

More evidence for a distribution of tunnel splittings in Mn₁₂-acetate

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In magnetic fields applied parallel to the anisotropy axis, the magnetization of Mn₁₂ has been measured in response to a field that is swept back and forth across the resonances corresponding to steps $N=4,5,\dots,9$. The fraction of molecules remaining in the metastable well after each sweep through the resonance is inconsistent with expectations for an ensemble of identical molecules. The data are consistent instead with the presence of a broad distribution of tunnel splittings. A very good fit is obtained for a Gaussian distribution of the second-order anisotropy tunneling parameter $X_E = -\ln(|E|/2D)$. We show that dipolar shuffling is a small effect and is not responsible for the nonexponential relaxation. © 2003 American Institute of Physics. [DOI: 10.1063/1.1543857]

In the single molecule magnet Mn₁₂-acetate, ([Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄]·2CH₃COOH·4H₂O), a recent study¹ of the magnetic relaxation at temperatures below 0.5 K for different sweep rates of a magnetic field applied along the longitudinal (easy) axis have yielded evidence that the symmetry breaking term that drives the tunneling in this material is locally varying, broadly distributed second-order anisotropy which is forbidden by the tetragonal symmetry of the Mn₁₂-acetate crystal, but which is present in real crystals due perhaps to long-range crystal dislocations² or local chemical environment.³ Other studies have yielded corroborating evidence.⁴ The distributed second-order transverse anisotropy gives rise to a distribution of tunnel splittings. In this article, we present additional experimental evidence that the tunnel splittings are broadly distributed.

The Hamiltonian for Mn₁₂-acetate is given by $\mathcal{H} = -DS_z^2 - AS_z^4 - g_z\mu_B H_z S_z + V_T$, where the anisotropy $D = 0.548(3)K$, the fourth-order longitudinal anisotropy $A = 1.173(4) \times 10^{-3} K$, g_z is estimated to be 1.94(1),⁵ and V_T contains all symmetry-breaking terms responsible for the observed tunneling. For temperatures below approximately 0.5 K, it has been shown that essentially all the tunneling proceeds from the ground state level $m' = -10$ of the metastable well.⁶ Ground state tunneling, indicated by the arrow in the double-well structure in Fig. 1, occurs at magnetic fields: $H_z = N(D/g_z\mu_B)[1 + (A/D)(N^2 - 20N + 200)]$, where $N = -(m + m')$ is the step number. The data reported in this article were obtained at 0.25 K, where only ground state tunneling is observed.

The magnetization of small single crystals of Mn₁₂-acetate was determined by methods described elsewhere.⁷ The relaxation of the magnetization was studied for each observable ground state resonance as follows: starting from zero magnetization, the external field was swept from zero up to and beyond a given resonance N . When the field reached the middle of the plateau just above step N , it was reversed and swept back across this resonance. When the field reached the middle of the previous plateau, the field was swept back up and the process was repeated many times.⁸ The same procedure was repeated for all observed resonances, $N=4,5,\dots,9$, as shown in the normalized magnetization curves of Fig. 1. The turning points were chosen so

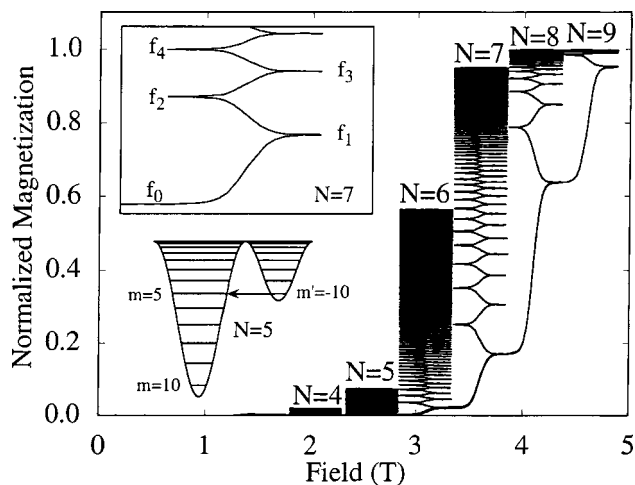


FIG. 1. Normalized magnetization vs magnetic field for a field that is swept back and forth across each resonance. The field was swept at a rate of $|dH_z/dt| = 5.83$ mT/s. The upper inset shows the labeling described for the first few oscillations for $N=7$. The arrow in the lower inset designates tunneling from the ground state of the metastable well for step $N=5$.

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that the amplitude of the field oscillations were the same for each N and the turning points of the field occurred near the center of a plateau. The field was swept at a rate $|dH_z/dt| = 5.83$ mT/s.

As the field is swept back and forth across the field resonance, the magnetization relaxes in steps. The manner in which it relaxes is expected to be different for a set of identical molecules than for the case of a distribution of tunnel splittings. We will show below that an ensemble of identical molecules cannot describe the data presented here. A method of fitting different distributions to the magnetization data will be developed, and an excellent fit is obtained for a lognormal Gaussian distribution. It will also be argued that dipolar shuffling⁹ would produce an asymmetry in the steps which is not observed.

The fraction of molecules remaining after each step can be determined from the magnetization curves. At the turning points labeled by f_0, f_1, f_2, \dots , for $N=7$, shown in the upper inset of Fig. 1, the fraction of molecules remaining in the metastable well is related to the normalized magnetization by $f_j = (1 - M_j)/2$, where M_j is the normalized magnetization at the turning points of the field. For each N , Fig. 2 shows the fraction of molecules remaining in the metastable well after each field pass plotted as a function of how many times, j , the field was swept past the resonance. The issue is whether or not the fraction remaining after each field sweep is consistent with the behavior expected for a sample comprised of an ensemble of identical molecules.

For a set of identical molecules, the probability P_N of remaining in the metastable well for resonance N is the same for each molecule. If the fraction of molecules in the metastable well before sweeping past the N th resonance is $f_{N,0}$, then the fraction of molecules remaining in the metastable well after sweeping the field through the resonance after j passes of the field is: $f_{N,j} = f_{N,0}(P_N)^j$. This form implies that for a set of identical molecules, $f_{N,j}$ would depend exponentially on j , and a semilog plot of the remaining fraction $f_{N,j}$ versus the number of oscillations j should yield straight lines for each N . As can be seen in Fig. 3, which shows the data of Fig. 2 on a semilogarithmic scale, this is not the case. The simple assumption that all the molecules are identical is clearly inconsistent with our data.

We now consider the case of a distribution of tunnel splittings. Chudnovsky and Garanin² calculated the effect of such a distribution due to transverse anisotropies caused by crystal dislocations which produce deformations that require inclusion of a magnetoelastic term in the Hamiltonian. The dislocations give rise to a transverse anisotropy, $E(S_x^2 - S_y^2)$ that varies with the distance from the dislocation. Thus, the second order transverse anisotropy prefactor E is distributed. Alternatively, Cornia *et al.*³ have pointed out that there are six different isomers of Mn_{12} -acetate, four of which are only twofold symmetric. This lowers the symmetry group for the Hamiltonian and also permits inclusion of locally varying second-order transverse anisotropy terms. In either case, a distribution of second-order anisotropy gives rise to a distribution of tunnel splittings. The following analysis is valid regardless of the origin of such a distribution of the second order transverse anisotropy prefactor E .

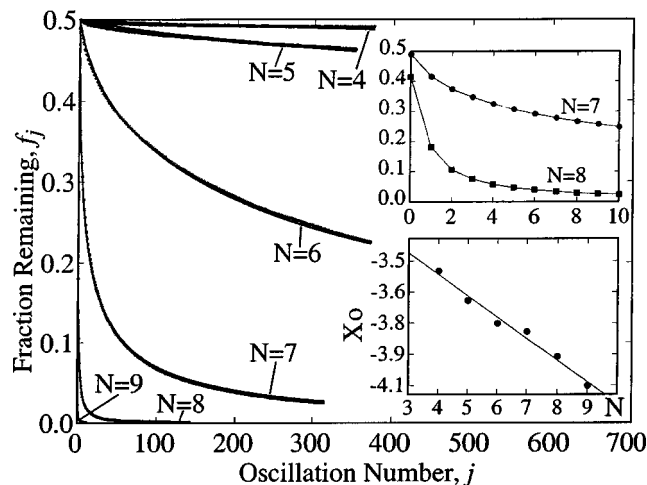


FIG. 2. Fraction of molecules remaining in the metastable well as a function of the oscillation number j . With a Gaussian distribution of $X_E = -\ln(|E|/2D)$, the fits to Eq. (1) for each N shown by the solid lines are nearly indistinguishable from the measured data. The upper inset shows the first few data points for $N=7$ and 8 on a linear scale to illustrate that dipolar shuffling has minimal effects. The lower inset shows the dependence of the fitting parameter X_0 on N .

The probability of remaining in the metastable well is given by the incoherent¹⁰ Landau-Zener-Stueckelberg formula,¹¹ $P_N = \exp(-\pi\Delta_N^2/2\hbar|v_N|)$, where Δ_N is the tunnel splitting and $v_N = (2S - N)g_z\mu_B dH_z/dt$ is the energy sweep rate. The tunnel splitting can be calculated through high order degenerate perturbation theory. For the case of second order transverse anisotropy (neglecting the fourth order longitudinal anisotropy), the tunnel splitting has the form, $\Delta_N = \eta_N g_N (|E|/2D)^{\xi_N}$, where

$$g_N = \frac{2D}{[(2S - N - 2)!!]^2} \sqrt{\frac{(2S - N)!(2S)!}{(N!)}}$$

and we set $D = 0.65$ K (instead of $D = 0.548$ K) to compen-

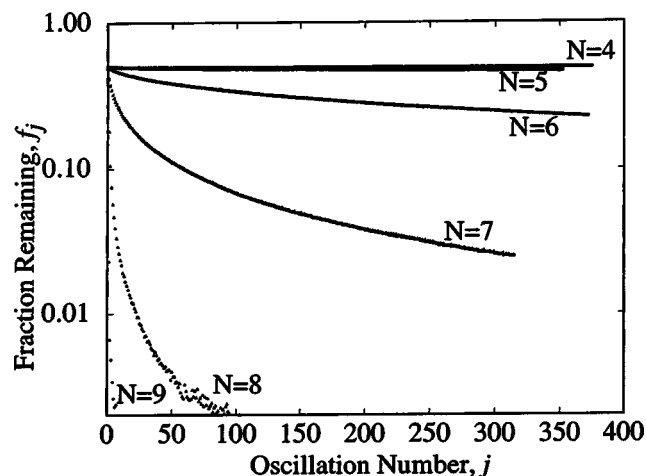


FIG. 3. The fraction of molecules remaining in the metastable well should have an exponential dependence on the oscillation number, j , for an ensemble of identical molecules. Since the data is not linear on a semilogarithmic plot, our results are inconsistent with expectations for identical molecules.

sate for the neglect of the fourth order term. For even N , $\xi_N = S - N/2$ and $\eta_N = 1$. For odd N , $\xi_N = S - (N-1)/2$ and $\eta_N = N/2$.^{2,1}

For an arbitrary initial distribution $\tilde{f}_0(E)$ the fraction of molecules remaining in the metastable well with a transverse anisotropy prefactor between E and $E+dE$ is $\tilde{f}_1(E)dE = P_1(E)\tilde{f}_0(E)dE$, where $P_1(E)$ is the probability of remaining in the metastable well for the $N=1$ resonance. Integrating over all possible transverse anisotropy prefactors, one obtains the fraction of molecules remaining in the metastable well after having swept the field entirely through the resonance, $f_1 = \int_{-\infty}^{+\infty} P_1(E)\tilde{f}_0(E)dE$. The total fraction of molecules remaining in the metastable well after having swept the field back and forth across the $N=1$ resonance j times is, $f_{1,j} = \int_{-\infty}^{+\infty} (P_1(E))^j \tilde{f}_0(E)dE$. Note that for $N>1$, the field is swept once through each of the lower resonances. Therefore, the fraction of molecules remaining in the metastable well, after sweeping the field back and forth j times across resonance N is given by

$$f_{N,j} = \int_{-\infty}^{+\infty} \prod_{k=0}^{N-1} P_k(E) (P_N(E))^j \tilde{f}_0(E) dE, \quad (1)$$

where $\prod_{k=0}^{N-1} P_k(E)$ determines how much of the distribution remains after having swept through the previous $N-1$ resonances and $P_N(E)$ is the probability of remaining in the metastable well for the N th resonance. Equation (1) can be used to model the data shown in Fig. 2. Different distributions $\tilde{f}_0(E)$ can be chosen and all the curves in Fig. 2 should be fit simultaneously for the same choice of parameters defining the shape of $\tilde{f}_0(E)$.

An excellent fit to the data is obtained for a log-normal distribution of the form¹ $\tilde{f}(X_E) = e^{-(X_E - X_0)^2/4\sigma^2}$, where $X_E = -\ln(|E|/2D)$. This form captures the behavior remarkably well for all observed resonances, and is indistinguishable from the data shown in Figs. 2 and 3. However, rather than being constant, the parameter X_0 required for a best fit was found to vary weakly with step number N . The values of X_0 chosen for each N in the fit are shown in the lower inset to Fig. 2. The width of the distribution $\sigma = 0.09814$ was constrained to be constant for the fit. The variation of X_0 with N could be due perhaps to the existence of other symmetry-breaking terms in the Hamiltonian. In our previous studies,¹ deviations from full scaling were attributed to a small admixture of tunneling due to transverse magnetic fields.

“Dipolar shuffling” has been recently proposed as an explanation for an unexpected dependence of tunnel splittings on sweep rate.¹⁰ This effect refers to the fact that when a molecule tunnels, the internal dipole fields are locally altered so that some molecules that were previously below are

now above the resonance field and vice versa. For the long thin sample studied here ($a \approx 40 \mu\text{m}$, $b \approx 40 \mu\text{m}$, $c \approx 150 \mu\text{m}$), this is expected to introduce an asymmetry between up and down sweeps: during an up sweep many of the dipole-shuffled molecules will skip the resonant field resulting in a lower tunneling rate while during a down sweep molecules will have additional opportunities to tunnel giving an enhanced tunneling rate. This would yield a tilted staircase for the curves shown in Fig. 2, with successive points lying above and below the curve expected in the absence of dipolar shuffling. The data plotted on an expanded scale in the upper inset of the figure show that the fraction remaining varies smoothly with oscillation number. We conclude that for the zero-field cooled samples studied here, dipolar shuffling is not responsible for the nonexponential behavior.

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