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Phonon-Assisted Tunneling in the Quantum Regime of Mn₁₂ Acetate

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Longitudinal or transverse magnetic fields applied on a crystal of Mn₁₂ acetate allows one to observe independent tunnel transitions between $m = -S + p$ and $m = S - n - p$ ($n = 6-10$, $p = 0-2$ in longitudinal field and $n = p = 0$ in transverse field). We observe a smooth transition (in longitudinal) from coherent ground-state to thermally activated tunneling. Furthermore, two ground-state relaxation regimes show a crossover between quantum spin relaxation far from equilibrium and near equilibrium, when the environment destroys multimolecule correlations. Finally, we stress that the complete Hamiltonian of Mn₁₂ should contain odd spin operators of low order.

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The system Mn₁₂ acetate (Mn₁₂-ac) is constituted of magnetic molecules in each of which 12 Mn ions (8 spins-2 and 4 spins-3/2) are strongly coupled by superexchange interactions [1]. The resulting spin $S = 10$, containing 10^3 atoms of different species (Mn, O, C, H) has volume ≈ 1 nm³. The Hilbert space dimension D_H describing the entangled spin states of the molecule is huge: $D_H = 10^8$. In the mesoscopic approach to Mn₁₂-ac most observations can be explained with $D_H = 2S + 1 = 21$ (for a review, see [2]). The large energy barrier DS_z^2 gives extremely small ground-state splitting. The consequence is that quantum relaxation is slow and strongly influenced by fluctuations of the environment. Above 1.5 K a single crystal of Mn₁₂-ac shows staircase-like hysteresis loops when the magnetic field is applied along the c -easy axis of magnetization [3] (for powder experiments, see [4-7]). Tunneling rates, deduced from relaxation and ac-susceptibility experiments, give sharp maxima precisely at the fields where hysteresis loops are steep: $B_n \approx 0.44n$ (in Teslas), with $n = 0, 1, 2, \dots$. All these results constituted the first evidence for thermally assisted tunneling in large spin molecules. Later we studied the effects of spin and phonon baths in this tunneling regime and the passage to the classically activated regime ([8,9] and [10] for a low spin molecule).

In this Letter we give a similar study, but at lower temperatures. We determine the nature of the crossover between thermally assisted and ground-state tunneling and show an interesting quantum behavior of the molecule spin dynamics, related to spin-phonon transitions. Furthermore, we suggest that odd spin operators [11], consistent with the tetragonal S_4 point symmetry of Mn₁₂-ac [1] should be taken into account in the Hamiltonian of this system. The magnetization of a small single crystal of Mn₁₂-ac in high fields and at sub-Kelvin temperatures was obtained from magnetic torque experiments, performed at the Grenoble High Magnetic Field Laboratory. The way to extract the longitudinal or transverse magnetization (parallel or perpendicular to the easy c axis) from the measured torque

Γ is analytical and unambiguous. The applied magnetic field creates a torque, which at equilibrium, is compensated by a mechanical drawback one. In a longitudinal field the system of nonlinear equations linearizes. To find a hysteresis loop we first perform a two-parameter linear fit (u and v) of the saturation region with $B_0/\Gamma = u + vB_0$ and then we calculate the normalized magnetic moment $m = M_{\parallel}/M_S = u/(B_0/\Gamma - vB_0)$. In the transverse case, $M_{\perp}$ is, to a good enough approximation, given by $M_{\perp} = \Gamma/B_0$.

Figure 1 shows several staircaselike hysteresis loops in a longitudinal field, below 1.3 K. The angle between the

FIG. 1. Hysteresis loops of Mn₁₂-ac, derived from torque measurements with an applied field along the c axis (sweeping rate $r = 11$ mT/s). Below ≈ 0.7 K, the curves are temperature independent, indicating quantum tunneling without thermal activation. Transition widths result from the distribution of dipolar fields. Inset: dm/dB_0 where $m = M_{\parallel}/M_S$ for the resonance $n = 8$ at three temperatures: 0.90 K (dots), 0.95 K (dashed line), and 1.00 K (continuous line). The resonance is split in two: tunneling from the ground state $m = -10$ and from the first excited state $m = 9$. Note the change of the height of each peak, when varying the temperature. Similar behavior was found for all the other resonances.

applied field and the easy axis, due to some inherent misalignment in the experimental setup, was $\lesssim 2.5^\circ$. The corresponding transverse field component, smaller than 0.2 T, is almost not affecting the transitions with $2m - n$ a multiple of 4 (m is the S_z eigenvalue), because of the leading C term in the transverse anisotropy (see the caption of Fig. 2b) or with $n \leq 6$. The observed B_n are independent of temperature (Fig. 2), an effect which was also observed in [12] but below ≈ 0.7 K only. This suggests that tunneling takes place from the metastable state $m = -10$ to final states $m = 10 - n$ ($n = 6$ to 10). As shown in the Fig. 1 inset for $n = 8$, the B_n are determined accurately enough to see that each resonance is constituted of several temperature-independent peaks (resonance groups). Their widths ≈ 0.15 T are close to the one observed at high temperature and come from the distribution of dipolar fields [3,9]. A comparison between the measured and calculated B_n makes their interpretation obvious. The calculated B_n are given by level crossings in Fig. 2b (the Hamiltonian, given in the caption of Fig. 2b, was found by EPR experiments [13]). Intercepts of the $m = S = -10$ state with $m = 3, 2, 1$, and 0, give the B_n indicated by horizontal lines $n = 0$ in Fig. 2a. Similar intercepts of the first excited level $m = -9$ with $m = 2, 1, 0$, and -1 , are also given. This shows unambiguously that tunneling occurs, when increasing temperature, first from $m = -10$, then from the first excited state $m = -9$, then from $m = -8, \dots$. Tunneling transitions with smaller m are closer and closer and may appear to be temperature dependent if the field resolution is not good enough. Regarding peak intensities, the area of deconvoluted Lorentzian peaks in each resonance group, characterized by the same index n , determines the fraction of tunneling events taking place from the ground state (index $p = 0$), from the

first excited state ($p = 1$), $\dots$. One can define an experimental crossover temperature $T_{c,n}$ for which the two peaks ($n = 0$ and $n = 1$) have the same area; for example, for $n = 8$ we found 0.95 K. Accounting for the proportionality of the tunneling rate with Δ^2 , where Δ is the tunnel splitting [14], this crossover can be written $kT_{c,n} \approx E_{0,1,n}/2 \ln(\Delta_{n-1}/\Delta_{n-0})$, where $E_{0,1,n}$ is the separation between the ground state and the first excited state, near the n th crossing. For the resonances with $n = 8$ and $E_{0,1,8} \approx 7.3$ K, calculated by exact diagonalization, we get $\ln(\Delta_{8-1}/\Delta_{8-0}) = 3.88$ corresponding to a transverse field of ≈ 0.31 T (a misalignment of $\approx 4.5^\circ$). Obviously, such a transverse field is larger than what is expected from our experimental setup. Similar discrepancies are also observed with other resonances. The important effect of small transverse fields is not sufficient to give an overall agreement, in particular when $2m - n$ is not a multiple of 4 and when $n \geq 6$. Finally, early observation of a crossover temperature of ≈ 2 K in zero field [4,8,15] is now confirmed by the extrapolation of $T_{c,n}$ (Fig. 2a), giving $T_{c,0} \approx 1.7$ K (the same type of extrapolation shows that the continuous process of ground-state to activated tunneling up to the top of the barrier spreads between ≈ 1.7 and ≈ 2.4 K). However, this requires a ground-state splitting $\approx 3 \times 10^{-10}$ K instead of the $\approx 10^{-11}$ K as calculated in [9]. All that suggests a lack of knowledge of the transverse spin operator coefficients of the Hamiltonian used for $\text{Mn}_{12}\text{-ac}$ (Fig. 2b). Besides the fact that all crystal field parameters of order larger than 4 are unknown, we must mention that all operators with odd order are missing. The S_4 point symmetry of $\text{Mn}_{12}\text{-ac}$ [1] leads to the following Hamiltonian [11]: $H = B_2^0 O_2^0 + B_3^0 O_3^2 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_5^0 O_5^2 + B_6^0 O_6^0 + B_6^4 O_6^4 + \dots$ where the O_l^m are the Stevens' equivalent operators [16]. The complete Hamiltonian should also contain magnetic field and the effect of Dzyaloshinsky-Moriya terms [15,17,18]. Interestingly, the new odd terms have no diagonal contribution, which is consistent with the good agreement we obtain regarding the resonance positions. This also shows that diagonal terms of order ≥ 6 are negligible.

Let us now consider the case when the field is applied perpendicularly to the easy axis. The symmetry of the double well is preserved allowing one to observe tunneling between the ground states $|S, +S\rangle$ and $|S, -S\rangle$. The sample was first saturated along the c axis of the crystal. Then, the field was set to zero and the sample rotated to $90^\circ \pm 1^\circ$. During the experiments, the applied field B_0 was varied between 0 and 5 T with a transverse component B_T nearly equal to B_0 , and a longitudinal one B_L varying between 0 and ≈ -0.07 T. When $B_L \approx -0.04$ T $\approx$ the Lorentz internal field of $\text{Mn}_{12}\text{-ac}$, the internal field is canceled. Nevertheless, level widths being ≈ 0.15 T, the spin-up and spin-down density of states were in coincidence during the whole variation of the applied field. Hysteresis loops of the transverse magnetization are plotted in Fig. 3. They show only one jump and are nearly independent of temperature, indicating that spin reversals

FIG. 2. (a) Measured positions of peak maxima vs temperature. Horizontal lines indicate the calculated crossing fields. (b) Energy levels spectrum calculated by exact diagonalization of the Hamiltonian $H = -DS_z^2 - BS_z^4 - C(S_+^4 + S_-^4) - g\mu_B S_z H_z$ for a spin $S = 10$ and the parameters $D = 0.56$ K, $B = 1.1$ mK, $C = 3 \times 10^{-2}$ mK obtained in EPR. The term B shifts the resonances belonging to same n and different m to lower fields when m decreases.

FIG. 3. Half hysteresis loop in transverse field at three different temperatures (sweeping rate $r = 11$ mT/s). $M_{\perp}$ is given by the measured torque divided by field. The crystal was first saturated in a large negative field. Inset: the geometry of the experiment.

take place by single coherent ground-state tunneling events. This loop can be understood easily. In transverse fields smaller than ≈ 4 T, tunneling rate Γ_0 between symmetrical ground states is too small and nothing happens. The tunneling gap increasing almost exponentially with B_T [19], Γ_0 becomes rapidly very large, and when $B_T \approx 4.5$ T the spins tunnel to the other well during the time of the experiment; due to a small misalignment from the ideal transverse geometry, as shown in Fig. 3 inset, after tunneling the molecules are kept within the final well (the sample is again saturated). The observation of tunneling requires Γ_0^{-1} to fall in the experimental window $1 - 10^3$ s. Such values for the tunneling rate, which depend on the level splitting and the hyperfine field fluctuations [14], are realistic according to NMR results on Mn_{12} [20] and for tunnel splittings calculated between 4 and 4.5 T.

Magnetic relaxation experiments give direct access to tunneling rates. An example is given in Fig. 4, in longitudinal and transverse applied fields. In both cases and below 1.2 K, the relaxation is a square root of time at short times: $M(0) - M(t) = M_s \sqrt{\Gamma_{\text{sqrt}} t}$. This law, already observed in Fe_8 [21] or Mn_{12} -ac above 1.5 K [8], was predicted by Prokof'ev and Stamp [14]. It is characteristic of quantum tunneling in the presence of dipolar interactions and fast hyperfine fluctuations and ends for times $\approx \Gamma_{\text{sqrt}}^{-1}$ due to the building of multimolecule spin correlations. At longer times more and more important correlations, should in principle lead to nonexponential relaxation (see Fig. 1 in [14]). However, this is not what we observe in Fig. 4, where the quantum relaxation regime, succeeding the square root one at long times, is exponential. We believe that this is because during the smooth transition between the square root and exponential regimes, couplings to the environment (spins, phonons...) have enough time to erase multimolecule spin correlations, an effect which could be called "environmental annealing."

FIG. 4. Relaxation curves in a transverse (longitudinal) field of 4.42 T (4.02 T) for the resonance $n = 0$ at $T = 0.5$ K ($n = 8$ at $T = 0.9$ K). In both cases the square root regime (dashed line) is observed only at short time scales, then the relaxation becomes exponential (dotted line). Note that experiments are done far from saturation. Inset: Temperature dependence of the square root tunneling rate in transverse (squares— Γ_T) and longitudinal field (circles— Γ_L).

The crossover time t_c (when the dashed fit intercepts the dotted fit in Fig. 4), depends on many parameters and will be analyzed in further studies. Regarding the first regime and for our present experimental conditions (sample in good contact with the cryostat), $\Gamma_{T,L}(T)^{-1}$ is always of the order of t_c , showing that fast recovery has the same origin as fast spin relaxation, i.e., not too small tunnel splittings and large hyperfine field fluctuations [14,22]. As shown above spin-phonon transitions also contribute to $\Gamma_{T,L}$ and thus to recovery near $T_{c,n}$ by adding new, thermally excited channels, with larger tunnel splittings and faster relaxation rates.

In Fig. 4 (inset) are shown the square-root relaxation rates plotted vs temperature, measured at the 8-0 resonance (Fig. 2) in longitudinal geometry (full circles— Γ_L) and in transverse geometry for the 0-0 resonance (full squares— Γ_T). As expected from the first part of this paper, Γ_L increases above ≈ 0.6 K, then it goes through a maximum and then decreases. The increase of $\Gamma_L(T)$ is due to the proximity of the resonance 8-1. The field separation between this resonance at 3.90 T and the resonance 8-0 at which $\Gamma_L(T)$ is measured at 4.02 T, being of the order of level broadening by dipolar interactions, spin-phonon transitions between them are allowed. This is what we observe and what constitutes a clear example of phonon-assisted tunneling in the quantum regime. Regarding peak intensities, near equilibrium the rate increases like $\Gamma_L(T) \approx \Gamma_{L,8-0} + \Gamma_{L,8-1} \exp(-E_{0,1,8}/kT)$. As an example, for $T = 0.7$ K and $\Gamma_{L,8-0} = \Gamma_L(0.55)$, we obtain $\ln(\Delta_{8-1}/\Delta_{8-0}) \approx 5.35$ too large to be explained numerically. As we already mentioned, new terms in the spin Hamiltonian of Mn_{12} could lead to a better agreement. The decreasing part of $\Gamma_L(T)$ simply comes from a decreasing

of the number of states available for phonon-assisted tunneling, due to the magnetization decrease when the field sweeps across the 8-1 resonance. Like Γ_L , the square-root relaxation rate Γ_T , measured in transverse geometry, is independent of temperature at lowest temperatures, as expected for ground-state tunneling. Above ≈ 0.7 K the tunneling rate increases with temperature. However, this is a very smooth effect which cannot be due to activated tunneling on levels $m = 9$ and $m = 8$. It is rather due to tunneling assisted by spin-phonon transitions between $m \approx \pm 10$ states, split by dipolar fields (and integrated over the spin-up and spin-down distributions). This assumption is supported by the fact that the corresponding energy scale of ≈ 0.5 K for increasing Γ_T is close to the dipolar energy ($g\mu_B SB_{\text{dipolar}} \approx 0.5$ K). This is another example of phonon-assisted tunneling in the quantum regime.

In conclusion, we have shown that in $\text{Mn}_{12}\text{-ac}$ with a longitudinal field ($n \neq 0$), the transition between coherent tunneling on the ground state and on upper states (with thermal activation) takes place, level after level, when they come into coincidence in an applied sweeping field. This is an obvious consequence of the 4th order anisotropy term BS_z^4 , which prevents the spin-up and spin-down level schemes coinciding. In any case, the experiments show a continuous transition, even in a constant field, contrary to Ref. [23]. More interestingly, phonon-assisted tunneling is evidenced between $m = -10$ and $m = 10$ splitted by dipolar fields in the transverse case or between $m = -10$ and $m = 1$ in the longitudinal one. "Annealing" of multimolecule spin correlations in the quantum regime result from spin relaxation itself and from spin-phonon transitions near the crossover to excited states. Such an exponential phonon-mediated relaxation crossover was predicted for a single-molecule relaxation [22], but no theoretical work exists which takes into account dipolar interactions. It would be of great interest to see a theoretical treatment of the long time quantum relaxation in the presence of phonons and dipolar interactions. Finally, we suggest not to forget that spin operators with odd powers are allowed by the S_4 symmetry of the $\text{Mn}_{12}\text{-ac}$ molecule.

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