Field-dependence of the Magnetic Relaxation in Mn$_{12}$-Acetate: A New Form of Spectroscopy

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We report point by point measurements below the blocking temperature of the magnetic relaxation of Mn$_{12}$-acetate as a function of magnetic field applied along the easy axis of magnetization. Unexpectedly complex structure is observed which we attribute to the effect of higher-order terms of the spin Hamiltonian on the tunneling process.

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The high-spin molecular magnets Mn$_{12}$-acetate (Mn$_{12}$) and Fe$_8$ have received considerable attention as model systems for the study of Quantum Tunneling of Magnetization (QTM). With a total spin $S = 10$ and a large uniaxial magnetic anisotropy $\mathcal{E}$, Mn$_{12}$ molecules crystallize into a body-centered tetragonal lattice where the $c$-axis is along the molecules’ easy axis. Strong anisotropy breaks each molecule’s 21-fold zero-field degeneracy and results in a double-well potential with energy levels that correspond to different projections of the spin along the easy axis. Strong evidence for QTM in Mn$_{12}$ was obtained in the form of a series of steps at regular intervals of magnetic field in the hysteresis loops of Mn$_{12}$ below the blocking temperature of $\approx 3$ K. Based on the observation that the relaxation follows an Arrhenius law above 2 K, this process has been attributed to thermally-assisted tunneling: at these intermediate temperatures the magnetization is thermally activated to some level (or group of adjacent levels) near the top of the anisotropy barrier where the tunneling from metastable to stable potential wells proceeds. Similar steps in the hysteresis loops have been observed in Fe$_8$, where the quantum mechanical nature of the relaxation process has been established unambiguously through experiments demonstrating phase interference and parity effects in response to externally applied transverse fields.

Measurements of steps in the hysteresis loops do not provide the resolution or control necessary for a detailed study. In measurements of the hysteresis, the external magnetic field is swept continuously at some predetermined rate so that the magnetic response is generally probed only on short time scales. For reasons that are only partially understood, the initial response of the magnetization in Mn$_{12}$ is not characteristic of the long-time behavior of the relaxation. We note also that there is a time-varying internal field associated with the time-varying sample magnetization which must be added to the externally applied field to obtain the total field $H_{\text{total}} = H + \alpha(4\pi M)$, where $\alpha$ is a constant between 0 and 1, depending on sample shape and size. The transient conditions of a hysteresis measurement make it particularly difficult to take this effect into account.

In this paper we report point-by-point measurements of the magnetic relaxation of Mn$_{12}$ in fixed external magnetic fields applied along the uniaxial anisotropy direction which reveal that the resonances corresponding to steps in the hysteresis loop consist of rich and quite complex substructures of resolved peaks. We attribute the observed splittings to the higher order longitudinal anisotropy term $AS^2$ in the spin Hamiltonian, a small anharmonic contribution that causes different pairs of energy levels on opposite side of the anisotropy barrier to be in resonance at slightly different values of magnetic field. Odd-even asymmetry between steps indicates that higher order transverse anisotropy also plays a role in Mn$_{12}$.

Millimeter size single crystals of Mn$_{12}$ were prepared according to the published procedure. Parallel and perpendicular components of the DC magnetization were obtained with a Quantum Design MPMS-5 magnetometer. A sample rotator was used to align the crystal $c$-axis parallel to the magnetic field in increments of 0.1°. The ratio between perpendicular and parallel SQUID readings was typically $10^{-3}$, corresponding to 20 Oe at 2 Tesla. Cooling the sample in zero magnetic field before each sweep, full curves of the magnetic relaxation were recorded as a function of time in a series of fixed externally applied longitudinal magnetic fields in the temperature range between 1.8 K and 2.6 K. Following our previous method of data analysis, we obtained the characteristic rate by fitting the long time relaxation to a single exponential. The overall change in magnetization is small after about 2000 s, corresponding to a negligible change in the average internal field $\alpha(4\pi M)$ compared to the sizable (fixed) external field $H$. 

FIG. 1. Relaxation rate as a function of magnetic field $H_{\text{total}}$ applied along the easy axis of a single crystal of Mn$_{12}$. Here $H_{\text{total}} = H + \alpha (4\pi M)$ with $\alpha = 0.57$.

The relaxation rates at several temperatures between 1.8 K and 2.6 K are plotted in Figs. 1 and 2 as a function of the total longitudinal magnetic field $H_{\text{total}} = H + \alpha (4\pi M)$; here the first term is the externally applied field $H$ and the second term is the contribution due to the sample’s magnetization. We used $\alpha = 0.57$ obtained from earlier measurements by Friedman [11] on similar samples.

Several observations can be readily made from the data. (1) The main features of the curves confirm the results obtained from hysteresis measurements: there is faster relaxation at approximately regularly spaced values of the magnetic field. Within the temperature range of our experiments five peaks or resonances are observed, labeled by “step numbers” $N = 0, 1, 2, 3, 4$. (2) Some of the resonance peaks corresponding to the “steps” in the hysteresis loops exhibit additional internal structure. Most noticeably, the $N = 2$ and $N = 4$ peaks split into two or more small peaks at the higher temperatures. The $N = 1$ and $N = 3$ resonances have much simpler structure. However, a careful examination of the $N = 3$ resonance at $T = 2.20$ K reveals that it also consists of two closely spaced peaks. The $N = 0$ peak exhibits no apparent structure at 2.60 K, or at other temperatures measured earlier [12]. (3) Unlike most spectra, which generally become sharper and more detailed as the temperature is reduced, it is interesting to note that the structure is more complex at higher temperatures. This is particularly clear for the $N = 4$ resonance where three maxima are clearly seen at 2.00 K, while only one major peak (probably with a small right shoulder) is present at 1.80 K. (4) The separation of approximately 0.10 T between two neighboring peaks of the $N = 4$ resonance is twice as large as in the case of the $N = 2$ resonance, where it is about 0.05 T (see the $T = 2.00$ K and 2.47 K curves, respectively).

Hysteresis and earlier relaxation studies of Mn$_{12}$ indicated relatively simple structure in the form of a series of clean steps, each due to energy coincidences of pairs of levels on opposite sides of the anisotropy barrier corresponding to different spin projections. In contrast, our detailed studies reveal that each resonance corresponding to a step displays rather complex structure. We suggest that these spectroscopic features are due to the non-simultaneous crossing of different pairs of magnetic sublevels, as explained below.

Up to fourth order terms, the spin Hamiltonian that describes Mn$_{12}$ can be written as:
\[ H = -DS_z^2 - \mu_B H \cdot g \cdot S - A S_z^4 + C(S_z^4 + S_z^4) \]  
(1)

where \( D = 0.548(3) \) K is the anisotropy constant, the second term represents the Zeeman energy, and the remaining are higher-order terms in the crystalline anisotropy allowed by tetragonal symmetry. A level in the metastable potential well with magnetic quantum number \( m \) comes into resonance with level \( m' \) in the stable well at a longitudinal magnetic field \( H_z \) given by:

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

Electron paramagnetic resonance (EPR) [14] and inelastic neutron scattering experiments in Mn\(_{12}\) [15] have shown there is a sizable fourth order term, \( AS_z^2 \), with \( A = 1.173(4) \times 10^{-3} \) K. As a consequence, different pairs of levels \( m, m' \) on opposite sides of the anisotropy barrier come into resonance at slightly different magnetic fields for the same step number \( N = |m + m'| \). Note that higher fields are necessary to bring lower-energy pairs (bigger \( |m| \)) into resonance, an effect that is more pronounced for peaks with higher numbered steps (due to the multiplicative factor \( N \) in Eq. (2)) [17]. Using the parameters \( D, A \) and \( g_z \) obtained by inelastic neutron scattering [16] and EPR measurements [14], the magnetic fields at which pairs of levels \( m, m' \) come into resonance calculated from Eq. (2) are listed in Table I.

Several features of the data are consistent with this model. In agreement with Eq. (2), the separation between neighboring peaks is generally larger within the higher number steps: the splitting for \( N = 4 \) is twice that for \( N = 2 \), there is no substantial splitting (or shift) for the \( N = 1 \) resonance, and none at all for \( N = 0 \). Also, since the tunneling is thermally assisted in this temperature regime, one might expect that spin reversal through resonant levels near the top of the potential well will become more active, introducing additional channels for tunneling as the temperature is raised. This could account for the fact that more complex structure is observed at higher temperatures. Quantitative comparison of the measured peak positions and the calculated resonant fields listed in Table I requires a reliable determination of the value of \( \alpha \) used to calculate the total field \( H_{total} = H + \alpha(4\pi M) \). Using \( \alpha = 0.57 \) found in earlier experiments on similar material [11], we suggest that the \( N = 1 \) peak centered at about 0.437 T at 2.60 K is associated with tunneling from \( m = -3 \) and/or \( -4 \) in the metastable well, while at the lower temperatures of 2.47 K and 2.42 K, the \( N = 1 \) maximum observed at 0.446 T is very close to the field 0.443 T listed in Table I for tunneling from \( m = -4 \) to \( m' = 3 \).

Other features of the data are more difficult to understand and warrant further discussion. One is that there appears to be considerably more structure in even \((N = 2, 4)\) than in odd \((N = 1, 3)\) resonances within the range of field and temperature of our measurements. It is puzzling, for example, that the \( N = 3 \) peak shows much less structure than the \( N = 2 \) resonance (note the multiplicative factor \( N \) of Eq. (1)). A second interesting feature is that the splitting within the \( N = 2 \) and \( N = 4 \) steps are too large to correspond to the difference in magnetic fields for two immediately neighboring level crossings (i.e. tunneling from \( m \) and \( (m - 1) \)). Instead, they correspond more closely to the field difference for every other level crossing (i.e. tunneling from \( m \) and \( (m - 2) \)). In contrast, the \( N = 3 \) resonance has negligible splitting and its two closely-merged peaks are probably due to immediately neighboring level crossings. These effects suggest that higher-order transverse anisotropy is important in the tunneling process.

Two symmetry-breaking terms that could be responsible for tunneling have been considered: (1) a transverse magnetic field (of hyperfine/dipolar origin, or externally applied); and (2) an anisotropy term of the form \( C(S_z^4 + S_z^4) \), the lowest order allowed by the tetragonal symmetry of Mn\(_{12}\). Our data presents a clear enigma. On the one hand, the odd-even asymmetry between steps and level-skipping within even-numbered steps both suggest that transverse anisotropy plays an important role in the tunneling. On the other hand, the odd and even-numbered resonances have comparable amplitudes, albeit at different temperatures. This implies that the tunneling is due to transverse magnetic fields. A simple model calculation for the tunneling rates that includes both symmetry-breaking terms does not fit the experimental results for any values of the parameters: the odd-even asymmetry requires that transverse anisotropy dominate, while the comparable amplitudes require that a transverse field be the dominant symmetry-breaking term. Which mechanism is responsible for tunneling in this material is an interesting question that has yet to be resolved.

Leuenberger and Loss [14] and Poljola and Schoeller [20] recently presented a comprehensive theory of the magnetization relaxation in Mn\(_{12}\) in the thermally assisted tunneling regime. The relaxation rate as a function of longitudinal magnetic field was calculated using a Hamiltonian that includes spin-phonon interactions, quartic magnetic anisotropy and a weak transverse field. They obtained satellite peaks qualitatively similar to those shown in Figs. 2 and 3 whose amplitude and width they investigated [19] for various angles between the sample easy axis and the field direction. Quantitative agreement between their theory and our experimental observations requires a substantial transverse magnetic field, due perhaps to mosaic spread or unintentional misalignment of the sample with respect to the magnetic field direction. However, the mosaic spread of approximately 0.4° [21] found for Mn-12 crystals is too small to account for our observations, and the degree of misalignment required to give a sufficiently large transverse component.
is well outside our experimental margin of uncertainty and would yield different results each time a sample is mounted and aligned.

In closing, we note that the point-by-point relaxation measurements presented in this paper represent a novel form of spectroscopy. “Spectra” obtained from such measurements allow detailed studies of the tunneling process, and provide important information regarding the dominant tunneling paths at different temperatures and magnetic fields.

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| \( N = 1 \) | \( N = 2 \) | \( N = 3 \) | \( N = 4 \) |
|---|---|---|---|
| \( m \) | \( m' \) | \( H \) | \( \text{T} \) | \( m' \) | \( H \) | \( \text{T} \) | \( m' \) | \( H \) | \( \text{T} \) |
| -1 | 0 | 0.422 | - | - | - | - | - | - | - |
| -2 | 1 | 0.425 | 0 | 0.848 | -1 | 1.275 | - | - | - |
| -3 | 2 | 0.432 | 1 | 0.859 | 0 | 1.286 | -1 | 1.719 | - |
| -4 | 3 | 0.443 | 2 | 0.877 | 1 | 1.308 | 0 | 1.740 | - |
| -5 | 4 | 0.458 | 3 | 0.902 | 2 | 1.340 | 1 | 1.776 | - |
| -6 | 5 | 0.476 | 4 | 0.935 | 3 | 1.383 | 2 | 1.827 | - |
| -7 | 6 | 0.497 | 5 | 0.974 | 4 | 1.437 | 3 | 1.891 | - |
| -8 | 7 | 0.522 | 6 | 1.021 | 5 | 1.502 | 4 | 1.971 | - |
| -9 | 8 | 0.551 | 7 | 1.075 | 6 | 1.578 | 5 | 2.064 | - |
| -10 | 9 | 0.584 | 8 | 1.137 | 7 | 1.664 | 6 | 2.172 | - |

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