# Spin-phonon avalanches in $Mn_{12}$ acetate

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We report experimental studies and suggest a quantitative model of spin relaxation in $Mn_{12}$ acetate in a pulsed magnetic field in the temperature range 1.9–5.0 K. When the field applied along the anisotropy axis is swept at 140 T/s through a nonmagnetized $Mn_{12}$ acetate sample, the sample's magnetization switches, within a few milliseconds, from zero to saturation at a well-defined field whose value depends on temperature but is quantized in units of 0.46 T. A quantitative explanation of the effect is given in terms of a spin-phonon avalanche combined with thermally assisted resonant spin tunneling. [S0163-1829(99)11529-7]

$Mn_{12}$ acetate exhibits resonant spin tunneling which has been the subject of intensive experimental[1–9] and theoretical[10–15] studies in the last few years. The low temperature magnetic structure of this molecule persists well above 50 K,[8] indicating that the exchange interaction is strong enough for the molecule to be treated in the kelvin regime as a very small single domain particle having spin 10. The symmetry of the molecule and of the lattice results in the strong uniaxial anisotropy along the $c$ axis.[1,3] Magnetic avalanches that switch, below 1 K, the magnetization of the $Mn_{12}$ sample from zero to saturation in a few milliseconds were first reported by Paulsen and Park.[1] Their observation came before the spin relaxation in $Mn_{12}$ was understood, so no quantitative explanation of avalanches was given. Nevertheless, Paulsen and Park correctly suggested that ''the avalanches were caused by a kind of chain reaction or thermal runaway.'' Recently, Fominaya *et al.*[2] have also directly recorded heat emissions at the resonant fields.

The sweeping rate of the magnetic field used in our experiments (140 T/s) was much higher than that used in the experiments of Paulsen and Park[1] and Fominaya *et al.*[2] We prove that the strength of the avalanche depends on temperature and on the speed at which the magnetic field is swept through the sample. At lower temperatures the avalanches shift to higher fields. The purpose of this paper is the experimental and theoretical demonstration of the fact that the avalanche, besides being a ''thermal runaway,'' is also a quantum effect caused by thermally assisted resonant spin tunneling.

Let us briefly review the theory of $Mn_{12}$. The $Mn_{12}$ acetate crystal consists of weakly interacting molecules of spin 10, whose low-energy Hamiltonian in the presence of the magnetic field **H** directed along the anisotropy axis is

$$\mathcal{H}=-DS_z^2-g\mu_B H_z S_z+\mathcal{H}', \tag{1}$$

where $D$ is about 0.6 K, $g$ is close to 2, and $\mathcal{H}'$ is the perturbation that violates the commutation of $S_z$ with the Hamiltonian.

The physics of the thermally assisted resonant spin tunneling is illustrated in Fig. 1. The system can be most easily interpreted in terms of the eigenstates of $S_z$, $-10<m<10$, and in terms of the energy barrier caused by the magnetic anisotropy. At zero magnetic field the two levels of the minimal energy belong to the two opposite orientations of the spin along the anisotropy axis, with $m=10$ and $m=-10$, respectively. The classical energy barrier between the states with $m=10$ and $m=-10$, due to the magnetic anisotropy, is about 60 K. When the magnetic field is applied in the positive $z$ direction (parallel to the $c$ axis), the state with $m=10$ is energetically more favorable than the $m=-10$ state. At field values, $H_z=nH_R$ with $H_R=D/g\mu_B\simeq 0.46$ T $(n=-10,-9,\ldots,-1,0,1,\ldots,9,10)$ the levels $m$ and $n-m$ match (see Fig. 1) and the resonant tunneling between these levels occurs. At low temperature $Mn_{12}$ molecules predominantly occupy the low-lying $m$ levels. Unless a large transverse field is applied, the tunneling between these levels is negligible. To tunnel across the barrier, the molecule must be first activated to an excited level. The tunneling from upper levels can be very fast. This effectively reduces the height of the energy barrier when the $m$ levels are in resonance. Quantitative kinetic models have been developed[11–13] which give a reasonably good description of experimental data. However, the simplest picture one can obtain by assuming that the rate of the magnetic relaxation is proportional to the Arrhenius factor, $\Gamma=\nu_0\exp(-U_{eff}/k_BT)$, with $U_{eff}(H)$ being the full barrier when the system is off resonance and a reduced barrier, due to tunneling, on resonance. That is, $U_{eff}=E_{m_B}-E_{-10}$, where $m_B$ is the so-called blocking level corresponding to the first level from the top for which the tunneling rate becomes small, compared with the thermal activation rate. The experimental value of the prefactor[4,5] is

 

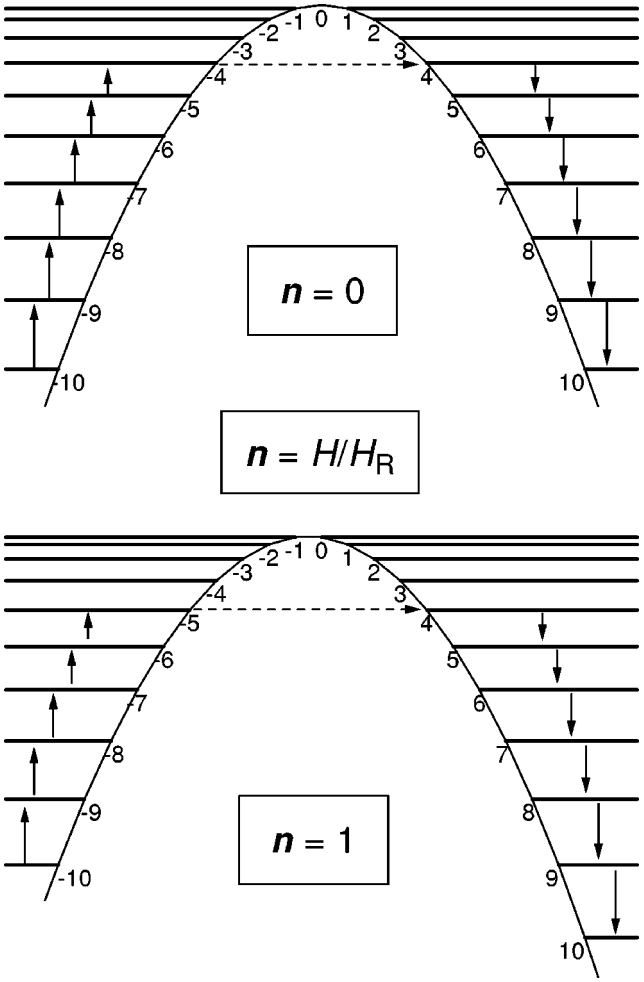


FIG. 1. Thermally assisted resonant spin tunneling in $Mn_{12}$ Acetate.

$\nu_0 = 10^7\ s^{-1}$. The experimental field dependence of the effective barrier that we will be using in this paper is shown in Fig. 2. It has been extracted[16] from the measurements of the magnetic relaxation in a field applied along the easy axis of the molecules at a fixed temperature. The relaxation followed the exponential law, $M(t) = M_0 \exp[-\Gamma(H,T)t]$, from which $U_{eff}(H,T)$ was directly obtained. The minima of $U_{eff}$ do not depend on temperature and occur at exactly the same values of the field, $H = nH_R$, as those obtained from the hysteresis measurements.[4]

The samples that we studied consisted of small crystallites of approximately 10 $\mu$m length and the aspect ratio of about ten, prepared according to Ref. 17. Measurements were performed on the oriented powder sample having the easy axis of all crystallites predominantly in one direction. The orientation (with an angular distribution of about 15°) was achieved by embedding the microcrystals in Araldite epoxy in a 5 T magnetic field for 24 h. The orientation was confirmed visually in an optical microscope at a 1000 $\times$magnification. The measurements were performed at the facilities of the SNCMP, INSA, Complexe Scientifique de Rangueil, Toulouse. The magnetization was measured using two concentric series-opposing pick-up coils. Two measurements have been made: the first one with the sample inside the coils and the second one without the sample. The latter

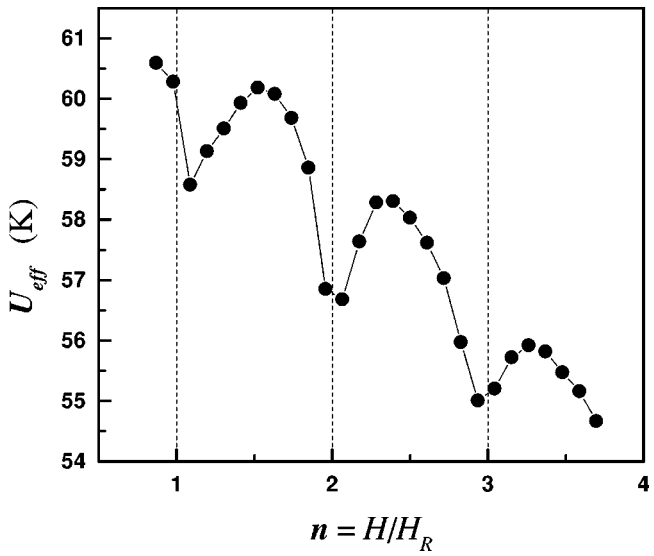


FIG. 2. Effective barrier vs applied field $H$, obtained from the relaxation measurements (Ref. 16). $H_R \approx 0.46$ T is the interval between resonant fields.

signal was subtracted from the former to obtain the magnetization of the sample. The data were taken continuously during 0.1 s when the field was rising. In Fig. 3 we show the field variation. At $H < 5$ T (see the inset in Fig. 3) $H(t) = \alpha t$, with $\alpha = 140$ T/s, is a good approximation.

Experimental results at different temperatures are shown in Fig. 4. The most striking observation is that the magnetization switches from zero to almost total saturation near one of the quantum resonance fields, $H_z = nH_R$. The actual number $n$ of the resonance responsible for the switch depends on temperature. It increases as the temperature goes down. This can be easily understood if one recalls that the population of the excited levels which contribute to tunneling goes down exponentially as the temperature is lowered. Consequently, a higher resonance field is needed to decrease the gap between the $m = -10$ level and the tunneling level at lower temperatures (see Fig. 1). The $n$ values of the observed resonances at lower sweeping rates are smaller.[4] In what follows

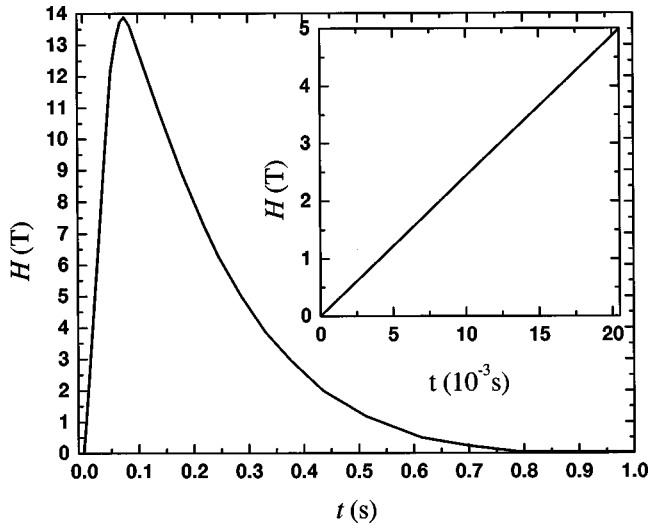


FIG. 3. Evolution of the pulse field with time. The inset shows the linear variation of the field between 0 and 5 T.

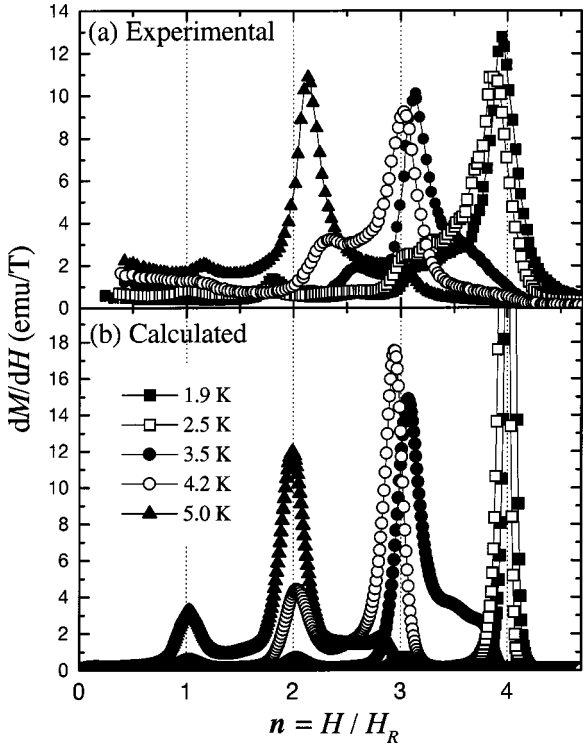


FIG. 4. Comparison between measured and calculated $dM/dH$ at different temperatures for high sweeping rate, $\alpha = 140$ T/s.

we suggest a quantitative explanation for the fact that the quantum hysteresis curve observed[4] at a low sweeping rate becomes one giant magnetization jump at a high sweeping rate.

The detailed theory of the magnetic relaxation in $Mn_{12}$ acetate[11–13] is rather involved as it includes the kinetics of the transitions between different spin levels. A simple quantitative description of the dynamics of the magnetization of a set of $Mn_{12}$ molecules with parallel easy axis can be given in terms of the differential equation

$$dM/dH = (1/\alpha)(dM/dt) = (\Gamma(H,T)/\alpha)(M - M_{eq}), \quad (2)$$

where $M_{eq} = M_{sat}\tanh(g\mu_B SH/k_B T)$ is the equilibrium magnetization, $M_{sat}$ is the saturation magnetization, and $\Gamma(H,T)$ is the rate obtained from independent measurements of the magnetic relaxation[16] at fixed $H$ and $T$.

At the microscopic level, a $Mn_{12}$ molecule must be activated from the $m = -10$ level to the lowest $m$ level (Fig. 1) from which tunneling becomes significant on the time scale of the experiment. The spin of the molecule then tunnels across the energy barrier and relaxes down the spin-level staircase to the $m = 10$ state, that is, towards the direction of the external magnetic field. The corresponding energy difference between the $m = -10$ state and the $m = 10$ state is released in the form of phonons. Phonons released by the molecule going down the staircase in the right well of Fig. 1, in principle, can be absorbed, in a resonant way, by neighboring molecules, which would drive these molecules up the spin-level staircase in the left well. It has been suggested[18] that such a process may result in a chain-reaction coflipping of spins towards the direction of the field. We consider such a scenario unlikely because of the weakness of the spin-phonon interaction. The phonon-induced resonant coflipping

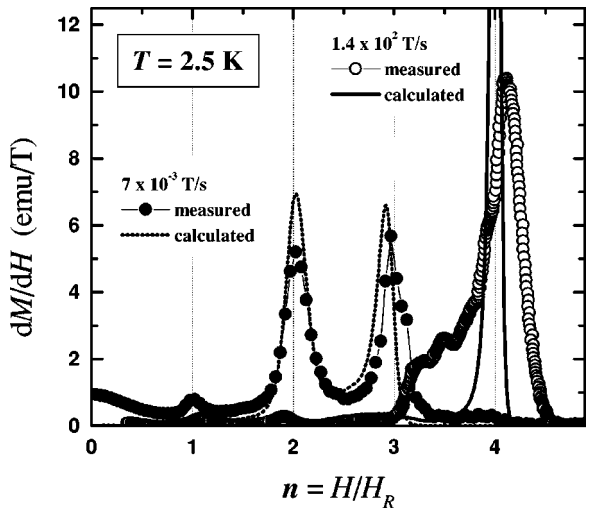


FIG. 5. Comparison between measured and calculated $dM/dH$ at two different sweeping rates.

of the spins would be equivalent to the propagation of a spin wave through $Mn_{12}$ acetate, which is impossible because the system is paramagnetic and the interaction between neighboring spins is very weak. For that reason we shall assume that the released phonons are thermalized, causing the sample to warm up. Equation (2) must then be accompanied by the equation of the heat balance

$$mc\frac{dT}{dt} = P(t) - Q, \quad (3)$$

where $P(t) = (d/dt)(\vec{M}\cdot\vec{H}) = M(dH/dt) + H(dM/dt)$ is the heat introduced into the system, $Q$ is the heat flow out of the system due to the thermal conductivity, and $m$ and $c(T)$ are the mass and the specific heat of the sample, respectively. The exact value of $Q$ should be obtained by solving the equation of the heat conductance for $Mn_{12}$ crystallites and the matrix, which is rather involved. Instead, we will use a rough estimate, $Q = \kappa l(T - T_0)$, where $\kappa = \gamma T^3$ is the effective coefficient of thermal conductivity of the entire sample of length $l \sim 0.1$ mm, and $T_0$ is the temperature of the system before the field variation began.

There are two limiting regimes:

(1) The limit of the low sweeping rate, when the heat release in the sample is slow enough to allow the effective exchange with the heat bath, so that the temperature of the sample remains almost constant.

(2) The limit of the fast sweeping rate, when the heat released during the relaxation process effectively remains inside the sample.

Avalanches should be expected in the second regime. Note, however, that the sweeping rate separating the two regimes strongly depends on temperature through temperature dependences of $c$, $\kappa$, and $\Gamma$. The lower the temperature, the lower is the sweeping rate that produces avalanches. Below we compare present results obtained in pulse fields with the hysteresis measurements at a low sweeping rate performed in earlier experiments.[4,16]

Equations (2) and (3) were solved for different sweeping rates using $\gamma$ as the only fitting parameter. The same value of $\gamma$ has been used for all the curves in Fig. 4. For $\alpha = 140$ T/s

and $T=2.5$ K our fitting procedure produced $\kappa=8$ W/K m, which is a reasonable value of the thermal conductivity for our dielectric sample in the kelvin range. The actual dependence of the specific heat on temperature,[9] $c \propto T^3$, has been used. The expression $\Gamma=\nu_0 \exp(-U_{eff}/k_B T)$ has been used in the calculation, with $U_{eff}$ taken from independent relaxation measurements,[16] see Fig. 2. The fit of the experimental data for two sweeping rates at $T=2.5$ K is shown in Fig. 5. There is a quantitative agreement between theory and experiment on the positions of the avalanches and their relative intensities. The widths of the maxima are more difficult to capture since they depend on the degree of the orientation of $Mn_{12}$ crystallites. Figure 4 shows measured and calculated curves for five different temperatures at $\alpha=140$ T/s. In both Figs. 4 and 5, the degree of the agreement between theory and experiment is amazing given the crude approximation used.

Two additional observations are in order. First, since the specific heat rapidly goes down as the temperature is lowered, the critical sweeping rate separating the two regimes can be rather low at low temperature. This is why avalanches were observed at a relatively low sweeping rate in the millikelvin range.[1] Second, the critical sweeping rate can also be low for small values of the thermal conductivity. For that reason avalanches have been recently observed at a low sweeping rate in the kelvin range when a single crystal of $Mn_{12}$ was in vacuum inside the Hall probe setup.[19]

In conclusion, we have demonstrated, both experimentally and by quantitative modeling, that avalanches in the magnetization reversal of $Mn_{12}$ acetate are produced by the spin-phonon relaxation which is caused by thermally assisted resonant spin tunneling.

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