Transition between thermally assisted relaxation and quantum tunneling in a molecular magnet

K. M. Mertes, Y. Zhong, and M. P. Sarachik[a)]
Department of Physics, City College of the City University of New York, New York, New York 10031

Y. Paltiel, H. Shtrikman, and E. Zeldov
Department of Condensed Matter Physics, The Weizmann Institute of Science, Rehovot 76100 Israel

E. Rumberger and D. N. Hendrickson
Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, California 92093

We report Hall sensor measurements of the magnetic relaxation of Mn_{12}–acetate as a function of magnetic field applied along the easy axis of magnetization. Data taken at a series of closely spaced temperatures between 0.24 and 1.9 K provide new clues for understanding the physics of quantum tunneling of magnetization in Mn_{12}–acetate.
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I. INTRODUCTION

Despite considerable interest and attention, a full understanding has not emerged of the magnetic relaxation of the single molecule magnet ($[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$). The magnetic core of Mn_{12}–acetate consists of 12 superexchange-coupled Mn atoms to give a sizable $S=10$ spin magnetic moment that is stable at temperatures of the order of 10 K and below. These magnetic clusters are arranged on a tetragonal lattice, and strong uniaxial anisotropy (of the order of 65 K) yields a double well potential with doubly degenerate ground states in zero field and a set of excited levels corresponding to different projections $m_s=\pm 10,\pm 9,\ldots,0$ of the total spin along the easy c axis of the crystal. Measurements below the blocking temperature of 3 K have revealed a series of steep steps in the curves of M versus H at roughly equal intervals of magnetic field, as shown in Fig. 1, due to enhanced relaxation of the magnetization whenever levels on opposite sides of the anisotropy barrier coincide in energy. In the present article we report detailed measurements of the magnetization of Mn_{12}–acetate as a function of magnetic field applied along the easy axis of magnetization at a series of very closely spaced temperatures. We show that there is an abrupt change in the character of the magnetic relaxation over a narrow range of temperature. Our results provide valuable new clues that may provide the key to understanding the mechanism of tunneling in Mn_{12}–acetate.

Identification of the levels that participate in tunneling is based on the following considerations. The spin Hamiltonian for Mn_{12} is given by:

$$\mathcal{H}=-DS_z^2-g_z\mu_B H_z S_z-AS_z^4+\cdots, \tag{1}$$

where D is the anisotropy, the second term is the Zeeman energy, and the third on the right-hand side represents the next higher-order term in longitudinal anisotropy; additional contributions (e.g., transverse internal magnetic fields, transverse anisotropy) are not explicitly shown. Tunneling occurs from level m' in the metastable well to level m in the stable potential well for magnetic fields:

$$H_z=N\frac{D}{g_z\mu_B}\left[1+\frac{A}{D}(m^2+m'^2)\right], \tag{2}$$

where $N=|m+m'|$ is the Nth level crossing or step number. The second term in brackets is small compared to 1. Thus, when an external magnetic field is increased from zero at some fixed rate, steps N_i occur at intervals of magnetic field, $\approx D/(g_z\mu_B)\approx 0.42\,\mathrm{T}$ corresponding to faster relaxation at fields where levels on opposite sides of the potential barrier coincide in energy; for a given step all pairs of levels cross at roughly the same magnetic field. However, careful measurements show that there is structure within each step due to the presence of the term AS_z^4; as indicated in Eq. (2), the levels do not cross simultaneously, an effect that is more pronounced for levels that are deeper in the well. EPR[1] and neutron scattering[2–4] experiments have yielded precise values of $A=1.173(4)\times 10^{-3}$ K and $D=0.548(3)$K, and an estimate for g_z of $1.94(1)$. Comparison of the measured magnetic fields with those calculated from Eq. (2) therefore

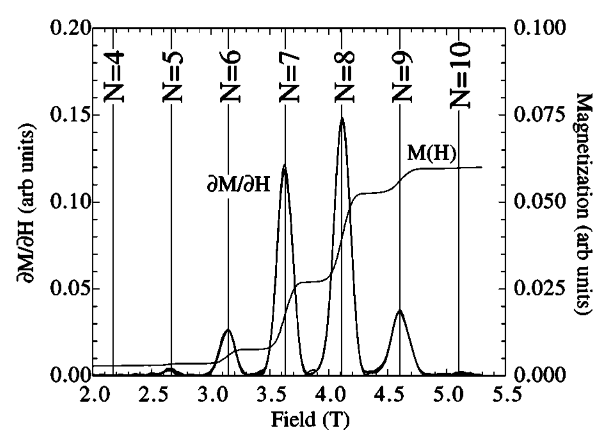

FIG. 1. For a set of closely spaced temperatures between 0.24 and 0.52 K, M and $\partial M/\partial H$ are plotted as a function of magnetic field.

[a)]Author to whom correspondence should be addressed; electronic mail: sarachik@sci.ccny.cuny.edu

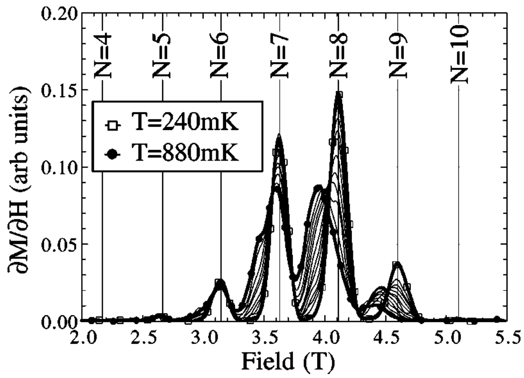

FIG. 2. As the temperature is raised above 0.52 K, we see the transition from ground state tunneling to thermally assisted tunneling.

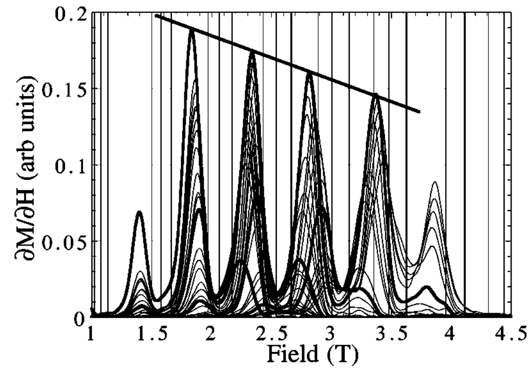

FIG. 3. For temperatures between 1.00 K and 1.90 K, the maximum height associated for each transition increases as N decreases. The temperature extrapolates toward the blocking temperature as the field is reduced to zero.

provides an experimental tool that allows identification of the states that are predominantly responsible for the tunneling.

II. EXPERIMENTAL RESULTS

The magnetization of small single crystals of Mn_{12}–acetate was determined from measurements of the local magnetic induction at the sample surface using a $10 \times 10\,\mu m^2$ Hall sensor composed of a two-dimensional electron gas (2DEG) in a GaAs/AlGaAs heterostructure. The 2DEG was aligned parallel to the external magnetic field, and the Hall sensor was used to detect the perpendicular component (only) of the magnetic field arising from the sample magnetization.[5]

Our results are shown in the next few figures. For different temperatures between 0.24 and 0.52 K, Fig. 1 shows the first derivative $\partial M/\partial H$ of the magnetization M with respect to the externally applied magnetic field H; the amplitude of these curves is a measure of the relaxation rate. Maxima occur at magnetic fields corresponding to faster magnetic relaxation due to level crossings on opposite sides of the anisotropy barrier. In the temperature range of these measurements, peaks are observed for $N=|m+m'|=5$–9; the curves all coincide for $T<0.52$. The position of the maxima corresponds accurately to the fields predicted for tunneling from the lowest state in the metastable well ($m'=-10$). This, and the fact that the rate of relaxation is independent of temperature, are clear indications that the tunneling occurs from the ground state in the metastable well for different step numbers N. The maxima of Fig. 1 can be fit to Gaussians of equal widths.

As the temperature is raised, the amplitudes of the maxima decrease and shoulders develop at lower fields near each peak (Fig. 2). We attribute this to the onset of thermally assisted tunneling from excited levels in the metastable potential well. One would expect that this shoulder is due to the emergence of a peak centered around the $m'=-9$ anticrossing point, with progressively larger admixtures of peaks centered about $m'=-8$, $m'=-7$, and so on, as the temperature increases. However, all attempts to fit the data by a sum of such Gaussian (or Lorentzian) distributions have been unsuccessful to date. Instead, the data are consistent with a superposition of two terms: a Gaussian fixed at the field corresponding to tunneling from $m'=-10$ and a second maximum that is approximately consistent with a Gaussian that moves continuously to lower fields as the temperature is raised. Although this behavior is enigmatic and requires further study, it is clearly inconsistent with the gradual evolution expected for a continuous second-order transition between thermally assisted and pure quantum tunneling.

As the temperature is raised even further, the maxima corresponding to ground state tunneling disappear and the excited state peaks grow in amplitude (Fig. 3). Note that the excited state peaks associated with each step do not grow indefinitely: at some step-dependent temperature the peak reaches a maximum and then decreases in amplitude. This is easily understood: as the temperature is increased the populations of higher energy levels (where tunneling is easier) increase, and a larger fraction of the magnetization relaxes toward its equilibrium value at smaller fields.

Moreover, one expects the maximum amplitude to increase with increasing temperature since tunneling is easier near the top of the potential well. Figure 3 shows that the temperature at which the excited state peaks exhibit a maximum increases linearly with decreasing field, and extrapolates to the blocking temperature at zero field. This illustrates the evolution from over-the-barrier relaxation of the magnetization in the superparamagnetic regime to the thermally assisted magnetic quantum tunneling regime. Interestingly, the position of the excited state peaks continue to move to lower fields. Each maximum in $\partial M/\partial H$ can still be approximately fit to a single Gaussian, although a second shoulder appears to develop, which is difficult to distinguish from the noise.

The position of the maxima is shown as a function of temperature in Fig. 4. Here we clearly see that the field corresponding to ground state tunneling is independent of temperature while the field associated with thermally assisted tunneling decreases approximately linearly with temperature.

III. CONCLUSION

To summarize, measurements in Mn_{12}–acetate taken at closely spaced intervals of temperature show that the magnetic relaxation exhibits an abrupt change in character over a narrow temperature range to rapid magnetic relaxation at a

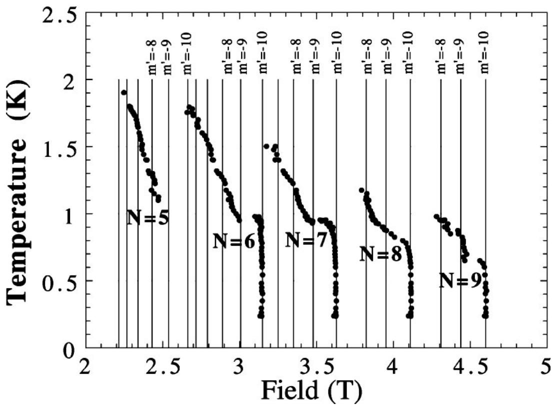

FIG. 4. Field values for each peak in $\partial M/\partial H$ plotted as a function of temperature. The positions clearly demonstrate the temperature independence of the peaks associated with tunneling from the $m' = -10$ ground state in the metastable potential well.

''resonant'' magnetic field corresponding to tunneling from the lowest state, $m' = -10$, of the metastable potential well; this resonant field is independent of temperature as the temperature is reduced further. For each step N, the maximum in $\partial M/\partial H$ for ground state tunneling can be fit to a Gaussian centered at the field corresponding to tunneling from the $m' = -10$ state of the metastable well. However, the peaks in $\partial M/\partial H$ in the thermally assisted tunneling regime cannot be decomposed into a sum of Gaussian peaks centered at the position of the excited state crossings. Rather, our data indicate that these maxima shift continuously to lower field and can be approximately fit to a single Gaussian. Our measurements provide valuable clues that may lead to a full understanding of the process of quantum tunneling in Mn_{12}–acetate.

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