Steps in the hysteresis loops of a high-spin molecule

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We report the first observation of steps in the hysteresis loop of a high-spin molecular magnet. We propose that the steps, which occur every 0.46 T, are due to thermally assisted resonant tunneling between different quantum spin states. Magnetic relaxation increases dramatically when the field is in the neighborhood of a step. A simple model accounts for the observations and predicts a value for the anisotropy barrier consistent with that inferred from the superparamagnetic blocking temperature. © 1996 American Institute of Physics.

INTRODUCTION

The large-spin molecule Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄, has been the subject of much experimental¹⁻⁵,10 and theoretical⁶,⁷ work since it was first synthesized by Lis⁸ in 1980. This molecule (often referred to as Mn₁₂) contains four Mn⁴⁺ (S = 3/2) ions and eight Mn³⁺ (S = 2) ions. Experiments¹ indicate that it has an S = 10 ground state. These molecules crystallize into a tetragonal lattice in which magnetic interactions between molecules are thought to be negligible.³ All experimental work¹⁻⁵,10 to date on this system indicates that it has a large magnetocrystalline anisotropy. Superparamagneticlike behavior has been reported.¹⁻⁴ Below a blocking temperature of ~3 K, hysteresis is observed³ and slow exponential relaxation of the magnetization has been found³ with relaxation times that obey an Arrhenius law, \( \tau = \tau_0 e^{ΔE/k_BT} \), down to 2.1 K; studies⁴,¹⁰ at temperatures down to 175 mK show deviations from this form that have been interpreted as possible signs of temperature-independent quantum tunneling.

In this article, we report the observation of steps in the hysteresis loops of a powdered sample of Mn₁₂. We suggest that the steps are manifestations of thermally assisted, field-tuned resonant tunneling through the molecule’s anisotropy barrier. We show that the relaxation rate increases dramatically when the applied field is tuned to a field at which one of the steps occurs.

EXPERIMENTS AND RESULTS

The sample was prepared following the published procedure⁸ and was then ground into a powder consisting of submicron-sized crystallites. The powdered sample was mixed into Stycast 1266 and allowed to set in a field of 5.5 T at 300 K. This served to orient the crystallites suspended in the epoxy such that their easy axes aligned with the field due to the anisotropy of the susceptibility tensor. No corrections were made for the diamagnetism of the epoxy, which was considered negligible. The dc magnetization measurements were taken at temperatures between 1.7 and 15 K with a Quantum Design MPMS5 magnetometer equipped with a 5.5-T superconducting magnet.

Figure 1 shows the hysteresis loops taken with the field applied along the easy axis of the oriented sample at six different temperatures from 1.7 to 2.8 K, as indicated. The steps in the loops are clearly visible. In contrast, no steps were seen in a control sample prepared in the absence of a field. It is noteworthy that after the system is saturated and the field is reduced back to zero field, the curve is temperature independent and no steps are apparent. The steps occur only at specific values of magnetic field. The inset to Fig. 1 shows the field at which a step occurs plotted versus step number, where the steps are labeled by integers and the fields plotted are the points in the hysteresis curves where the slope, \( dM/dH \), is maximal. The excellent linear fit indicates that a step occurs at approximately every 0.46 T. If data from all temperatures are used, then a total of seven steps, including the one at zero field, are observed and it is quite possible that more would be seen at lower temperatures. We note that as temperature is lowered, steps that were apparent at higher temperatures seem to disappear. These steps can still be observed, however, if the rate at which the field is swept is
the straight lines in Fig. 3. The fit yields time constants, \( \tau \), of 1048 and 2072 s at 0.9 and 0.95 T, respectively.

**DISCUSSION**

We suggest that the observed steps are due to thermally assisted resonant tunneling between quantum spin states in the Mn12 system. In zero field, the molecule has two degenerate ground states, corresponding to the spin being parallel (\( m = S \)) or antiparallel (\( m = -S \)) to the easy axis. An anisotropy barrier separates the states and a magnetic field breaks the symmetry, making one state a true ground state and the other a metastable ground state. This model is illustrated in Fig. 4. When an excited level in the right well is resonant with the metastable ground state on the left, transitions across the barrier are induced. Once the system has crossed the barrier, there is presumably a rapid spontaneous decay from the excited state to the ground state. In this way the metastable state is depleted and the system enters the \( m = -S \) state.

The simplest Hamiltonian for this system is

\[ \mathcal{H} = -D S_z^2 - g \mu_B S \cdot H, \]  

(1)

**FIG. 4.** A schematic representation of the resonant tunneling mechanism proposed to explain the observations. Tunneling from the metastable state \( m = S \) to an excited state \( m = -S + n \) is followed by a rapid spontaneous decay into the ground state.
where $D$ represents the anisotropy energy that breaks the zero-field Zeeman degeneracy. If the field is applied along the easy axis, then the eigenstates of this Hamiltonian are $|S, m\rangle$. The first term in Eq. (1) implies that the ground state will be $m = \pm S$, as expected; the sign depends on the direction of the field. For clarity, we take $|S, S\rangle$ as the initial state of the system. We propose that a step occurs when the energy of this state is equal to the energy of a state on the other side of the anisotropy barrier. A simple calculation reveals that the field at which the state $|S, S\rangle$ crosses the state $|S, -S + n\rangle$, is

$$H_{S, -S + n} = \frac{-Dn}{g \mu_B}. \tag{2}$$

Thus, steps occur at even intervals of field, as observed. Interestingly, when the field is tuned such that the metastable ground state in the left well is resonant with a state in the right well, all of the excited states in the left well are also resonant with states on the other side of the barrier. Thus, a multiple resonance is set up whenever the field is tuned to a step. Using the fact that a step occurs every 0.46 T, we find $D/g = 0.21$ cm$^{-1}$, which is consistent with the published values$^{6}$ of $D \sim 0.5$ cm$^{-1}$ and $g \sim 1.9$ cm$^{-1}$. As a further check of this model, we can estimate the size of the anisotropy barrier: at zero field, the barrier is $g(D/g)S^2 \sim 41$ cm$^{-1}$, consistent with the estimate of 45 cm$^{-1}$ obtained above from the blocking temperature data. Given that $S = 10$ in this system, there should be exactly 21 steps ($n = 0, 20$), the last corresponding to the elimination of the barrier. Measurements at lower temperatures are needed to observe additional steps.

As noted above, as temperature is reduced, any given step becomes less prominent and the transition rate decreases rapidly. This implies that the resonant tunneling mechanism responsible for the steps is thermally assisted. It is possible that acoustic phonons provide the angular momentum necessary for the transition between different spin states. As temperature is lowered, the population of phonons (or other excitations) drops and the transition rate decreases. More work is needed to understand precisely what role thermal excitations play in this resonant process.

We would like to stress that the above model of field-tuned, thermally assisted resonant tunneling out of a metastable spin state explains many of the observations presented herein. When the field is reduced from saturation, no steps are seen because the system is already in the true ground state $m = S$. It is only when the field is reduced to near zero or reversed that the state becomes metastable allowing resonant transitions and the corresponding steps. The higher-numbered steps have progressively faster magnetic relaxation times since the tunnel barrier is lowered by the applied field.

In summary, we have found steps in the hysteresis curves of Mn$_2$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$ and propose that they result from thermally assisted resonant transitions between spin states. The magnetic relaxation rate of the system increases dramatically when the field is tuned to a step; that is, when there is a level crossing. A simple model has been proposed that accounts for the even interval of field between neighboring steps and is in quantitative agreement with measurements of the anisotropy barrier.

Note added in proof: Since we submitted this manuscript, two papers$^{11,12}$ have appeared on Mn$_2$O$_{12}$, reporting anomalously fast relaxation rates at zero field$^{11,12}$ and 0.3 T. Novak and Sessoli$^{12}$ suggest that these results are due to thermally assisted resonant tunneling. A similar suggestion has been made previously by Barbara et al.$^{10}$ to explain the zero-field anomaly.

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