Mixed Quantum-Thermal Relaxation in Mn_{12} Acetate Molecules

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We present a theoretical and experimental study of the magnetic field dependence of the relaxation of the $Mn_{12}O_{12}$ acetate compound. For $T \geq 2$ K the molecule which starts from the $|-S\rangle$ state climbs to the excited states by means of thermal mechanism, while the remaining barrier is crossed by tunneling. This mixed quantum-thermal mechanism shows a critical dependence of the relaxation time with respect to the external magnetic field. [S0031-9007(97)05090-4]

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The magnetic relaxation time of molecular clusters can become very large at low temperatures. The most impressive example is the $Mn_{12}O_{12}$ group, with a spin $S = 10$, whose relaxation time τ reaches two months [1] in the acetate compound (Mn_{12} acetate), in zero magnetic field at 2 K. Above this temperature $2 \leq T \leq 6$ K, τ follows an Arrhenius law [1,2] $\tau = \tau_0 \exp(\Delta/k_B T)$ with $\Delta/k_B = 61$ K while the prefactor $\tau_0 \approx 10^{-8}$ s is extraordinarily large. This behavior results from thermally activated Orbach processes [3,4]: the molecule must overcome the energy barrier Δ given by the anisotropy allowed by the tetragonal symmetry. At very low temperatures, relaxation measurements show that the Arrhenius law is not satisfied and τ goes to a finite limit [5] when $T \to 0$. This was interpreted as a resonant quantum tunneling of the magnetization between the lowest lying energy states [6,7] but a quantitative comparison between theory and experiment is difficult because of the smallness of the relaxation rate.

Experimental results are usually analyzed [1–3,9–13] assuming a second-order anisotropy: $-AS_z^2$. However, recent high field electron paramagnetic resonance (EPR) data [8] suggest the presence of a significant fourth-order term, so that an approximate spin Hamiltonian appropriate to Mn_{12} acetate in the presence of an external field H parallel to the fourfold axis z, is

$$\mathcal{H}_0 = -AS_z^2 - BS_z^4 - hS_z\,, \qquad (1)$$

with $h = g\mu_B H$ and $g = 2$, while $A/k_B = 0.556$ K and $B/k_B = 1.1 \times 10^{-3}$ K. Its eigenvectors $|m\rangle$ are those of S_z and its eigenvalues are $E_m = -Am^2 - Bm^4 - hm$. Recently, hysteresis loops were recorded [2,9–11] for $T > 2$ K, which show steps at roughly constant field intervals $\Delta H \simeq 4$–5 kOe. This implies that $\tau(H)$ has minima as a function of H for these values of the field. These results are irreconcilable with the activated relaxation process proposed in Ref. [3] (which implies a monotonic decrease of τ when increasing the field) and suggest a field-tuned resonant tunneling between two excited states of (1) when two eigenvalues E_m and $E_{m'}$ are equal. This occurs when

$$h = g\mu_B H_p = Ap + Bp(p^2 + 2m^2 - 2mp)\,, \qquad (2)$$

where $p = m + m'$ is an integer.

In particular, the most pronounced minimum is observed for $H = 0$ followed by a first maximum for $H = H_{1,M} \simeq 1.5$ kOe with a high ratio $\tau(H_{1,M})/\tau(H = 0)$.

In this Letter we report the first theoretical study of τ vs H considering both activated and tunneling transitions. We analyze in detail the low field range, $H < H_{p=1}$. In this case, the lowest order spin Hamiltonian allowed by tetragonal symmetry which does not commute with S_z,

$$\mathcal{H}_1 = -C[S_+^4 + S_-^4]\,, \qquad (3)$$

is sufficient for tunneling transitions. This term only allows tunneling between energy levels E_{-m} and E_{m-p} when $2m - p$ is a multiple of 4. A general treatment is a formidable task because also other interactions (dipolar, random fields, etc.) must be taken into account as well as spin-phonon terms. However, we shall also discuss qualitatively tunneling between $|-m\rangle$ and $|m - p\rangle$ for $p = 1$ in the presence of a transverse field. Our analysis permits us to understand the difference between the energy barrier obtained from relaxation measurements [1,2,5,9] and the larger one, $(E_0 - E_{10})/k_B = 66.6$ K, estimated from EPR [8] or inelastic neutron scattering [14] investigations. We show that the presence of a fourth-order term, $B \neq 0$, is necessary to reproduce the experimental T dependence of τ in the region $2 \leq T \leq 7$ K.

The time evolution of a spin is described by rate equations which should take into account possible transitions

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from any eigenstate $|m\rangle$ to other eigenstates [3]. At high enough temperature, these transitions are mainly due to the spin-phonon interaction, which will be written as [15]

$$\mathcal{H}_{\text{spin-phonon}} = g(\epsilon_{xz}\{S_x, S_z\} + \epsilon_{yz}\{S_y, S_z\}) + g_2[\epsilon_{xy}\{S_x, S_y\} + (\epsilon_{xx} - \epsilon_{yy})(S_x^2 - S_y^2)], \quad (4)$$

where ϵ_{ij} denote the components of the deformation tensor and $\{,\}$ indicates the anticommutator. The first term, when treated in second order perturbation theory (Fermi golden rule), [3] gives rise to transitions from $|m\rangle$ to $|m+1\rangle$ and $|m-1\rangle$ (we shall say that $\delta m = \pm 1$) with a transition probability proportional to $|\langle m \pm 1|S_z S_{\pm} 1|m\rangle|^2$ and to the density of phonons with energy: $(E_{m\pm1} - E_m)$. The second term of (4) (neglected by Villain *et al.* [3]) can be treated in the same way and gives rise to transitions with $\delta m = \pm 2$. The actual spin-phonon interaction contains other terms [7], which could be taken into account in the same way but would not introduce any new feature. The best fit between theory and experiment is obtained when one assumes $g_2/g = 2$.

The existence of sharp minima of the relaxation time as a function of H shows that tunneling has to be introduced. For the sake of simplicity, only tunneling between $|m\rangle$ and $|-m\rangle$ will be considered. This is correct if the field is sufficiently low, say $h < A/2$. The rate equations are

$$\frac{dN_m}{dt} = \sum_{p=1}^{2} N_{m-p}\gamma_{m-p}^{m} + \sum_{p=1}^{2} N_{m+p}\gamma_{m+p}^{m} - N_m \sum_{p=1}^{2}(\gamma_m^{m-p} + \gamma_m^{m+p}) + (N_{-m} - N_m)\Gamma_m, \quad (5)$$

where N_m is the number of molecules in spin state $|m\rangle$. γ_m^q is the relaxation rate from a state $|m\rangle$ to a state $|q\rangle$ due to the spin-phonon interaction and can be calculated through the golden rule [3]. Γ_m is the tunneling relaxation rate between the states $|m\rangle$ and $|-m\rangle$. It can be expressed in two steps. In the first step, one can ignore the spin-phonon interaction and consider the spin subject to its crystal field Hamiltonian $\mathcal{H}_0 + \mathcal{H}_1$. If $C \ll A$, the eigenvectors are generally localized in one of the two regions $m < 0$ or $m > 0$. For certain values of the field H, and in particular for $H = 0$, one or several pairs of eigenvectors are delocalized. This situation (which corresponds to the crossing of levels of the Hamiltonian) will be called a resonance. In the present Letter, only the resonance at $H = 0$ will be addressed. At the resonance between the states $|-m\rangle$ and $|m\rangle$, eigenvectors of the crystal field Hamiltonian can be formed as symmetric and antisymmetric combinations of $|-m\rangle$ and $|m\rangle$ plus small corrections. The energy difference $\hbar\omega_{Tm}^0$ between the symmetric and antisymmetric wave vectors can be calculated from perturbation theory [6,12,16] for an isolated spin at resonance. The result is

$$\hbar\omega_{Tm}^0 = \begin{cases} 2\langle -2|\mathcal{H}_1|2\rangle & \text{if } m = \pm 2, \\ 2\langle 4|\mathcal{H}_1|0\rangle^2/(16A + 256B) & \text{if } m = \pm 4, \\ 2\langle 6|\mathcal{H}_1|2\rangle^2\langle -2|\mathcal{H}_1|2\rangle/(32A + 1280B)^2, & \text{if } m = \pm 6, \end{cases} \quad (6)$$

while $\omega_{Tm}^0 = 0$ for odd values of m in the absence of transverse magnetic field. In the second step, spin-phonon interactions are taken into account through the lifetime τ_m of the excited states $|-m\rangle$ and $|m\rangle$ [17]. This lifetime is a simple function [17] of the coefficients $\gamma_m^{m'}$ and is presumably of the order of τ_0. Thus, the spin is subject to decay with rate $1/\tau_m$ and to an oscillation with frequency ω_{Tm}^0 between wells $S_z < 0$ and $S_z > 0$. For times longer than $1/\omega_{Tm}^0$, this process gives rise to the last term of (5), where Γ_m is given [17,18] by

$$\Gamma_m = \frac{4(\omega_{Tm}^0)^2\tau_m}{1 + \tau_m^2(E_m - E_{-m})^2/\hbar^2}. \quad (7)$$

This expression depends on the magnetic field H through $(E_m - E_{-m})$ and is peaked at $H = 0$. An order of magnitude of ω_{Tm}^0 can be obtained from (6) if one writes

$$\langle -2|\mathcal{H}_1|2\rangle \approx \langle 4|\mathcal{H}_1|0\rangle \approx Cs^4. \quad (8)$$

For $H = 0$ using the value $Cs^4/k_B = 3 \times 10^{-5}$ K estimated from EPR spectra [8] we obtain from (6) the values $\omega_{T2}^0 \approx 10^{11}\ \text{s}^{-1}$ and $\omega_{T4}^0 \approx 10^9\ \text{s}^{-1}$. These estimations are much larger (by 5 to 7 orders of magnitude) than those obtained by Hernández *et al.* [11], who assumed tunneling to be driven by a transverse field alone. Even though the transverse field due to hyperfine and dipole interaction is probably 3 to 5 times as large as the value 0.01 T assumed by Hernández *et al.*, the difference is large enough to rule out any interpretation of the experimental data merely based on the transverse field.

If a spin is thermally activated to the level $|-m\rangle$, it can (i) deactivate to the level $|-(m+1)\rangle$, (ii) climb to the next level $|-(m-1)\rangle$ [or of course to $|-(m-2)\rangle$, but this possibility will be disregarded for the sake of simplicity], or (iii) tunnel to the state $|m\rangle$. The event (i) is the most likely but irrelevant for relaxation. The respective probabilities per unit time of the second and third events are $\gamma_{-m}^{-(m-1)}$ and Γ_m, respectively. The transition probability $\gamma_{-m}^{-(m-1)}$ is the product of the Boltzmann factor $\exp[\beta(E_{-m} - E_{-(m-1)})]$ by a quantity which depends on the spin-phonon interaction, whose order of magnitude can reasonably be expected to be the prefactor $1/\tau_0$ of the Arrhenius law. Thus, tunneling is expected to dominate thermal activation if

$$\Gamma_m\tau_0 \exp[\beta(E_{-(m-1)} - E_{-m})] > 1. \quad (9)$$

This condition contains explicitly or implicitly three parameters: m, H, and T. At a given temperature between 3 and 5 K, and for a given value of $m = 2$ or 4, formulas (9) and (7) show that tunneling dominates thermal activation in a band of width ΔH_m centered at $H = 0$. This band is broad for small m and becomes narrower with increasing m. To go beyond these qualitative predictions, one should calculate the relaxation time τ from the rate equations. The calculation is similar to that of Villain *et al.* [3] but the final formula is much more complicated because of the transitions with $\delta m = 2$ and we shall only give the following qualitative expression valid at very low temperature when Γ_4 is sufficiently large while Γ_m is negligible for $m \geq 5$:

$$\tau \simeq \exp[\beta(E_{-4} - E_{-S})]/\gamma_4^5 . \qquad (10)$$

Only the coefficient γ_4^5 appears at very low temperature because the bottleneck lies in the last activated jump [3]. The energy barrier is no longer $E_0 - E_{-S}$ but $E_{-4} - E_{-S}$, which is equal to $84A + 19744B$. For $H = 0$, the molecule, which starts from the $|-S\rangle$ state, climbs to the excited state $|-4\rangle$ by means of thermal mechanism, while the remaining barrier is crossed by tunneling between $|-4\rangle$ and $|4\rangle$. In order to understand between which states tunneling occurs we note that the activation barrier obtained from relaxation experiments [1,4,7,9] is $\Delta(0)/k_B = 61$ K for $H = 0$, while EPR and neutron scattering results suggest that the total anisotropy barrier is $\sim 67-70$ K. Thus it is reasonable to hypothesize that this value should be obtained from relaxation experiment with $H = H_{1,M}$ and that tunneling occurs between $|-4\rangle$ and $|4\rangle$. The fact that the activation barrier $\Delta(H)$ is affected by tunneling implies that the corresponding tunnel frequency ω_{T4} should be larger than τ_0, so that (9) is satisfied at all temperatures. This is consistent with the value of the crystal field parameter $Cs^4/k_B = 3 \times 10^{-5}$ K estimated from EPR experiments. If $\omega_{Tm}\tau_0 < 1$, tunneling between $|-m\rangle$ to $|m\rangle$ affects relaxation at low temperature only.

The field dependence of the magnetization relaxation time was measured with a SQUID magnetometer on a sample comprising six small single crystals, prepared according to literature [19] and glued together on a glass support with the easy axis parallel to the applied field. The sample was cooled in a field of -2 T to achieve saturation, the field was then changed to the required positive value, and the magnetization measured at regular intervals in time. The decay is well described by a single exponential, except at very short times where a faster relaxation is observed. In Fig. 1 the experimental and theoretical field dependence of τ are shown for $T = 2.8$ and $T = 2.97$ K. A qualitative agreement with the experimental data is obtained and in particular the maximum position and the high ratio $\tau(H_{1,M})/\tau(H = 0)$ are correctly reproduced. It is worthwhile to note that the theoretical results are very sensitive to the choice of the value of C, and a lower value than the EPR one is necessary to adequately reproduce the experimental data. It should also be noted that our theory is correct for $H < 3$ kOe and consequently the experimental minima observed for $H = H_p$ (with $p \neq 0$) are not reproduced. In Fig. 2 the theoretical τ-temperature dependences for $H = 0$ and $H = H_{1,M}$ are shown. The calculated relaxation times strongly deviate from a single Arrhenius law $\tau = \tau_0 \exp(\Delta/k_B T)$. However, in the temperature region $2 \leq T \leq 7$ K, where experimental results have been analyzed, the theoretical results in zero field can be represented by an Arrhenius law with $\Delta/k_b = 62.12$ K and $\tau_0 = 2 \times 10^{-8}$ s, in excellent agreement with the experimental data [2,9]. It is noteworthy that, if B were assumed to be 0, the theoretical relaxation time would be fitted in the same temperature range, for $A = 0.726$ K, by an Arrhenius law with $\Delta/k_B = 70.7$ K and $\tau_0 = 2 \times 10^{-9}$ s, which is inconsistent with the experimental data. Equation (10) is not satisfied because the temperatures are too high and Γ_m is not large enough. However, the tunnel channel is still more efficient than the total thermal mechanism between $|-4\rangle \rightarrow |0\rangle$. For $H = H_{1,M}$ the activation barrier is close to the total anisotropy barrier, namely, $\Delta(H = H_{1,M}) = 67.3$ K. For $B = 0$ the result would be $\Delta(H = H_{1,M}) = 72.8$ K.

Although the present Letter is mainly devoted to the resonance at $h = 0$, it is necessary to say a few words about the resonance at $h = A$. Indeed, the model we have

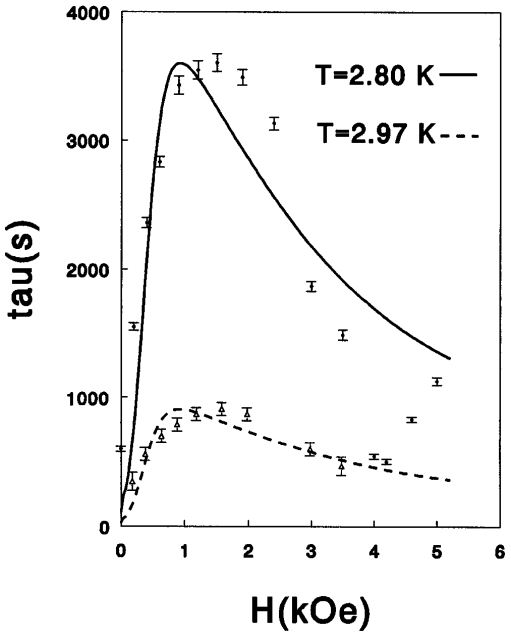

FIG. 1. Experimental field dependence of τ for $T = 2.8$ and $T = 2.97$ K, compared with the theoretical prediction calculated from (5). The values of the coefficients γ_m^p have been derived from the golden rule using formula (4) with $g/k_B = 15.4$ K and $g_2/g = 2$. The coefficients Γ_4 and Γ_2 have been deduced from (6) while coefficients Γ_m with $m > 4$ have been neglected. The value $C/k_B = 2 \times 10^{-6}$ K has been used, while A/k_B and B/k_B have their experimental ones (see text).

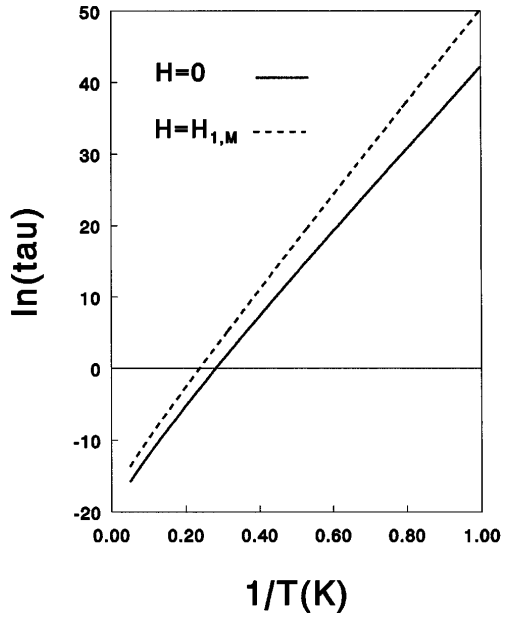

FIG. 2. T dependence of τ for $H = 0$ (solid line) and for $H = H_{1,M}$ (dashed line). The parameters are the same as in Fig. 1.

used to explain the resonance at $h = 0$ is based on formulas (1) and (3), which only allow tunneling between states $|m\rangle$ and $|m'\rangle$ for which the difference $\delta m = m' - m$ is a multiple of 4. This implies that m and m' should have the same parity, so that $p = m + m'$ is an even number in (2) and no resonance can occur near $h = A$ in the model used above. It is therefore necessary to modify the model and to assume that some transverse magnetic field is present [7]. This field can be either external [11] or the result of dipole interactions with other molecules [7,20] or of hyperfine interactions. As stated above, an external field alone is probably too weak to account for the order of magnitude of the observed tunneling. Both a transverse external field $H_x = h_x/(g\mu_B)$ and the anisotropy (3) are probably necessary. The former breaks the selection rule $\delta m =$ multiple of 4, and the latter provides the right order of magnitude. For instance, the tunneling frequency between $|-3\rangle$ and $|2\rangle$ at resonance (i.e., for $E_2^0 \approx E_{-3}^0$ or $h \approx A + 13B$) can be obtained from perturbation theory [12,16] as the absolute value of

$$\hbar\omega_{32}^{0T} = 2\,\frac{\langle -3|\mathcal{H}|1\rangle\langle 1|\mathcal{H}|2\rangle}{\langle 1|\mathcal{H} - E_2^0|1\rangle} + 2\,\frac{\langle -3|\mathcal{H}|-2\rangle\langle -2|\mathcal{H}|2\rangle}{\langle -2|\mathcal{H} - E_2^0|-2\rangle}, \qquad (11)$$

where $\mathcal{H}$ is the total spin Hamiltonian.

The tunneling frequencies at other resonances with odd values of $m - m'$ can also be obtained from perturbation theory. Quite generally, they are proportional to matrix elements of the type $\langle m|\mathcal{H}|m \pm 1\rangle$, and therefore to the transverse field H_x. This tunneling frequency is therefore expected to be much smaller (at least by a factor of 10) than the tunneling frequency for even $(m - m')$. This prediction does not seem to be experimentally confirmed. This seems to be the main question to be elucidated in the future.

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