magnetic field H is written

$$H = DS_z^2 - H_z S_z - H_x S_x , \tag{1}$$

where $\vec{H}$ abbreviates $g\mu_B \vec{H}$. The system is described by $2S+1$ levels that correspond to the different spin projections on the anisotropy axis z. The strength of the longitudinal component of the magnetic field H_z modifies the barrier height between the spin-up and the spin-down components. For the values $H_z = nD/g\mu_B$ $(n = -10, -9, \ldots, 9, 10)$ the levels m and $n-m$ match so that resonant tunneling between these levels should be expected. The transversal component of the Hamiltonian H_x to the first approximation, is responsible for the tunneling process.[9,10] The field needed to attain saturation (the so-called anisotropy field) equals $H_a = 2DS/g\mu_B$. In the case of zero applied field the spin tunneling transitions are due to the existence of transversal components of both hyperfine and dipole fields, which in average are of the order of 200 G. This small value of the transversal component makes the tunneling between the low-lying levels extraordinary slow and only thermally activated tunneling between the levels near the top of the barrier is detected.[19] High-field electron-paramagnetic resonance experiments[20,21] suggest the existence of a small fourth-order magnetic anisotropy, which would result in slightly different values of the energy levels. The spin-phonon interaction is the only one that can be possible for the spin relaxation.[9] That is, the leading processes at the temperatures of the experiments are the emission and absorption of phonons accompanied by the hopping of spins between the energy levels.

II. EXPERIMENTAL RESULTS

Heat-capacity measurements were performed using a Quantum Design physical property measurement system (PPMS). In these measurements the response of the sample to a small heat pulse was detected. The thermal relaxation of the sample is fitted to an exponential law with the time constant proportional to the heat capacity of the sample. The sample used in our experiments is a Mn_{12}-acetate single crystal of 2.6 mg, glued to the platform, with its magnetic easy direction parallel to the direction of the magnetic field. The magnetic contribution to the heat capacity is estimated by subtracting the zero field values from those obtained in the presence of magnetic field. In Figs. 1(a) and 1(b) we show the dependence of the heat capacity on the longitudinal field H_z at two different temperatures and for different ex-

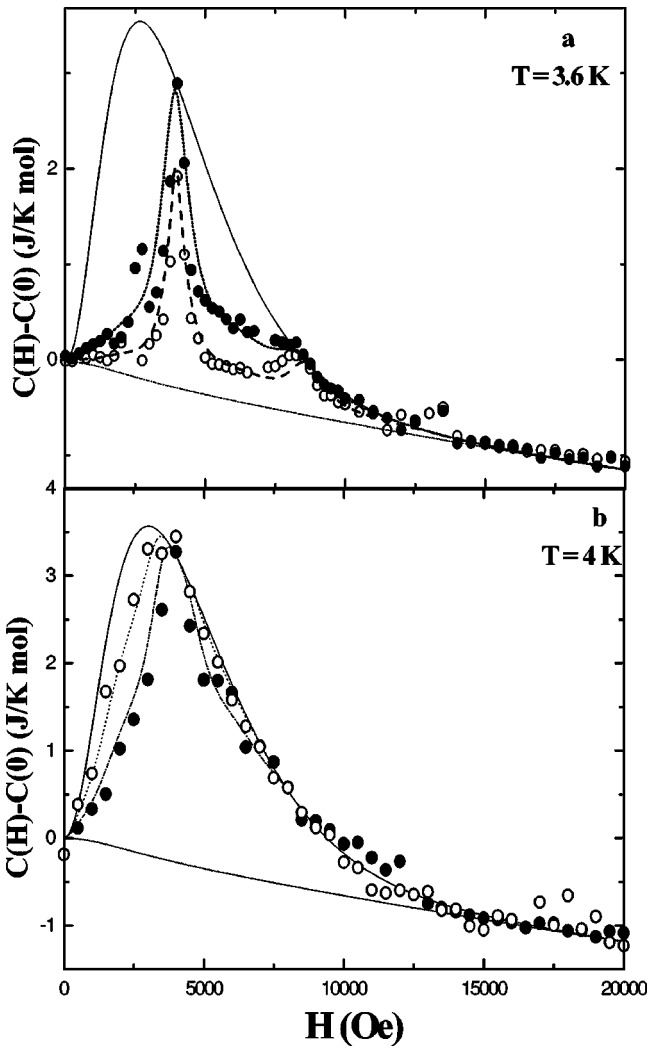

FIG. 1. Magnetic contribution to the heat capacity for a longitudinal applied field (0–2 T) at a temperature of 3.6 K (a) and 4 K (b). Experimental data for two resolution times (a). (○, 2 s; ●, 4 s, (b). (●, 2.3 s; ○, 4.5 s and theoretical calculations for different times (a) (– · –, 0 s;– –, 1.4 s;- - -, 3.8 s;—, equilibrium (10^{99} s), 1(b) – · –, 0 s;– –, 2.5 s; - - -, 4.6 s;—, equilibrium (10^{99} s).

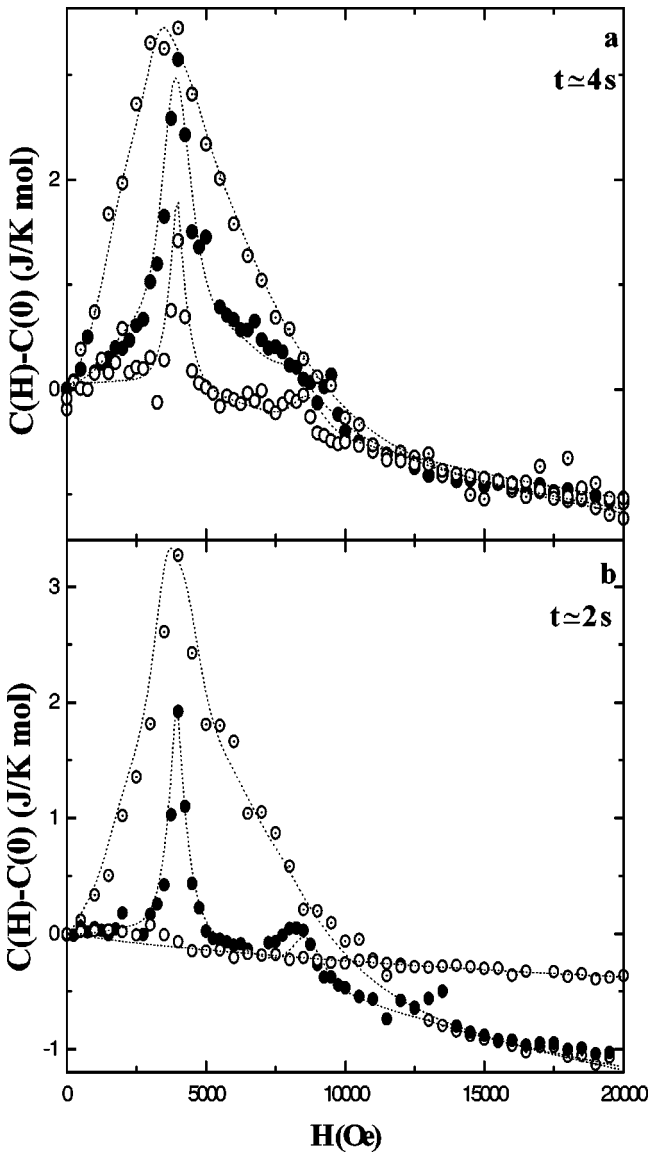

FIG. 2. Magnetic contribution to the heat capacity for a longitudinal applied field (0–2 T) at a fixed resolution time of 2 s (b) and 4 s (a) at different temperatures: (a) (○, 3.7 K; ●, 4 K; ⊙, 3.4 K), and (b) (○, 4 K; ●, 3.6 K; ⊙, 3.4 K. The dotted lines show the calculations for these resolution times and temperatures.

perimental resolution times. In Figs. 2(a) and 2(b) we show the dependence of the heat capacity on the longitudinal field for different temperatures at a fixed resolution time. The most remarkable observation is that the intensity and the width of the peaks at resonant fields $H_1=0.4$ T, $H_2=0.8$ T vary with time and temperature. Whether they are detected or not depends on the experimental time window (that is, the duration of the pulse), which depends on temperature. For very low temperatures, the thermal and quantum relaxation phenomena are so slow that very long pulses are needed to detect these peaks. At higher temperatures, the relaxation processes are so fast that the detection of the peaks needs the application of very short heat pulses, outside our experimental capabilities.

III. THEORY AND DISCUSSION

Traditionally, the heat capacity deduced experimentally is that of the system in equilibrium. In the case of our material and as a consequence of the existence of slow relaxation processes whose duration depends on both the temperature and magnetic field, it is possible to detect the thermal response of the sample before arriving at the global thermodynamic equilibrium. In this section we will explain how to calculate the heat capacity associated with the response to a heat pulse of duration t in relation to the parameters entering in the Hamiltonian given by Eq. (1). The thermal activation to a particular spin level $S_z=m=10,9,\ldots,0,\ldots,-9,-10$, is given by the Boltzmann rate

$$\Gamma=\nu\exp\{-[E(m)-E(-10)]\}, \tag{2}$$

where ν is the attempt frequency being of the order[3] of 10^{-7} s. The level from which the tunneling occurs is called blocking level m_b and is the first level from the top of the barrier for which the tunneling rate is small compared to the Boltzmann rate. That is, $U_{\text{eff}}=E(m_b)-E(-10)$ is the effective barrier at the resonance. The fact that m_b depends on T (ther-

mal activation), H_z (the longitudinal field determining the barrier height), and H_x (the transversal field on which depends the tunneling rate), allows us to detect different resonances. In our calculations we have used a phenomenological effective barrier obtained from relaxation measurements at a fixed field:[18]

$$U_{\text{eff}} = DS^2\left(1-\frac{H}{H_a}\right)^2 - b(1-|\sin \pi H/H_n|)^2, \qquad (3)$$

where H_n stands for the value at which the first resonance takes place, D is the uniaxial anisotropy constant, and b is associated with the quantum relaxation, that is, $DS_z^2 - b$ gives m_b. Therefore, this expression takes into account both thermal and tunneling processes. The relaxation time is

$$\tau = \tau_0 \exp(-U_{\text{eff}}/T). \qquad (4)$$

While the heat pulse is applied, the relaxation consists of two stages. In our calculations we have distinguished between two types of processes that take place on different time scales. During the first, short stage, the thermal equilibrium within each well is independently established. Then, on a larger time scale, transitions between the wells establish the global equilibrium of the system. Both processes are governed by Boltzmann's characteristic time $\tau \propto \exp \epsilon/T$, where ϵ_1 is 12 K, which is the energy gap between the lowest-lying levels. The levels involved in the second process are those at the top of the barrier[3–7] and therefore ϵ_2 is about 40 K. The great difference in the values of the characteristic time of the two processes allows us to assume that the time dependence is mostly determined by the tunneling process. The former process considers two separated potential wells with an infinite barrier whose temperature has increased from T to $T + \Delta T$, so that we have a local thermalization of the levels in each well. The population in each level is given by

$$n'_{i,\alpha} = n_{i,\alpha}(T)\frac{n_\alpha(T)}{n_\alpha(T+\Delta T)}, \qquad (5)$$

where $\alpha = 1,2$ is the well index, i is the considered level, $n_\alpha(T)$ is the population of the α well at T, and $n_{i,\alpha}(T)$ is the occupation number of the i level at T. Then we compute the energy increment of this thermalization process in each well as

$$\Delta E = \sum_{\alpha=1,2}\left[\sum_i e_{i,\alpha}[n'_{i,\alpha} - n_{i,\alpha}(T)]\right]. \qquad (6)$$

And thus obtaining the following contribution to the heat capacity,

$$C_{inst} = \lim_{\Delta T \to 0}\frac{\Delta E}{\Delta T}$$

$$= \frac{1}{T^2}\left[\sum_i e_i^2 n_i - Z\frac{\left(\sum_{i\in 1} e_i n_i\right)^2}{Z_1} + \frac{\left(\sum_{i\in 2} e_i n_i\right)^2}{Z_2}\right]. \qquad (7)$$

The latter takes into account the fact that the barrier is finite, so that there is an exchange of population between both wells, either thermal or quantum. At this stage we use the fact that the system has a unique relaxation rate. That is, just one level is responsible for the relaxation. We may consider, therefore, our two metastable wells as a two-level system whose populations evolve in time according to

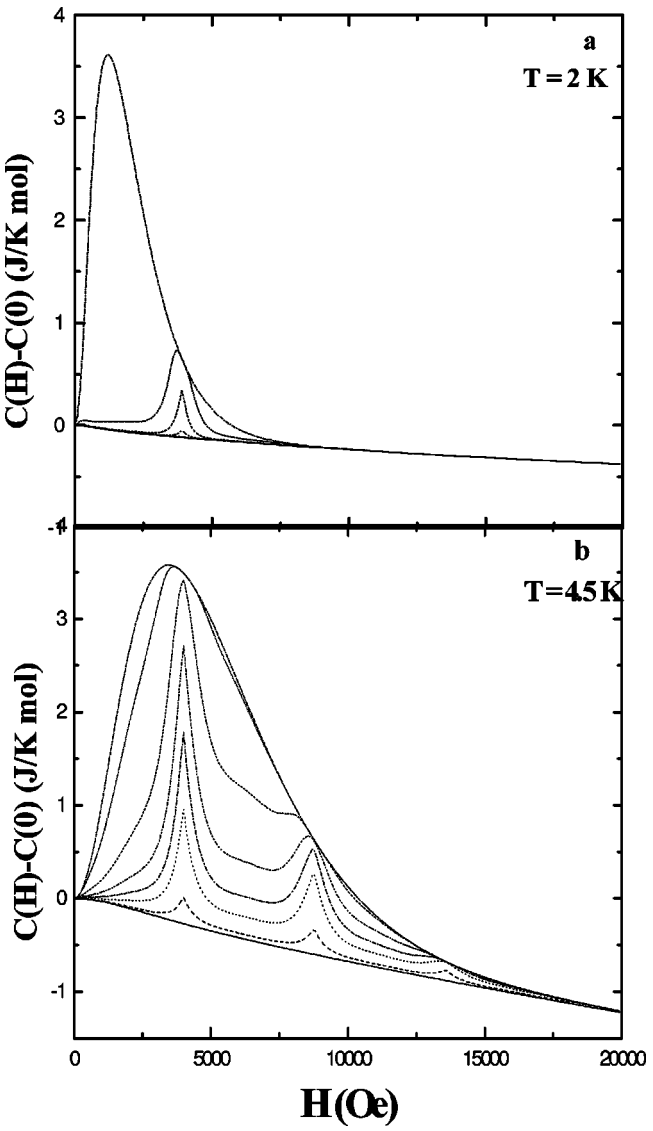

FIG. 3. Theoretical calculations of the magnetic specific heat as a function of longitudinal field at $T = 4.5$ K and $T = 2$ K, for different durations of the heat pulse: (a) —, 0 s; – –, 10 s; - -, 10^2 s; $-\cdot-$, 10^3; - · ·, 10^4 s; – –, 10^5 s, · · · ·, 10^6 s; —, equilibrium (10^{99} s), and (b) —, 0 s; – –, 510^{-3} s; - - -, 2.510^{-2} s; - · -, 510^{-2} s; - · ·, 0.1 s; – –, 0.25 s; · · ·, 1 s; —, equilibrium (10^{99} s).

$$\frac{dn_\alpha}{dt} = -\Gamma_{\alpha,\alpha'}n_\alpha + \Gamma_{\alpha',\alpha}n_{\alpha'} \qquad (8)$$

with $\alpha, \alpha' = 1,2$.

We arrive to the following occupation levels for each well:

$$n_\alpha(t) = n_\alpha(T+\Delta T)[1-\exp(-t/\tau)] + n_i(T)\exp(-t/\tau), \qquad (9)$$

where $1/\tau = \Gamma_{1,2} + \Gamma_{2,1}$ which is the relaxation rate defined in Eq. (4). By using Eq. (6) we compute the specific heat as

$$C=(C_{eq}-C_{inst})[1-\exp(-t/\tau)], \tag{10}$$

where

$$C_{eq}=\frac{1}{T^2}\left[\sum_i e_i^2 n_i-\left(\sum_i e_i n_i\right)^2\right]. \tag{11}$$

The total heat capacity is

$$C=C_{inst}+(C_{eq}-C_{inst})[1-\exp(-t/\tau)], \tag{12}$$

where t is the duration of the heat pulse.

In Figs. 1 and 2 we show the results of the fitting of experimental data to Eq. (12) using D, b, and τ_0 as fitting parameters. The values obtained for D and τ_0 are 0.66 K and 6.6×10^{-6} s, which agree with those obtained with other experimental techniques.[13] The value of $b=9$ K suggests that tunneling occurs from $m_b=4$ for the two first resonances observed experimentally at $H=0.4$ and 0.8 T, as has been previously reported.[3–5,10] Our fitting reproduces well the shape, the width, and the position of the peaks. The position of the peaks remains constant as they are due to quantum relaxation. However, for long heat pulses there is a slight shift of the peaks towards lower fields. The longer the resolution time, the closer our system is to the equilibrium configuration, which is the reason for the fictitious shifting of the relaxation peaks [Fig. 1(b) and Fig. 3(b)]. In Fig. 3(a) we show the heat capacity computed at $T=4.5$ K for resolution times ranging from zero to the time the system needs to reach equilibrium. For very short pulses, it was possible to detect three resonances whose intensity increases with time and eventually either shifts or disappears when they reach the equilibrium curve. However, at $T=2$ K, only one resonance could be observed, Fig. 3(b). The fact that relaxation increases with temperature results in a broadening of the peaks. The resonances that at low temperatures are not detectable appear at higher temperatures and vanish when the system gets close to the equilibrium, as it is shown in Fig. 2(a) and Fig. 2(b).

In conclusion we have shown experimental data concerning the time dependence of the heat capacity of Mn_{12} clusters. We have also provided theoretical calculations that explain the response of the system to different heat pulses at different temperature.

Despite the fact that in this paper we deal only with the specific heat of Mn_{12} clusters, our theoretical approach is valid for any magnetic system having a two-well energy-level configuration, this is, having an anisotropy energy barrier and a unique relaxation time, whether there is tunneling or not. The information of the processes governing the relaxation is included in the dependence of the relaxation time on the magnetic field. Equation (12) can, therefore, be applied to a broad spectrum of materials such as rare earth atoms.

ACKNOWLEDGMENTS

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