Tunneling splittings in Mn_{12}-acetate single crystals

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Abstract. – A Landau-Zener multi-crossing method has been used to investigate the tunnel splittings in high-quality Mn_{12}-acetate single crystals in the pure quantum relaxation regime and for fields applied parallel to the magnetic easy axis. With this method several individual tunneling resonances have been studied over a broad range of time scales. The relaxation is found to be non-exponential and a distribution of tunnel splittings is inferred from the data. The distributions suggest that the inhomogeneity in the tunneling rates is due to disorder that produces a non-zero mean value of the average transverse anisotropy, such as in a solvent disorder model. Further, the effect of intermolecular dipolar interaction on the magnetic relaxation has been studied.

Single-molecule magnets (SMMs) such as Mn_{12}, Fe_8 and Mn_4 have enabled new studies of the physics of magnetic nanostructures. These materials are ordered crystals of nominally identical high-spin ($S = 10$ and smaller) molecules with predominately uniaxial magnetic anisotropy. A particular focus has been put on quantum tunneling (QT) of the magnetization [1–10], with efforts aimed at understanding the origin of the tunneling phenomena in SMMs, the effect of intermolecular interactions in SMM crystals and the role of the environmental degrees of freedom in modulating QT (including phonons and nuclear spins) [11]. Even in the original, high-symmetry and high-magnetic-anisotropy barrier SMM, Mn_{12}-acetate, the QT phenomenon remains poorly understood. Primarily this is due to the fact that the magnetic properties do not reflect the tetragonal symmetry (S4 site symmetry) of the molecule. For example, QT transitions do not obey the selection rules imposed by this symmetry and the magnetic relaxation is clearly non-exponential, indicating inhomogeneity in the tunneling rates. It has become evident in recent research [12, 13] that disorder that lowers the molecule symmetry plays an essential role in the physics of QT in Mn_{12}-acetate single crystals, but the precise nature of the disorder remains unclear. Thus far, two alternative models of disorder have been proposed. The first is line-dislocations in crystals that produce long-range deformations and through magnetoelastic interactions lead to a distribution of the transverse

magnetic anisotropy. This leads to a very broad distribution in the tunnel splittings on a logarithmic scale [14]. The second is disorder in the solvent molecules that surround each Mn$_{12}$ core that lead to a discrete set of transverse anisotropies [15]. Each model has predictions that can be compared to experiment. In addition, intermolecular dipolar interactions are another important source of magnetic inhomogeneity that can be studied in experiment.

In this letter we present experimental results on the tunnel splittings in deuterated Mn$_{12}$-acetate single crystals in the pure quantum regime, in which relaxation is by QT without thermal activation [10]. Deuterated crystals have been studied because the purity of the chemicals used in the synthesis leads to very high-quality crystals [16]. We have used a modification of the Landau-Zener (LZ) method and a high-sensitivity micro-Hall effect magnetometer to study the magnetic relaxation in Mn$_{12}$. With this method we have determined the distribution of tunnel splittings for a *single* QT resonance in a manner that enables a critical comparison of the experimental data with models of disorder for Mn$_{12}$. We also show the effect of intermolecular dipolar interactions on the magnetic relaxation in Mn$_{12}$.

The effective spin Hamiltonian for Mn$_{12}$ is

$$\mathcal{H} = -DS_z^2 - BS_z^4 - g\mu_B \boldsymbol{H} \cdot S + \mathcal{H}', \tag{1}$$

where the parameters $D = 0.548(3)\,\text{K}$, and $B = 1.17(2) \times 10^{-3}\,\text{K}$, have been determined by EPR [7] and inelastic neutron spectroscopy experiments [8]. The first two terms represent the uniaxial anisotropy of the molecules, the third term is the Zeeman interaction of the spin with the magnetic field, $\boldsymbol{H}$, and the fourth term includes dipolar and hyperfine interactions and higher-order transverse anisotropy terms that do not commute with S_z. The observed steps in the magnetic hysteresis correspond to an enhancement of the relaxation towards the equilibrium magnetization when the eigenstates of S_z, m and m', on opposite sides of the barrier are nearly degenerate (see, for example, fig. 1 of ref. [10]). These resonances are labelled by the integer $k = m - m'$ and occur at longitudinal magnetic fields of approximately $H_k = kD/(g\mu_B) \sim k\ 0.42\,\text{T}$.

It has been shown that the LZ method is a powerful way to study tunnel splittings in SMM crystals [5]. The method consists in sweeping the longitudinal magnetic field at a constant rate, $\alpha = \mathrm{d}H/\mathrm{d}t$, across a QT resonance and measuring the fractional change in magnetization. For an ensemble of non-interacting identical SMMs, this fractional change in magnetization is related to the probability that an individual SMM has *remained* in the original metastable state after an avoided level crossing. The probability is $R = (M - M_{\text{eq}})/(M_{\text{ini}} - M_{\text{eq}})$, where M_{ini} is the magnetization before the crossing, M_{eq} is the equilibrium magnetization, and M is the magnetization measured after crossing the resonance. This probability is related to the quantum splitting Δ, through the LZ formula $R_{\text{lz}} = \exp[-\pi\Delta^2/2\nu_0\alpha]$, where $\nu_0 = g\mu_B(2S - k)$ and $\nu_0\alpha$ is the energy sweep rate. Clearly, for this formula to be valid the energy sweep rate that an individual SMM in a crystal experiences must be proportional to the sweep rate of the applied external field. This will only be true if changes in the internal magnetic field on each crossing are small ($R \approx 1$). For this reason, in our experiments, we cross a resonance (say, the k-th resonance) n-times at a constant and sufficiently fast sweep rate, so that on each crossing $R \approx 1$. Then we repeat this process for different sweep rates. In this case, the probability *to remain* in the metastable state after the n-th crossing is $R_k = \frac{M_n - M_{\text{eq}}}{M_{\text{ini}} - M_{\text{eq}}}$, where M_n is the magnetization after the n-th crossing of the resonance. The LZ probability after n-crossings is

$$R_{\text{lz}n} = \exp\left[-\frac{\pi\Delta^2}{2\nu_0}\frac{n}{\alpha}\right]. \tag{2}$$

Based on this formula, relaxation curves recorded at different sweeping rates should scale when plotted as a function of $\alpha_{\text{eff}} = \alpha/n$. In fig. 1 we show the data obtained for resonance
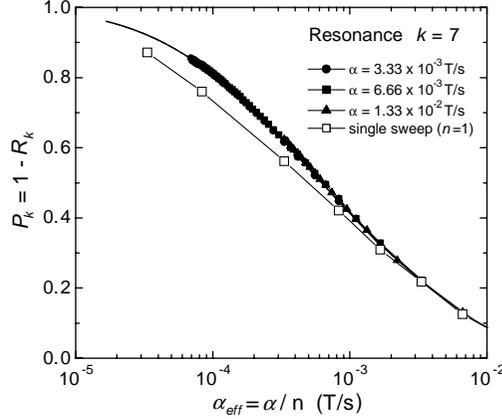
Fig. 1 – The tunneling probability for deuterated Mn_{12}-acetate as a function of the effective sweeping rate, $\alpha_{eff} = \alpha/n$, of the applied magnetic field in a LZ multi-crossing experiment recorded at different sweeping rates (closed symbols) for resonance $k = 7$ and at a temperature of 0.65 K. The open squares correspond to the tunnel probability in a LZ single-crossing experiment vs. the sweeping rate ($n = 1$). The difference between the two curves we associate with dipolar interaction between molecules [19].

$k = 7$ at different sweeping rates, $\alpha = 3.33 \times 10^{-3}$, 6.66×10^{-3} and 13.3×10^{-3} T/s in the pure quantum tunneling regime for this resonance, $T = 0.65$ K ($m = 10$, $m' = -3$). To do the measurements we saturated the system with a negative high magnetic field, $H = -5$ T, and then we swept the field to positive values until we arrived at the vicinity of this resonance ($H_7 = 3.55$ T), with the applied field aligned with the z-axis of the crystal [17]. Then we crossed the resonance n times ramping the field up and down within ± 0.2 tesla of the resonance at a given rate. This procedure was then repeated for different sweep rates. The scaling of the curves is clear, indicating that α_{eff} is the relevant parameter to characterize the data for this range of sweep rates. It is important to point out that the relaxation curve does not follow eq. (2), i.e., it is not an exponential function of α_{eff}, which we discuss in detail below.

For smaller sweep rates, changing internal magnetic fields should affect the magnetic relaxation. This was studied experimentally in Fe_8 [18], where the relaxation departs from the LZ behavior for sweep rates below $\sim 10^{-3}$ T/s, and was theoretically explained in terms of dipolar interactions by Liu et al. [19]. To study this in Mn_{12}, we have measured a single-crossing LZ relaxation at resonance $k = 7$ for different sweeping rates ranging from $\sim 10^{-5}$ to $\sim 10^{-2}$ T/s. The results are compared to the multi-crossing procedure in fig. 1 (open squares). The difference between these procedures is clear. The break point from the LZ single-crossing behavior is $\alpha_c \sim 10^{-3}$ T/s and is similar to that observed in Fe_8, while the deviations from the scaled data are smaller. This is due to the fact that dipolar interactions in Mn_{12} are smaller than in Fe_8 because of differences in the intermolecular distances and crystal structure [20]. We emphasize that the LZ multi-crossing procedure permits studies at very small effective sweep rates in a regime in which a single-crossing experiment would be complicated by intermolecular dipolar interactions.

We have carried out multi-crossings measurements of resonances $k = 6$, 7, and 8 at different sweep rates, $\alpha > \alpha_c$. The results are presented in fig. 2a starting from a saturated sample. Small differences were observed in the same procedure carried out on three different single crystals synthesized in the same way. The main results are the following: a) The behavior of the relaxation is clearly non-exponential; the relaxation is broad on a logarithm scale,
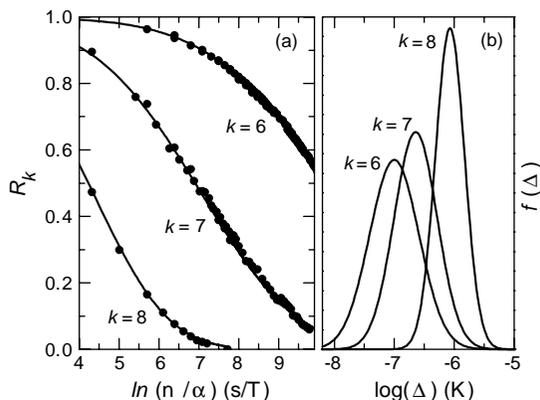
Fig. 2 – (a) Probability to remain in the metastable well in a LZ multi-crossing experiment using different sweep rates (3.33×10^{-3} T/s to 1.33×10^{-2} T/s) for different resonances, k. Lines are fits using a log-normal distribution of splittings. (b) Corresponding splitting distribution functions extracted using the fitting procedure described in the text. The centers, x_c, are -7.34, -6.54, and -6.07 and the widths, W, are 0.43, 0.36, and 0.24, for resonances, $k = 6$, 7, and 8, respectively.

indicating the presence of a distribution of quantum splittings in the crystal; and b) the data give direct information on the distribution width due to the fact that multi-crossings procedure allows us to measure a large fraction of the relaxation curve for each resonance. We have assumed a log-normal function to extract the distribution of the quantum splittings in Mn_{12}. We take the form $f(x) = A \exp[-(x - x_c)/2W^2]$, with $x = \log \Delta$, and we fit the relaxation curves with the following expression:

$$R(\alpha, n) = \int_{-\infty}^{\infty} R_{lz}(\alpha, \Delta, n) f(\log \Delta) \, d \log \Delta. \tag{3}$$

The fitting parameters are the center of the distribution x_c and the width of the distribution on a log scale, W. The fits with eq. (3) are represented by lines in fig. 1 and fig. 2a and are in excellent accord with the experimental data. The fitting parameters can be determined within an accuracy of 5%. The corresponding splitting distribution functions for each resonance are shown in fig. 2b. The mean value of the distribution increases with k, while the width remains more or less constant, being somewhat narrower for $k = 8$. This width is a factor of 2 (in $\log \Delta$) smaller than the width extracted in ref. [12], because of the higher quality of the deuterated crystals.

Recently, it has been proposed that line dislocations [14] or solvent disorder [15] should introduce a second-order anisotropy term, $E(S_x^2 - S_y^2)$, in the Hamiltonian of Mn_{12}, that increases the quantum tunneling probability. Line dislocations generate a broad distribution of the parameter E with mean value $\langle E \rangle = 0$, while disorder of the solvent molecules creates a discrete number of E values due to different Mn_{12} isomers existing in the crystal. Recent relaxation experiments have confirmed the existence of a broad splitting distribution [12, 13] as well as broad absorption lines [21] and discrete double absorption peaks [15, 22] have been observed by EPR experiments. In order to compare our experimental data to these models, we have tried to fit our relaxation curves to the distributions predicted by these models. In the distribution function predicted by the line dislocations model the mean value and width
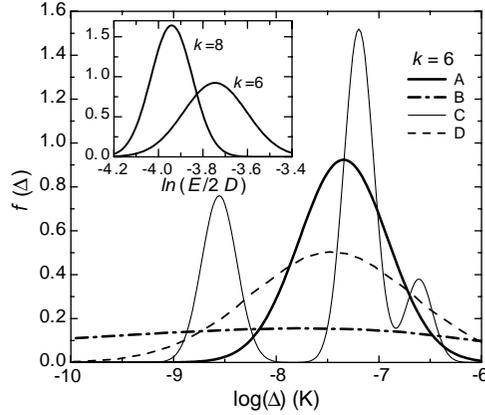
Fig. 3 – Splitting distributions function extracted using a log-normal distribution (A), the dislocation model (B), and the solvent disorder model (C). Distribution D was measured in a non-deuterated Mn_{12}-acetate single crystal (from ref. [12]). The inset shows the distribution of the second-order anisotropy parameter, E, extracted from the log-normal distribution of tunneling splittings using eq. (5) for $k = 6$ and $k = 8$.

of the distribution are not independent variables,

$$f_L(x) \cong \frac{1}{2\sqrt{\pi}\tilde{E}_{\tilde{c}}} \exp\left[x - \frac{e^{2x}}{\left(2\tilde{E}_{\tilde{c}}\right)^2}\right], \tag{4}$$

where $x \equiv \ln \tilde{E}$ with $\tilde{E} = E/2D$. $\tilde{E}_{\tilde{c}}$ is the width of the distribution of the anisotropy parameter $\tilde{E}$. $\tilde{E}_{\tilde{c}}$ depends on the geometry of the crystal and on the concentration of dislocations per unit cell, c. To fit to this function we use the following relation between Δ with E which follows from perturbation theory:

$$\ln\left(\Delta_k/g_k\right)/\xi_k = \ln\left(\frac{E}{2D}\right), \tag{5}$$

where g_k and ξ_k are determined by k, S, and D [14]. The only fitting parameter is $\tilde{E}_{\tilde{c}}$. The result of this fit for resonance $k = 6$ is shown in fig. 3 (dash-dotted line). It corresponds to a concentration of dislocations of around $c \sim 10^{-4}$. The mean value is chosen to coincide with the center of the log-normal distribution function (continuous thick line). Clearly, the width is many orders of magnitude too large to fit the experimental data. Physically, this is due to the fact that the transverse anisotropy distribution expected from the dislocations model alone is centered at $\langle E \rangle = 0$, which produces a large tail to small values of the tunnel splitting, and would produce a much broader relaxation curve than observed in experiment. As a consequence it is clear that a model that describes our data must have non-zero mean value of the transverse anisotropy distribution. For example, taking our log-normal distribution of Δ, the distribution of the transverse anisotropy parameter can be inferred. The results for $k = 6$ and $k = 8$ are shown in the inset of fig. 3. As these curves do not overlap (scale), it is clear that the origin of the tunnel splittings cannot *only* be due to a second-order transverse anisotropy. However, qualitatively, this would lead to a distribution of Δ that narrows for increasing k (which can be seen from perturbation theory, eq. (5)), as observed in fig. 2.

The solvent disorder model suggests a multi-peak discrete splitting distribution due to the presence of six different isomers of Mn_{12} with different E parameters. We have found that it is not possible to fit the experimental data with a sequence of delta-functions for the suggested values of E for each isomer. However, we have obtained a good fit to the data assuming a log-normal distribution with a very narrow width for each delta-function proposed in ref. [15]. The resulting distribution function has three well-defined peaks as can be observed in fig. 3 (continuous thin line). The values of the peak centers are $x_{c,1} = -7.19(-7.0525)$, $x_{c,2} = -8.55(-8.1749)$, and $x_{c,3} = -6.60(-6.7995)$, in accord with the reported values between parenthesis [23]. The width of each peak is $W_i = x_{c,i}/50$. The height of each peak is taken to be proportional to the measured population of its corresponding isomer. The data suggest that the solvent disorder model, which gives a non-zero value of the transverse anisotropy, together with some other type of disorder (like line dislocations or point defects) that introduces a small broadening of the anisotropy E parameter around these values are consistent with our relaxation data. We note other models that include higher-order transverse anisotropies (such as $C(S_x^2 - S_y^2)^2$) and disorder of some type will likely also have features necessary to understanding the relaxation in Mn_{12}. Of course, in order to explain the relaxation for odd resonances, there must be transverse fields due to small tilts of the anisotropy axis of the molecules or slight misalignments of the applied field.

To conclude, we have used a powerful method to study quantum splittings of SMM single crystals. We have reported for the first time the breakdown of LZ scaling due to dipolar interactions in Mn_{12}-acetate and we have estimated the order of magnitude of the interaction energy between molecules. Our results suggest that the quantum splitting distribution in Mn_{12}-acetate should be due to disorder which generates a transverse anisotropy distribution with a non-zero mean value, such as solvent disorder.

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