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Quantum tunneling of magnetization in Mn_{12} acetate clusters

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Abstract

The Mn cluster complex $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ exhibits macroscopic quantum tunneling of magnetic moment, as evidenced by pronounced steps in the magnetization curve at low temperatures.

The magnetization of Mn_{12} acetate single crystals, and the slow relaxation of the magnetic moment, was measured in the temperature range from 3 K down to 60 mK with a very sensitive cantilever magnetometer. The relaxation of the magnetic moment, at low temperatures and for magnetic fields near a step in the magnetization curve, is logarithmic and shows a complicated temperature dependence. In contrast, other investigations had found a temperature-independent relaxation, with a relaxation time saturated at 10^8 s.

Keywords: Mn_{12} acetate; Quantum tunneling of magnetization; Cantilever magnetometer; Logarithmic relaxation

1. Introduction

The Mn_{12} acetate compound first synthesized by Lis [1], $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ (Mn–Ac), has attracted interest because it exhibits macroscopic quantum tunneling of magnetic moment (QTM). At temperatures below about 3 K, steps are observed in the hysteresis loop of oriented powder samples [2–4] and single crystals [5]. The occurrence of these steps at a number of regularly spaced values of the magnetic field is a demonstration of the resonant nature of the magnetization reversal. Unlike superparamagnetic particles, where QTM was first observed [6], the crystals contain a large number of identical clusters, allowing much more accurate comparisons to be made.

The cluster consists of a tetrahedron of four Mn(IV) ions each in their $S = \frac{3}{2}$ state and coupled to yield $S = 6$, surrounded by eight Mn(III) ions each with $S = 2$, with their total moment $S = 16$ directed antiparallel to the spin of the inner ions. The cluster can be considered as a single $S = 10$ system, with the spin preferentially aligned along the c-axis due to a large axial crystal field anisotropy in the tetragonal lattice [7,8].

High field magnetization and electron paramagnetic resonance (EPR) have indicated that the

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ground state is $m = \pm 10$ [8]. At low temperatures, a magnetic field will remove the degeneracy, and the clusters will become completely polarized. If the field is then reduced to zero (or inverted), the magnetization has to decay (or reverse to the opposite polarization), and AC-susceptibility measurements have suggested that the decay is single exponential and thermally activated, $\tau = \tau_0 \exp(K/k_B T)$, with K ranging from 64 to 61 k_B and $\tau_0 = 2.6$–2.1×10^{-7} s [9,10]. This relaxation is unusually slow. Below 3 K the relaxation time starts to exceed the time of measurement, and below this so-called "blocking temperature", the magnetization becomes hysteretic. However, at low temperatures the relaxation time does not continue to grow exponentially but instead saturates at values of 10^7–10^8 s [11]. This was taken as evidence for QTM.

2. Experimental

We have used a cantilever magnetometer to study the magnetization of Mn–Ac single crystals, and the slow relaxation of the magnetic moment, in the temperature range from 3 K down to 60 mK. The cantilever technique is distinguished by its very high sensitivity, especially for axially oriented magnetic moments as in the case of the Mn–Ac with its high c-axis anisotropy energy. In such a case it can be applied in the torque mode, and the torque trying to align the magnetic moment along (when $\boldsymbol{m} \| \boldsymbol{B}$) or away from (when $-\boldsymbol{m} \| \boldsymbol{B}$) the direction of the applied magnetic field will result in a small, capacitively detected deflection of the thin silicon cantilever. Near zero field, however, the sensitivity vanishes, but for fields above 0.5 T we obtain a very satisfactory signal-to-noise ratio with single crystals as small as 20 μg. The data down to 450–500 mK were obtained using a ^{3}He cryostat in the resistive magnets at NHMFL, while for the millikelvin data a dilution refrigerator in a superconducting magnet was used.

The Mn–Ac was synthesized following the original procedure described by Lis [1] (reaction of Mn $(CH_3COO)_2$ with $KMnO_4$ in 60% CH_3COOH). The single crystals were grown by the slow evaporation technique, and grew in the form of rectangular parallelepipeds with the longest dimension as the c-axis (which is also the direction of easy magnetization). The crystals utilized were approximately 0.015 mm^3 with 0.8 mm as the largest dimension.

3. Results

Fig. 1 shows magnetization curves (normalized to the saturation value at higher fields) from 2.2 K down to millikelvin temperatures, and recorded at ramping rates of 0.0085 T/s. At higher temperatures, steps are seen to occur at lower indexed transitions, while at lower temperatures sharp transitions at indices $N = 7$ (albeit weak), 8, 9 and 10, and a broader transition around $N = 11$ are observed. The transition fields at which steps were found are plotted in the inset and they depend linearly on the index, giving a step size $\Delta B = 0.449$ T.

For an Ising spin Hamiltonian with axial anisotropy, and for the magnetic field parallel to the easy axis, many levels are crossing simultaneously for $B_N = N|D_1|/g\mu_B$, where N is the index of the transition, $D_1 \approx -0.64\, k_B$ the prefactor of the lowest-order anisotropy term and the g-factor $g \approx 2$. The resonances seem to occur at these energy level crossings. The value of ΔB derived with these values (0.48 T) is significantly larger than observed. We have indications that the experimental observations can be reconciled by invoking higher-order anisotropy (e.g. $D_4(S_x^4 + S_y^4)$ [12]).

The appearance of magnetization steps is dependent on whether the relaxation-time corresponds to the measuring time. It has been mentioned [3], for example, that as the processes slow down with temperature transitions at indices up to $N = 19$ should be observed when the temperature would be reduced to near 10 mK. We find that this does not occur: the highest index step observed is the $N = 11$ transition, this step appears below 750 mK and accounts for the last 5% of magnetization reversal all the way down to 60 mK. The reasons for this will be discussed in a forthcoming paper.

Here we will focus on the relaxation of the magnetic moment. It was found that the relaxation time at zero (or low) field is thermally activated from the lowest lying level $m = -10$ to the top of the

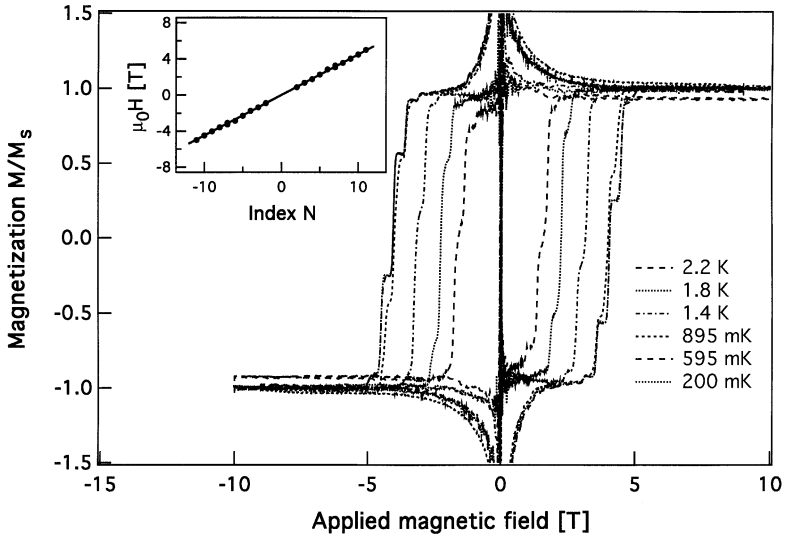

Fig. 1. Magnetization for a Mn_{12} acetate single crystal with the magnetic field aligned parallel to the easy axis. The sample is first fully magnetized; rapid changes in magnetization occur at regular intervals after the field has been reversed. The resonance fields are separated by $\Delta B = 0.449$ T (see inset).

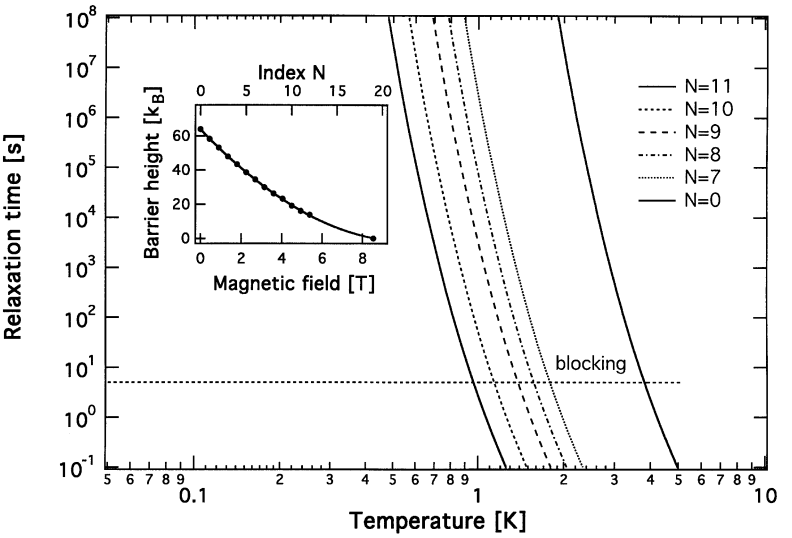

Fig. 2. Relaxation times corresponding to different barrier heights. At the higher index steps, i.e. at higher magnetic fields, the barrier height is reduced, and consequently thermal excitation across the anisotropy barrier strongly enhanced.

anisotropy barrier [9,10]. In Fig. 2 it is shown that then for measurements on time scales exceeding a few seconds, the relaxation is "blocked" below 3–4 K. The Zeeman energies will lead to an effective lowering of the energy barrier with field, until at $B \approx 8.5$ T it is reduced to zero, and at $N = 10$ the relaxation will be enhanced to $\tau < 100$ s for $T = 1$ K.

In the experiment, the crystal was first fully magnetized by applying a high enough magnetic field (around 9 T in our case), and then the field was reversed and ramped up to a value corresponding

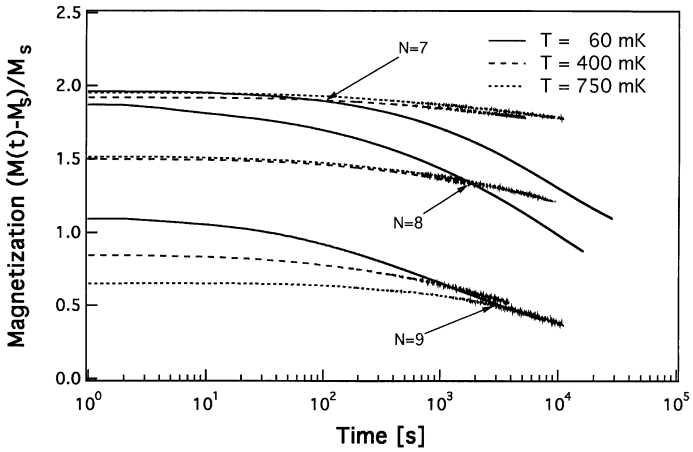

Fig. 3. Slow decay of the magnetization with the magnetic field held constant at the resonant field, at 60, 400 and 750 mK. Although exponential at short times, for longer times the decay is logarithmic.

to a step in the magnetization curve. Fig. 3 shows the relaxation of the magnetization observed at fields corresponding to $N = 7$, 8 and 9, and from 750 mK down to 60 mK. These data are representative of the relaxation near the resonant step in the magnetization. The relaxation is logarithmic with time, as is best illustrated by the 60 mK data. The relaxation thus does not represent the thermal excitation from the low-lying $m = -10$ level to the top of the barrier, which would have a relaxation time well in excess of 10^6 s in this field and temperature range. The observation of logarithmic decay near the resonant steps is in marked contrast with the saturated, exponential decay reported by Paulsen et al. [11], and indicates that a number of processes with widely varying barrier heights must be involved [13], possibly phonon assisted tunneling [12]. The data, shown in Fig. 3, indicate that at higher temperature any non-equilibrium population remaining in excited states after passing through the resonance is more rapidly depleted than at 60 mK.

4. Conclusions

The reversal of magnetization is very fast when the field is brought to resonance, and the step seems to end because the change in internal field eventually breaks the alignment of the tunneling energy levels. The excess population in excited levels then starts to decay partly down to the metastable $m = -10$ state partly, after phonon-assisted tunneling or thermal excitation over the top of the barrier, towards the stable $m = +10$ level. A number of processes must take part in this phase, so that the decay of excess population in excited states becomes logarithmic with time.

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References

[1] T. Lis, Acta Crystallogr. B 36 (1980) 2042.
[2] J.R. Friedman, M.P. Sarachik, J. Tejada, R. Ziolo, Phys. Rev. Lett. 76 (1996) 3830.
[3] J.M. Hernandez, X.X. Zhang, F. Luis, J. Tejada, J.R. Friedman, M.P. Sarachik, R. Ziolo, Phys. Rev. B 55 (1997) 5858.
[4] F. Luis, J. Bartolomé, J.F. Fernández, J. Tejada, J.M. Hernández, X.X. Zhang, R. Ziolo, Phys. Rev. B 55 (1997) 11448.
[5] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, Nature 383 (1996) 145.

[6] For a review of the field see contributions in Quantum Tunneling of Magnetization – QTM'94, L. Gunther, B. Barbara (Eds.), vol. 301, NATO ASI Series E: Applied Sciences, Kluwer, Dordrecht, 1995.
[7] R. Sessoli, H.-L. Tsai, A.R. Scake, S. Wang, J.B. Vincent, K. Folting, D. Gatteschi, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 115 (1993) 1804.
[8] A. Caneschi, D. Gatteschi, R. Sessoli, A.L. Barra, L.-C. Brunel, M. Guillot, J. Am. Chem. Soc. 113 (1991) 5873.
[9] M.A. Novak, R. Sessoli, A. Caneschi, D. Gatteschi, J. Magn. Magn. Mater. 146 (1995) 211.
[10] R. Sessoli, D. Gatteschi, A. Caneschi, M.A. Novak, Nature 365 (1993) 141.
[11] C. Paulsen, J.-G. Park, B. Barbara, R. Sessoli, A. Caneschi, J. Magn. Magn. Mater. 140–144 (1995) 379.
[12] P. Politi, A. Rettori, F. Hartmann-Boutron, J. Villain, Phys. Rev. Lett. 75 (1995) 537.
[13] L. Gunther, J. Am. Chem. Soc. 115 (1993) 413.