Observation of the distribution of molecular spin states by resonant quantum tunneling of the magnetization

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Below 360 mK, Fe₈ magnetic molecular clusters are in the pure quantum relaxation regime and we show that the predicted “square-root time” relaxation is obeyed, allowing us to develop a new method for watching the evolution of the distribution of molecular spin states in the sample. We measure as a function of applied field $H$ the statistical distribution $P(\xi_H)$ of magnetic energy bias $\xi_H$ acting on the molecules. Tunneling initially causes rapid transitions of molecules, thereby “digging a hole” in $P(\xi_H)$ (around the resonant condition $\xi_H = 0$). For small initial magnetization values, the hole width shows an intrinsic broadening which may be due to nuclear spins.

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Strong evidence now exists for thermally-activated quantum tunneling (QTM) in magnetic molecules such as Mn₁₂ac and Fe₈ [1,2]. Crystals of these materials can be thought of as ensembles of identical, iso-oriented nanomagnets of net spin $S = 10$ for both Mn₁₂ac and Fe₈, and with a strong Ising-like anisotropy. The energy barrier between the two lowest lying spin states with $S_z = \pm 10$ is about 60 K for Mn₁₂ac and 25 K for Fe₈ [3,4]. Theoretical discussion of thermally-activated QTM assumes that thermal processes (principally phonons) promote the molecules up to high levels, not far below the top of the energy barrier, and the molecules then tunnel inelastically to the other side. The transitions are therefore almost entirely accomplished via thermal excitations.

At temperatures below 360 mK, Fe₈ molecular clusters display a clear crossover from thermally activated relaxation to a temperature independent quantum regime, with a pronounced resonance structure of the relaxation time as a function of the external field [5]. This can be seen for example by hysteresis loop measurements (Fig. 1). In this regime only the two lowest levels of each molecule are occupied, and only “pure” quantum tunneling through the anisotropy barrier can cause direct transitions between these two states. It was surprising however that the observed relaxation of the magnetization in the quantum regime was found to be non-exponential and the resonance width orders of magnitude too large [6,7]. The key to understanding this seemingly anomalous behavior now appears to involve the ubiquitous hyperfine fields as well as the (inevitable) evolving distribution of the weak dipole fields of the nanomagnets themselves [8].

In this letter, we focus on the low temperature and low field limits, where phonon-mediated relaxation is astronomically long and can be neglected. In this limit, the $S_z = \pm 10$ spin states are coupled by a tunneling matrix element $\Delta_{tunnel}$ which is estimated to be about $10^{-8}$ K [9]. In order to tunnel between these states, the magnetic energy bias $\xi_H = g\mu_B S H$ due to the local magnetic field $H$ on a molecule must be smaller than $\Delta_{tunnel}$ implying a local field smaller than $10^{-9}$ T for Fe₈ clusters. Since the typical intermolecular dipole fields are of the order of 0.05 T, it seems at first that almost all molecules should be blocked from tunneling by a very large energy bias. Prokofev and Stamp have proposed a solution to this dilemma by assuming that fast dynamic nuclear fluctuations broaden the resonance, and the gradual adjustment of the dipole fields in the sample caused by the tunneling, brings other molecules into resonance and allows continuous relaxation [10]. A crucial prediction of the theory is that at a given longitudinal applied field $H$, the magnetization should relax at short times with a square-root time dependence:

$$M(H,t) = M_{in} + (M_{eq}(H) - M_{in})\sqrt{\Gamma_{sqrt}(\xi_H)t}$$

(1)

Here $M_{in}$ is the initial magnetization at time $t = 0$ (i.e. after a rapid field change), and $M_{eq}(H)$ is the equilibrium magnetization. The rate function $\Gamma_{sqrt}(\xi_H)$ is proportional to the normalized distribution $P(\xi_H)$ of energy bias in the sample:

$$\Gamma_{sqrt}(\xi_H) = c\frac{\Delta_{tunnel}^2}{\hbar} P(\xi_H)$$

(2)

where $\hbar$ is Planck’s constant and $c$ is a constant of the order of unity which depends on the sample shape. If these simple relations are true, then measurements of the short time relaxation as a function of the applied field $H$ gives experimentalist a powerful new method to directly observe the distribution $P(\xi_H)$. Indeed the predicted $\sqrt{t}$ relaxation (Eq. 1) has been seen in preliminary experiments on fully saturated Fe₈ crystals [11]. We
show here that it is accurately obeyed for saturated and non-saturated samples (Fig. 3) and we find that a remarkable structure emerges in $P(\xi_H)$ as presented in the following.

In order to carefully study $P(\xi_H)$ and its evolution as the sample relaxes, we have developed a unique magnetometer consisting of an array of micro-SQUIDs [10,11] on which we placed a single crystal of Fe$_8$ molecular clusters. The SQUIDs measure the magnetic field induced by the magnetization of the crystal (see inset of Fig. 4). The advantage of this magnetometer lies mainly in its high sensitivity and fast response, allowing short-time measurements down to 1 ms. Furthermore the magnetic field can be changed rapidly and along any direction.

Figure 2 shows a typical set of relaxation curves plotted against the square-root of time. However instead of saturating the sample before each relaxation measurement so that the initial magnetization $M_{in} = M_s$ as described in [3], these measurements were made by rapidly quenching the sample from 2 K in zero field (ZFC), i.e. for an initial magnetization $M_{in} = 0$. The quench takes approximately one second and thus the sample does not have time to relax, either by thermal activation or by quantum transitions, so that the high temperature “thermal equilibrium” spin distribution is effectively frozen in. Once the temperature is stable (in this case 40 mK) a measuring field is applied, the timer is set to $t = 0$, and the relaxation of the magnetization is recorded as a function of time. The entire procedure was repeated for each measuring field shown in Fig. 4. As can be seen for short times $t < 100$ s the square root relaxation is well obeyed. Note that all curves extrapolate back to $M = 0$ at $t = 0$. A fit of the data to Eq. (1) determines $\Gamma_{\text{squad}}$.

A plot of $\Gamma_{\text{squad}}$ vs. $H$ is shown in Fig. 3 for the zero field cooled data, as well as distributions for three other values of the initial magnetization which were obtained by quenching in small fixed fields (field cooled FC magnetization). The distribution or an initial magnetization close to the saturation value is clearly the most narrow reflecting the high degree of order starting from this state. The distributions become more broad as the initial magnetization becomes smaller reflecting the random fraction of reversed spins. The small satellite bumps are due to flipped nearest neighbor spins on the tri-clinic lattice as seen in computer simulations [3,12,13].

We can exploit this technique of measuring $P(\xi_H)$ in order to observe the evolution of molecular states in the sample during relaxation by quantum tunneling of the magnetization. We first field cooled the sample (thermally anneal) as described above in order to obtain the desired initial magnetization state. Then after applying a field $H_t$, we let the sample relax for a time $t_s$, which we call “tunneling field” and “tunneling time” respectively. During the tunneling time, a small fraction of the molecular spins tunnel and reverse their direction. Finally, we applied a small measuring field and record the short time relaxation which again can be fit to a square root law (Eq. (1)) yielding $\Gamma_{\text{squad}}$. The entire procedure is repeated many times for other measuring fields in order to probe the distribution as a function of field $H$, and thus we obtain the distribution $P(\xi_H, H_t, t_s)$ which we call a “tunneling distribution”.

Figure 4 shows tunneling distributions for field $H_t = 0$ and for tunneling times between 1 and 250 s for the case that the initial magnetization starts from the fully saturated state. Note the rapid depletion of molecular spin states around the resonant field $H_t = 0$ and how quickly the depletion depth and width increase with tunneling time. In effect, a “hole is dug” into the distribution function around $H_t$. The hole arises because only spins in resonance can tunnel. The hole is spread out because as the sample relaxes, the internal fields in the sample change such that spins which were close to the resonance condition may actually be brought into resonance. Notice however that “wings” are created on each side of the hole because other spins are pushed further away from resonance. These features are in good agreement with Monte Carlo simulations of the relaxation for non-spherical samples [3,12,13].

In Fig. 3(b) we see the extraordinary effect of sample annealing (i.e. for small values of the initial magnetization $M_{in}$) on the evolution of $P(\xi_H, H_t, t_s)$ with time. Now the depletion proceeds over an extremely narrow bias range. This is virtually incontestable experimental proof that we are seeing tunneling relaxation. The narrowing of the hole is because in the annealed sample further incremental relaxation hardly changes the internal demagnetization field. Notice that the initial line shape of $P(\xi_H)$ is very accurately fit to a Gaussian for the annealed samples, exactly as predicted for the dipole field distribution of a dense set of randomly oriented spins [14].

Further investigation of the effect of sample annealing led us to another remarkable discovery (Fig. 3). Progressive annealing such that $|M_{in}| < 0.5 M_s$, eventually leads to a hole linewidth which at short times is independent of further annealing, and has a half linewidth of 0.8 mT. It is interesting that such an intrinsic linewidth was predicted by Prokof’ev-Stamp [9]. It is claimed to come from the nuclear spins which would give rise to a linewidth $\xi_0$ of roughly the same order (although only 2% of natural iron has a nuclear moment, there are other nuclei in the clusters that can contribute to the hyperfine fields, i.e. more than 100 hydrogen, 18 nitrogen and 8 bromine atoms!). We notice that any intrinsic linewidth due to the tunneling matrix element itself is 5 orders of magnitude smaller, and would be quite unobservable. According to Eq. (3), the ratio $\Gamma_{\text{squad}}/E_D$ (where $E_D$ is the Gaussian half-width of $P(\xi_H)$ for strongly annealed samples) should be a constant, and thus allows us to estimate $\Delta_{\text{tunnel}}$ from our relaxation measurements. We find that it is indeed a constant (even though $E_D$ and $\Gamma_{\text{squad}}$
vary with $M_n$, and we extract $\Delta_{\text{tunnel}} \approx 5 \times 10^{-8}$ K for $|M_n| < 0.5M_s$, assuming $c = 1$. This agrees well with the expected value $\xi_0$.

In conclusion, we have developed a new measurement technique yielding $P(\xi_H)$ which is related to the internal dipole field distributions always present in crystals of molecular clusters. The distribution evolves during relaxation by tunneling in a non-trivial way, and can be monitored by our technique, revealing the details of how the tunneling is proceeding in the sample, which molecules are tunneling, and how the time-varying internal fields influence the relaxation. The shape of the hole for thermal annealed distributions indicates a fast dynamic relaxation over a field range of 0.8 mT which could correspond to the Prokof’ev-Stamp theory to the nuclear linewidth $\xi_0$. Although this is only indirect evidence of the nuclear mechanism, it is hard for us to see what else could be operating at these temperatures. Our evidence for the role of the dipole interactions is on the other hand very direct, and in good agreement with Monte Carlo simulations. We believe that our technique should work for other multi-particle spin systems in the quantum regime (like quantum spin glasses), and could give quite new information on the non-ergodic relaxation behavior typical of these systems.

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FIG. 1. Magnetic hysteresis curves for a crystal of Fe₈ molecular clusters in the quantum regime (40 mK) for three field sweeping rates. Resonant tunneling is evidenced by six equally separated steps. Note the strong dependence on the field sweeping rate. The measurements were made using an array of micro-SQUIDs (see inset) [000]. The high sensitivity of this magnetometer allows us to study single crystals of the order of 10 to 500 µm which are placed directly on the array.

FIG. 2. Typical square root of time relaxation curves for an Fe₈ crystal measured at 40 mK. For each curve, the sample was first thermally annealed at $H = 0$ (ZFC), then a small field was applied and the relaxation of magnetization was measured during $10^4$ s. The slope of the lines gives $\Gamma_{\text{sqrt}}$ when plotted against the square-root of $t$ as shown.

FIG. 3. Field dependence of the short time square root relaxation rates $\Gamma_{\text{sqrt}}(\xi_H)$ for three different values of the initial magnetization $M_n$. According to Eq. 3, the curves are proportional to the distribution $P(\xi_H)$ of magnetic energy bias $\xi_H$ due to local dipole field distributions in the sample. Note the logarithmic scale for $\Gamma_{\text{sqrt}}$. The peaked distribution labeled $M_n = -0.998M_s$ was obtained by saturating the sample, whereas the other distributions were obtained by thermal annealing (FC or ZFC). $M_n = 0.870M_s$ is distorted by nearest neighbor lattice effects.
FIG. 4. Tunneling distributions: the field dependence of the short time square root relaxation rates $\Gamma_{\text{sqrt}}(\xi H)$ are presented on a logarithmic scale showing the depletion of the molecular spin states by quantum tunneling at $H = 0$ for various tunneling times.

(a) Tunneling distributions for the initial magnetization starting from saturation $M_{\text{in}} = M_s$. For each point, the sample was first saturated in a field of -1.4 T and at a temperature of about 2 K and then rapidly cooled to 40 mK. After applying a “tunneling field” of $H_t = 0$, we let the sample relax for a “tunneling time” $t_t$ (after $t_t = 2, 10, 50$ and 250 s, the reversed fraction of magnetization is 0.008, 0.030, 0.077, 0.159 of $M_s$, respectively). Finally, we applied a small field to measure the short time relaxation which could be fit accurately to a square root law yielding $\Gamma_{\text{sqrt}}$. Because $\Gamma_{\text{sqrt}}$ is proportional to the spins which are still free to tunnel, one obtains the distribution $P(\xi H, H_t, t_t)$. (b) Tunneling distributions as in (a), but now for each point, the sample was first annealed (FC) to a value $M_{\text{in}} = -0.2 M_s$. After $t_t = 5, 10, 20$ and 40 s, the reversed fraction of the magnetization is 0.0012, 0.0020, 0.0032, 0.0049 of $M_s$, respectively. At the resonance, the depletion develops very rapidly with elapsed time, even though the total magnetization and the internal demagnetization field hardly change during this time. Notice that parabolic shape of $\Gamma_{\text{sqrt}}(\xi H)$ shows it is accurately Gaussian, with a half-width of 0.03 T. This Gaussian profile is found for $|M_{\text{in}}| < |0.5 M_s|$ (but with a half-width $E_D$ depending on $M_{\text{in}}$).

FIG. 5. Detail showing the depletion of molecular spin states by quantum tunneling for different values of annealing (FC). The difference between the initial thermally quenched distribution (i.e. $t_t = 0$) and the tunneling distribution obtained after allowing the sample to relax for $t_t = 16$ s are plotted. For initial FC magnetization values close to saturation, the depletion is larger and asymmetric whereas it is narrow and symmetric for initial magnetization values which are smaller than $0.5 M_s$. Note that in the latter case the hole is independent of initial magnetization, yielding an intrinsic hole width of about 0.8 mT (see also fig. 4b).
$M/M_s$ vs. $\mu_0 H(T)$

- $140$ mT/s
- $14$ mT/s
- $2.8$ mT/s

$T = 40$ mK

Sample with array of SQUIDs
$T = 40\text{mK}$

$M_{in} = 0$

$M / M_s$ vs $\sqrt{t(s)}$ with magnetic fields of 0mT, 0.56mT, 1.12mT, 2.24mT, 2.80mT, 3.36mT, and 3.92mT.
\[ \Gamma_{\text{sqrt}(s^{-1})} \]

\[ T = 40\text{mK} \]

\[ \mu_0 H(T) \]

- \[ M_{\text{in}} = 0.998 \ M_s \]
- \[ M_{\text{in}} = 0.870 \ M_s \]
- \[ M_{\text{in}} = 0 \ M_s \]
\[ \Gamma_{\text{sqrt}}(s^{-1}) \]

\[ T = 40 \text{mK} \]

\[ \mu_0 H(T) \]
\[ \Gamma_{s\sqrt{t}}(s^{-1}) \]

\[ M_{in} = -0.2 M_s \]

- \( t_t = 0 \text{s} \)
- \( t_t = 5 \text{s} \)
- \( t_t = 10 \text{s} \)
- \( t_t = 20 \text{s} \)
- \( t_t = 40 \text{s} \)
\[(\Gamma_{\text{tunnel}} - \Gamma_{\text{init}}) \text{ (} s^{-1} \text{)}\]

\[T = 40\text{mk} \quad t_t = 16\text{s}\]

\[\begin{align*}
M_{in} = -0.71 \quad M_s \\
M_{in} = -0.81 \quad M_s \\
M_{in} = -0.90 \quad M_s \\
M_{in} = -0.99 \quad M_s \\
M_{in} = -0.55 \quad M_s \\
M_{in} = -0.36 \quad M_s \\
M_{in} = -0.22 \quad M_s \\
M_{in} = -0.07 \quad M_s
\end{align*}\]