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Thermally activated and field-tuned tunneling in $Mn_{12}Ac$ studied by ac magnetic susceptibility

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The magnetic ac susceptibility χ of oriented $Mn_{12}Ac$ crystallites has been measured as a function of temperature, field, and frequency. The field has been applied at different values of the angle θ with respect to the sample easy axis. For $T=5$ K, the isothermal and adiabatic χ limits have been determined as a function of field. For $\theta=0°$ and intermediate frequencies, Lorentzian-shaped peaks have been observed at magnetic field values $H_n=nH_1$ with $n=0$, 1, and 2 where $H_1=4.1$ kOe. As θ increases these maxima shift to higher fields, that satisfy $H_n\cos\theta=\mathrm{const}$, and decrease in amplitude. The relaxation time τ_1 follows Arrhenius' law with respect to temperature and decreases sharply at $H=H_n$. The observed phenomenology unambiguously proves the existence of field-tuned tunneling between excited magnetic states which are thermally populated. At 5 K, the effective activation energy and the spin states involved in the tunneling process have been obtained. [S0163-1829(97)09317-X]

I. INTRODUCTION

Since the report on the $Mn_{12}Ac$ complex magnetic bistability and the possibility that this molecule provides a magnetic quantum tunneling[1] (MQT) model system, extensive work has been performed on it. Magnetic dc susceptibility experiments characterized $Mn_{12}Ac$ as a superparamagnet, with blocking temperature $T_B=3$ K. It was found that this compound has only one relaxation time τ, which depends exponentially on the temperature $\tau=\tau_0\exp(QV/k_BT)$, with $\tau_0=2.1\times10^{-7}$ s and $QV/k_B=61$ K. The saturation of the relaxation time to a constant value below 2 K was interpreted as a new indication of the crossover to MQT below that temperature.[2]

The bistability property was based on the appearance of a broad magnetic hysteresis loop below T_B.[1] Later, ''avalanche'' processes appeared in hysteresis loops measured below 2.5 K.[3] Recently[4–6] hysteresis loop measurements on a sample of oriented crystals showed the onset of steps at field intervals of $\Delta H=4.6$ kOe, which were attributed to resonant tunneling of the magnetization between different excited quantum states. This process differs from MQT between the lowest-lying energy states for the two magnetization directions. However, both processes are related since the MQT is the mechanism which gives rise to magnetic relaxation of the molecule.

A well-established technique to study magnetic relaxation times is ac susceptibility. Indeed, the complex susceptibility was studied on this molecule as a function of frequency and temperature, confirming the values of QV/k_B and τ_0 reported earlier.[7] Of more interest is the field dependence of the relaxation time measured by means of ac susceptibility.[8] In Ref. 8 it is described that when the magnetic field is applied on an oriented sample along the c axis, the relaxation time shows two dips at $H=0$ and $H=3$ kOe, respectively. The authors inferred the existence of tunneling between thermally populated up, $|+m\rangle$, and down, $|-m\rangle$, magnetization states, which are nearly degenerate at zero field. When a field is applied, the increase in τ could be related to the detuning produced by the Zeeman splitting of the $|\pm m\rangle$ doublet. A relaxation time minimum would appear when energy levels corresponding to states of opposite spin orientation cross and a new tuning condition is achieved.

Although the value $H_c=3$ kOe is different from $\Delta H=4.6$ kOe we may conjecture that the step in magnetization and the dip in τ are simply related. To ascertain this, ac susceptibility measurements have been performed on the same sample for which the steps had been previously detected. The magnetic field, frequency, and temperature dependence of the complex susceptibility have been explored in the neighborhood of the tuning regions ($H=0$ and 4.6 kOe), as a function of sample orientation. Briefly, the presence of susceptibility peaks at the tuning fields, with a Lorentzian dependence on the applied field, has been observed. From the temperature and field dependence of the relaxation time, the existence of tunneling between thermally populated excited levels at these fields has been unambiguously concluded. The relaxation time depends on the orientation of the easy axis of the sample with respect to the applied magnetic field.

II. SAMPLE PREPARATION AND EXPERIMENT

The compound $Mn_{12}Ac$, brief for

$$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot2CH_3COOH\cdot4H_2O,$$

is an organometallic molecular crystal with 8 Mn III ($S=2$) and 4 Mn IV ($S=3/2$) ions, which form a magnetic cluster of effective spin $S=10$ (Ref. 9). The sample was synthesized as described in Ref. 10 and its quality was

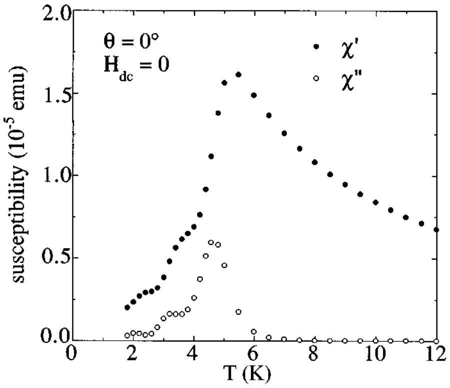

FIG. 1. Magnetic ac susceptibility measured at $\nu = 5$ Hz along the z axis of the sample; ●, real component; ○, imaginary component.

checked by x-ray diffraction. The obtained crystallites were about 10 μm long and aspect ratio of about 10, the long axis being parallel to the c axis. The crystallites were embedded in Araldite epoxy and submitted to a 5.5 T field at room temperature. Since at this temperature the sample is superparamagnetic, an effective orientation of the crystallites with the c axis parallel to the field direction was achieved. The orientation was confirmed visually under a microscope at 1000× magnification. We estimate that the crystallites' c axis lie within a cone of about ±7° wide, around the field direction.

Cylindrical samples of this sample/epoxy solid were measured in a Quantum Design superconducting quantum interference device magnetometer with ac susceptibility option. The excitation field was 4 Oe for all experimental runs. The frequency ν was varied between 0.025 and 980 Hz and the temperature stability was maintained within 1% of the absolute temperature. Measurements were also performed with the orientation axis (taken as the z axis of the sample) forming an angle $0 < \theta < 90°$ with the applied field. For this the sample holder was cut to form the desired angle and the sample glued on that surface. We estimate that the angle between the sample axis and the field direction was determined to 5°.

III. EXPERIMENTAL RESULTS

The ac susceptibility measured under a 5 Hz ac magnetic field applied along the z axis of the sample is shown in Fig. 1. As it has been recently reported by several authors[1,2,8] it follows the characteristic behavior of an ideal superparamagnetic system with a well defined relaxation time. Between 6 and 12 K the total susceptibility is real and follows the Curie-Weiss law $\chi = C/(T - T_C)$ whereas it reaches a maximum at the blocking temperature $T_B = 5.5$ K and decreases at lower temperatures. The imaginary part of the susceptibility χ'' departs from zero near T_B and shows a peak at $T = 4.5$ K. At this temperature, the relaxation time τ_1 of the Mn_{12}Ac molecules equals the inverse of the angular frequency ($\omega = 2\pi\nu$) of the ac magnetic field. On the other hand, the characteristic measuring time of dc magnetic experiments is about 100 s and, consequently, the dc blocking temperature $T_B = 3$ K, obtained from the peak of the dc zero-field-cooled magnetization curve,[1] and the value reported here are very different.

It should be noted that two shoulders appear in $\chi'(T)$ and $\chi''(T)$ below 4 K. These two peaks are related to relaxation processes with relaxation times τ_2 and τ_3, respectively, shorter than τ_1. The existence of these processes has also been inferred from magnetic relaxation experiments performed below 3 K (Ref. 2). Our $\chi'(\omega)$ measurements performed above 4 K reveal that these faster relaxing parts of the magnetization contribute to χ' with their equilibrium susceptibility for the whole measuring frequency and dc field range. Then, it follows that $\tau_1 \gg \tau_2 \gg \tau_3$ and we focus our study on the slowest relaxation mechanism.

Our ac susceptibility measurements under a dc field have been performed at $T > 3$ K. Furthermore, the magnetization reaches the thermal equilibrium value M_{eq}; consequently, magnetic relaxation effects are only due to the ac magnetic field. For practical purposes, the frequency-dependent susceptibility can be written as follows:[11]

$$\chi_{\mathrm{ac}}(H,T,\theta,\omega) = \chi_{\mathrm{hf}}(H,T,\theta) + \frac{\chi_0(H,T,\theta) - \chi_{\mathrm{hf}}(H,T,\theta)}{1 + i[\omega\tau_1(H,T,\theta)]}, \tag{1}$$

where θ is the angle of the applied dc and ac magnetic fields with respect to the easy axis of the sample. Usually, the dynamic behavior of an uniaxial single domain magnetic particle is analyzed using Arrhenius' law for the relaxation time:[12,13]

$$\tau_1 = \tau_0 \exp\left[\frac{U(H,\theta)}{k_B T}\right] \tag{2}$$

where the energy barrier $U(H,\theta)$ for thermal activation, in the case of uniaxial magnetic anisotropy, is given by[14,15]

$$U(H,\theta) = QV[1 - H/H_Q(\theta)]^{x(\theta)}. \tag{3}$$

Here Q is the density of anisotropy energy, V is the volume of the particle, and $H_Q(\theta)$ is the critical field at which the energy barrier becomes zero. For $\theta = 0°$, this field equals the anisotropy field which was estimated[8] to be around 100 kOe. The exponent $x(\theta) = 0.86 + 1.14\, H_Q(\theta)/H_Q(0)$ tends to 2 as θ goes to zero.

At the low-frequency limit $\omega\tau_1(T,H) \ll 1$ the susceptibility given by Eq. (1) is real and reaches the thermal equilibrium value χ_0, usually called the isothermal susceptibility. The Mn_{12}Ac equilibrium susceptibility can be obtained numerically differentiating the magnetization versus field curve measured above 3 K, i.e., when all the molecules are superparamagnetic for the characteristic dc measuring times. The equilibrium susceptibility so obtained, at $T = 5$ K and $\theta = 0°$, is shown in Fig. 2.

At high enough frequencies $\omega\tau_1 \gg 1$ the susceptibility given by Eq. (1) tends to χ_{hf}. This theoretical limit was experimentally achieved at $T = 5$ K and $\theta = 0°$ measuring the susceptibility at the highest accessible frequency, $\nu = 980$ Hz; the results are also represented in Fig. 2. Finally, in the same figure, the $\chi'(H)$ measurements for $\nu = 15$ Hz at $T = 5$ K and $\theta = 0°$ are shown. They lie between both limits for all the applied fields and approximate the isothermal limit

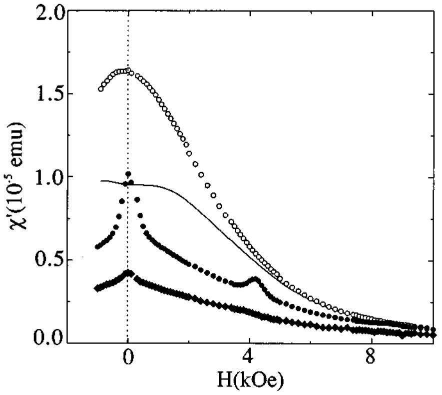

FIG. 2. Field dependence of the real part of the susceptibility χ' at $\theta=0°$ and $T=5$ K; ◆, high-frequency limit ($\nu=980$ Hz); ○, isothermal limit ($\nu=0$); ●, intermediate case ($\nu=15$ Hz); (–) estimation of the susceptibility caused by overbarrier thermally activated relaxation (see text).

as H increases (although this limit in fact decreases with increasing H and becomes very close to $\chi_{\rm hf}$ above 9 kOe).

For classical thermally activated relaxation, the field dependence of χ' is determined by the decrease of the anisotropy energy barrier U as H increases [cf. Eq. (3) above]. The effective relaxation time τ_1 given by Arrhenius' law is then shorter and, according to Eq. (1), the system should approach the equilibrium susceptibility value. Although experimental $\chi'(H)$ data indeed approach $\chi_0(H)$ at high fields, the $\chi'(H)$ curve also shows two sharp peaks centered around $H_0=0$ and $H_1=4.1(1)$ kOe [$B_1=H_1+4\pi M_{\rm eq}=5.1(1)$ kG]. We note that B_1, that is, the internal field which is seen by the molecule, is very similar to the value $B_1=5$ kG, where the first jump appears in magnetic hysteresis loops measured at low temperatures.[4,5] To amplify the $\chi'(H)$ and $\chi''(H)$ peaks at H_1 we first determined, at each temperature, the relaxation time $\tau_1(H_1)$ from the inflection point of the $\chi'(\omega)$ experimental curve. We then measured $\chi''(H)$ and $\chi'(H)$ in each isotherm at the frequency which verifies $\omega\tau_1\approx 1$. In other words, we synchronized our experimental exciting frequency to the relaxation rate of the molecules at $H=H_1$. In this condition, according to Eq. (1), $d\chi'/d(\omega\tau_1)$ has a maximum. Thus, the susceptibility becomes very sensitive to the dependence of the relaxation time on H. If Eq. (1) is again considered, the origin of the two $\chi'(H)$ peaks could be either the existence of narrow maxima in the equilibrium susceptibility, which are not experimentally observed, or a sudden speeding up of the magnetic relaxation near H_0 and H_1. In order to clarify this point, we estimated, using Eq. (1) to interpolate between the low-frequency $\chi_0(H)$ and high-frequency $\chi_{\rm hf}(H)$ limits obtained experimentally, the field dependence that $\chi'(\nu=15\ {\rm Hz})$ would follow if the relaxation mechanism at $T=5$ K was the thermal activation of the magnetic moment over the anisotropy barrier. The parameters τ_0 and $U(H=0)$ for $\theta=0°$, which are given in Table I, were substituted in Eqs. (2) and (3) to obtain $\tau(H)$. This $\chi'(H)$ estimation is shown as a continuous line in Fig. 2. From inspection of Fig. 2, it is clear that the calculated susceptibility differs with the experiment. Thus, Eqs. (1)–(3) do not predict the existence of a sharp χ' peak at a finite field $H_1=4.1$ kOe. It follows that the field dependence of τ_1 disagrees with the classical expectation for a thermally activated relaxation mechanism.

TABLE I. Activation energy $U_{\rm eff}$, and prefactor τ_0, Arrhenius law [Eq. (2)] parameters obtained from the fit of $\tau_1(T)$ data, for different strengths and orientations of the applied field. ($U=100$, $D=73$ K).

θ (deg.)	H (kOe)	$U_{\rm eff}$ (K)	τ_0 (s)
0	0.0	61 (2)	6 (2)$\times10^{-8}$
0	4.1	57 (1)	1.1 (2)$\times10^{-7}$
25	0.0	61 (2)	5 (4)$\times10^{-8}$
25	4.5	51 (2)	2 (1)$\times10^{-7}$
25	5.0	60 (2)	6 (3)$\times10^{-8}$

In order to determine unambiguously that the ac susceptibility peaks are due to a nonclassical field dependence of the relaxation time, we performed ac susceptibility measurements as a function of the frequency in the 0.025 Hz$<\nu<$1000 Hz range. We obtained the relaxation time τ_1 fitting the $\chi'(\omega)$ and $\chi''(\omega)$ experimental curves to Eq. (1). Typical experimental curves measured at different field values around $H_1=4.1$ kOe are shown in Fig. 3. We note first that the fits are reasonably good except at the high-frequency region. This discrepancy indicates that there are other faster relaxation mechanisms for the magnetic moments, as we expected from the $\chi_{\rm ac}(T)$ data (see Fig. 1). However, it is clear in Fig. 3 that the $\chi''(\omega)$ maximum appears at a higher frequency for $H_1=4.1$ kOe than for $H=3.5$ and 5 kOe. The field dependence of τ_1 at $T=5$ K is shown in Fig. 4. We

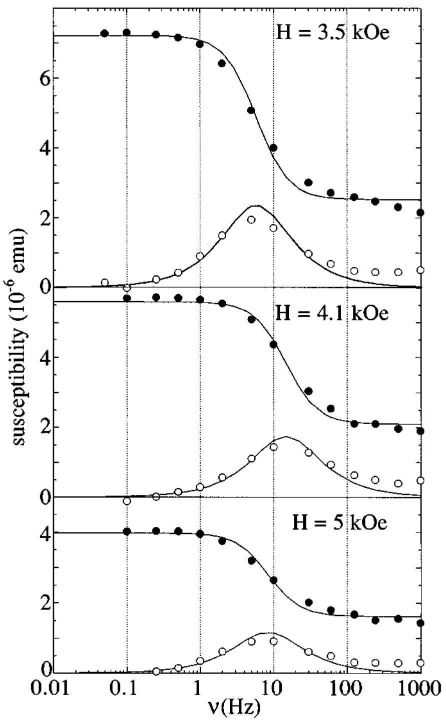

FIG. 3. Magnetic ac susceptibility as a function of frequency, measured at $\theta=0°$, $T=5$ K, and fields at and about $H_1=4.1$ kOe; ●, real component; ○, imaginary component; (–) fits to Eq. (1) to obtain τ_1.

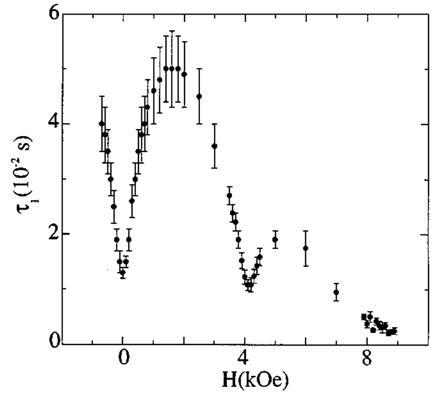

FIG. 4. Field dependence of the relaxation time for $T=5$ K and $\theta=0°$.

emphasize that τ_1 does not have a monotonic decrease as H increases but shows minima at $H_0=0$ and $H_1=4.1$ kOe, in contrast with the classical expectation for a pure thermally activated relaxation process.

The $\chi'(H)$ experimental data can be fitted near $H_0=0$ and $H_1=4.1$ kOe to a Lorentzian curve (Fig. 5):

$$\chi'(H)=\chi_B(H)+\frac{A}{1+[(H-H_n)/\Delta_n]^2}, \tag{4}$$

where Δ_n can be interpreted as the field range around H_n ($n=0$,1) for which the relaxation time increases with the absolute value of $H-H_n$. $\chi_B(H)$ describes the field dependence of the susceptibility far from $H=H_n$. In order to fit the experimental data to Eq. (4), $\chi_B(H)$ was chosen to be a constant value for the H_0 peak and a second-order polynomial near H_1. At $T=5$ K and $\theta=0°$, we obtain $\Delta_0=270(3)$ Oe and $\Delta_1=351(9)$ Oe, respectively, (see Fig. 5). Δ_1 is larger than Δ_0 for all T and θ.

Experimental $\chi'(H)$ and $\chi''(H)$ curves corresponding to $\theta=25°$ and three different temperatures $T=4.3$, 5, and 5.5 K are shown in Fig. 6. We note that χ' and χ'' also show two peaks near $H_0=0$ and $H_1=4.5$ kOe; i.e., the field value H_1 does not depend significantly on temperature. On the other hand, Δ_1 increases by 24% as the temperatures raises from 4.3 to 5.5 K whereas Δ_0 remains approximately constant.

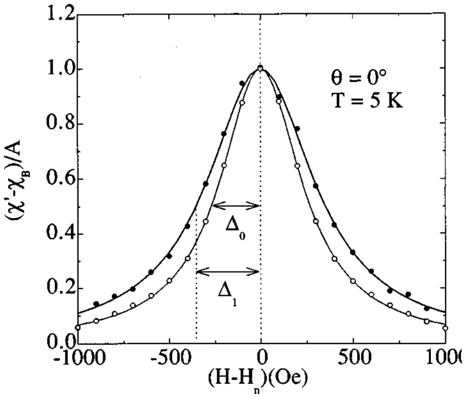

FIG. 5. The susceptibility peak at $T=5$ K and $\nu=15$ Hz, about H_0 and H_1, fitted to a Lorentzian function [Eq. (4)]; half width at half maximum's $\Delta_0=270(3)$ Oe, $\Delta_1=351(9)$ Oe.

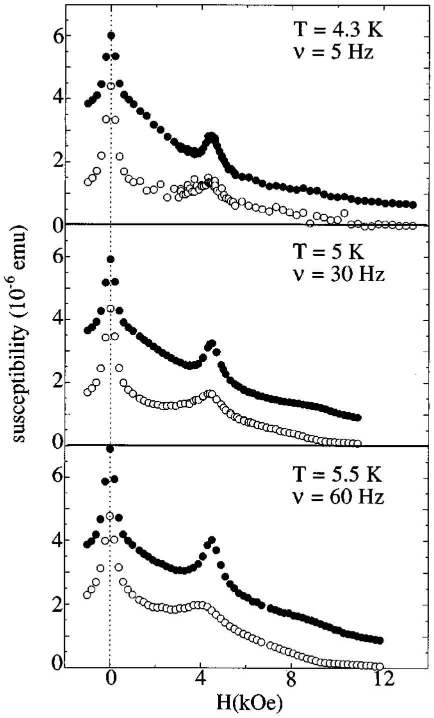

FIG. 6. Magnetic ac susceptibility isotherms ($\theta=25°$) measured at those frequencies that maximize the $H=H_1$ peak; ●, real component; ○, imaginary component.

At any value and orientation of the dc applied magnetic field, the relaxation time strongly increases as the temperature decreases. In fact, the temperature dependence of τ_1 can be fitted to Arrhenius' law as shown in Fig. 7 for $\theta=25°$. The values of the activation energy U_{eff} and time constant τ_0 parameters obtained from this fit of τ_1 are given in Table I. It is interesting to note that, in agreement with previously reported data,[8] the order of magnitude of the microscopic time τ_0 does not change with the applied field. We note that for $\theta=25°$, U is smaller at $H_1=4.5$ kOe, which corresponds

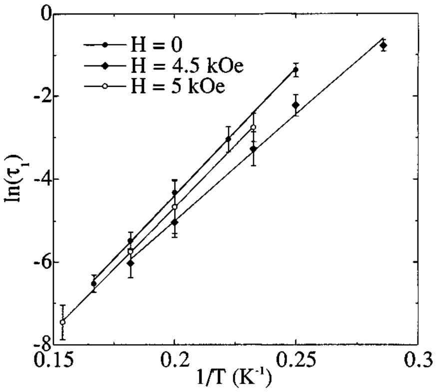

FIG. 7. Temperature dependence of the relaxation time for ($\theta=25°$); (−) fits to Arrhenius law: ●, for $H_0=0$; ○, for $H_1=4.5$ kOe; ◆, for $H=5$ kOe. (Note that its slope is higher than for $H_1=4.5$ kOe.)

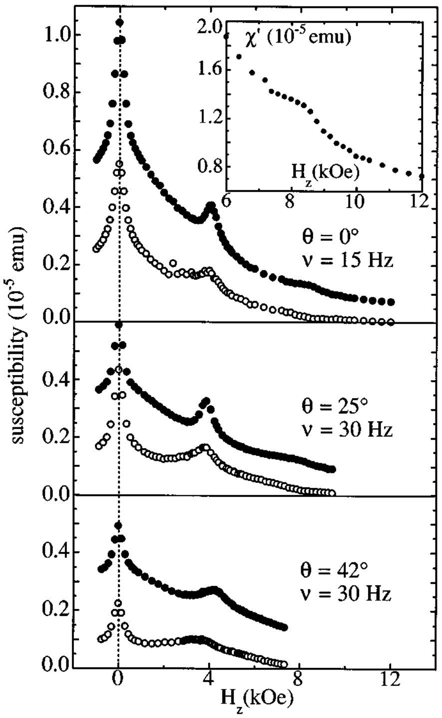

FIG. 8. Magnetic ac susceptibility isotherms measured at different orientations θ, plotted as a function of the component of the applied field H_z which is parallel to the easy axis of the sample; ●, real component; ○, imaginary component. Inset: Enlarged view of the H_2 peak measured at $\theta=0°$, $T=5$ K, and $\nu=15$ Hz.

to the second peak in Fig. 6, than the value obtained for a slightly larger field value $H=5$ kOe; i.e., the value of U_{eff} is smaller in-tune condition than off-tune condition. Moreover, the relaxation time τ_1 and the activation energy U obtained at $H_0=0$ (for $\theta=0°$ and $\theta=25°$) are larger than the same parameters measured at $H=H_1(\theta)$ ($H_1=4.1$ kOe for $\theta=0°$ and $H_1=4.5$ kOe for $\theta=25°$). The observation that $U(H)$ is smaller at H_n, with $n=0,1$, than at fields that are off-tune condition is crucial for this work since it points towards the physical origin of the relaxation time minima at $\tau_1(H_n)$, as we discuss in the next section. Again, this experimental result disagrees with the decrease of $U(H)$ as H increases predicted for classical thermally activated relaxation [Eq. (3)].

In order to investigate the effect of the transverse component of the applied field H_x on the magnetic relaxation of Mn$_{12}$Ac, we repeated the same set of ac susceptibility experiments for $\theta\neq 0$. The $\chi'(H)$ and $\chi''(H)$ experimental curves show two maxima at $H=H_0$ and $H=H_1$ for all θ values (see Fig. 8). The first χ' peak is always centered about $H_0=0$ whereas $H_1(\theta)$ increases as θ increases. It is very relevant to note that the field value $H_1(\theta)$ at which the first peak appears is such that its component parallel to the z axis is nearly independent on θ for $\theta\leqslant 60°$ and approximately satisfies $(H_1)_z=H_1\cos\theta\approx 4.1$ kOe (see Figs. 8 and 9). For larger angles the width of the $\chi'(H)$ peak is too large to define the position of the critical field with enough precision as to assure this statement. In spite of this experimental shortcoming, we infer that the existence of a sharp minimum in $\tau_1(H)$ at $H=H_1(\theta)$ is determined by the value of the $(H_1)_z$ rather than by the total applied field $H_1(\theta)$. It is also

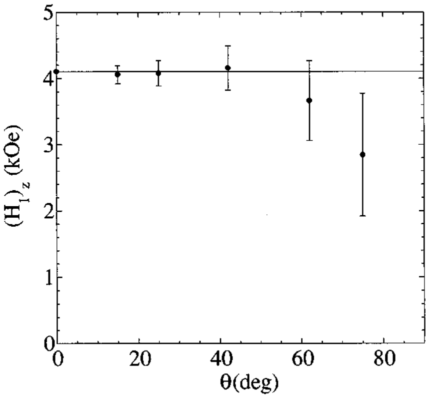

FIG. 9. Angular dependence of the crossing field component parallel to the easy axis $(H_1)_z$. The continuous line represents the condition $(H_1)_z=4.1$ kOe.

evident from the data exhibited in Fig. 8 that the χ' and χ'' maxima become broader and lower as θ departs from zero. The relaxation time measured under the condition $H_z=(H_1)_z$ fixed, which is shown in Fig. 10, decreases as H_x increases, in contrast with low-temperature magnetic relaxation experiments which detected no dependence of τ_1 on θ.[16] This discrepancy can be due to the very different experimental conditions under which both series of experiments were performed: $T=200$ mK and variable H_z in the experiment of Paulsen and Park $T=5$ K and $H_z=$ const in ours.

When the applied field was parallel to the z axis of the sample, we observed a third peak of χ' near $H_2=8.4$ kOe ($B_2=9.7$ kG). This peak is shown in the inset of Fig. 8. The value B_2 is not far from the magnetic-field value $B\approx 10$ kG where a jump is observed in the hysteresis loop.[4,5] The possibility of observing peaks at multiple values of H_1 higher than two is hindered by the merging, above $H=9$ kOe, of the isothermal and high-frequency limits of the susceptibility. In Ref. 8, a deep minimum of the relaxation time about $H=0$ and a second one at $H=3$ kOe, quite smaller than our $H_1=4.1$ kOe value, were observed. The authors suggested the existence of a fine structure of maxima

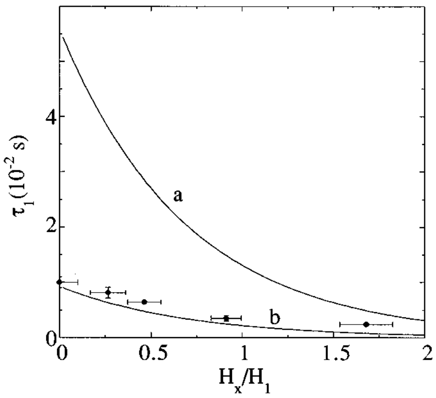

FIG. 10. Dependence of the relaxation time τ_1 measured at $T=5$ K and fixed $H_z=(H_1)_z$ on the component of the applied field H_x perpendicular to the easy axis of the sample; Curve a, estimated dependence for classical overbarrier hopping; Curve b, estimated dependence for resonant tunneling through levels lying 9 K below the classical barrier.

and minima below 5 kOe. From our data (cf. Figs. 4 and 8) it seems that the relaxation time minima appear only at $H_z \approx n\ H_1(0)$, where n is an integer.

IV. DISCUSSION

Our main experimental results are (1) When the field is applied parallel to the anisotropy axis of the sample, we observe sharp susceptibility maxima at $H=0$, 4.1, and 8.4 kOe, which we denominate H_n, with $n=0$, 1, and 2, respectively. They correspond to internal fields B_n that are in excellent agreement with the values at which steps have been observed in hysteresis loop measurements.[4–6] This is clear evidence for the existence of a common underlying mechanism. (2) The relaxation time shows minima at these field values. (3) Despite its rather striking field dependence, the relaxation time decreases as T increases, and follows Arrhenius' law for all fields. (4) The corresponding activation energy U_{eff} depends on H; it is lower at the tuning field values $H=H_n$ than for off-tune fields. (5) The tuning condition only depends on the component of the field along the anisotropy axis, and is fulfilled at least when $(H_1)_z=H_1\cos\theta \approx 4.1$ kOe. (6) At this tuning field value we have verified that the relaxation time becomes shorter as the transverse component H_x increases. (6) The relaxation time at $H_n = nH_1$, decreases as n increases, at least for $n=0$, 1, and 2.

The following spin Hamiltonian has been proposed for this system:[18,19]

$$\mathcal{H}=-DS_z^2+g\mu_B S_z H+\mathcal{H}' \tag{5}$$

where D is the anisotropy energy constant. The values $D \approx 0.73$ K and $g\approx 1.9$, determined by means of magnetization and high-field ESR experiments, will be used here.[17] The first term is an uniaxial anisotropy energy, the second term corresponds to the interaction of the magnetic moment with the z component of the applied field, and $\mathcal{H}'$ is a perturbation which does not commute with S_z. We treat the molecule as a $S=10$ object since, at low temperatures, the population of the $S=9$ excited multiplet is expected to be small. The eigenstates $|m\rangle$ of S_z are also eigenstates of the unperturbed Hamiltonian. The unperturbed ground state, in the absence of an applied magnetic field, is the $|\pm 10\rangle$ doublet, and all $|\pm m\rangle$ states are degenerate. The perturbation $\mathcal{H}'$ induces tunneling between states of opposite spin orientation.

The Zeeman term $g\mu_B S_z H_z$ breaks the zero-field degeneracy of the anisotropy term. It follows that one of the two anisotropy energy wells, in which $m>0$ for $H_z>0$, becomes metastable (see Fig. 11). For increasing field values the $|+m\rangle$ state increases, while the $|-m\rangle$ decreases in energy and both cross with the adjacent states. According to Eq. (5), all unperturbed energy levels on both sides of the energy barrier match at $H_z=nH_1(0)$, where $H_1(0)=D/g\mu_B$ (see Fig. 12) and n is an integer. Using the values of D and g given above, we obtain $H_1(0)=5.7$ kOe, larger than the observed value by 37%, approximately. The origin of this large discrepancy can be the difference between the externally applied field H and the magnetic field $B=H+4\pi M$ which really interacts with the magnetic moment of the molecule. Therefore, the difference between the applied field H_1 and the corresponding internal field B_1 is expected to be larger if the magnetization of the sample attains its equilibrium value, as in our ac experiments. The theoretical value $B_1(0) = 5.7$ kG is only about 10% larger than the crossing field $B_1(0)=5.1$ kG obtained from either ac or dc experiments.[4,5]

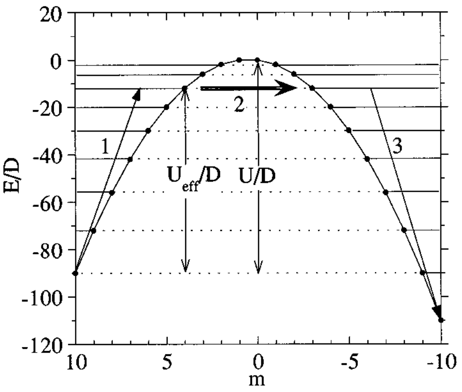

FIG. 11. Energy levels scheme of the unperturbed Hamiltonian $\mathcal{H}-\mathcal{H}'$ [see Eq. (5)] at $H_z=H_1(0)$. The tunneling process proposed in the text is shown schematically: (1) Thermal activation from the initial state $|m=10\rangle$ to the excited state $|m=4\rangle$, (2) tunneling to $|m=-3\rangle$, and (3) decay to the ground state $|m=-10\rangle$. U and U_{eff} are the energy barriers for classical thermally activated relaxation and tunneling between excited states, respectively.

In our experiment, we apply an oscillating field parallel to the dc field. Therefore, the observed time evolution of the magnetization is induced by the oscillating applied field. During this time evolution, the magnetization approaches its equilibrium value and, consequently, a continuous redistribution of the spin states population follows. Several possible mechanisms have been proposed to explain this evolution for Mn_{12}Ac molecules. Below we compare them to our experimental results.

At high temperature, the relaxation time measured experimentally follows Arrhenius' law (see Fig. 7). It has been proposed[18] that the molecule follows a series of thermally activated Orbach processes to overcome the anisotropy energy barrier U. In each Orbach process, the molecule changes from an initial $|m\rangle$ state to a final $|m\pm 1\rangle$ state. U is defined as the distance from the bottom of the metastable

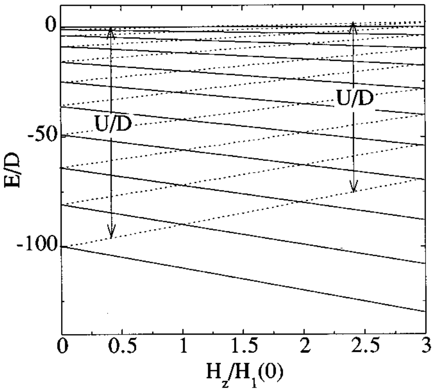

FIG. 12. Energy levels of $\mathcal{H}-\mathcal{H}'$ as a function of the z component of the applied field scaled to the first crossing field $H_1(0)$; continuous lines: lower potential well $(m<0)$; dashed lines: upper potential well $(m>0)$. The energy barrier for the thermally activated relaxation process is shown at two different field values.

energy well to the top of the barrier (see Fig. 11). At zero applied field, $U=100D\approx73$ K which is the energy difference between the unperturbed states $|m=0\rangle$ and $|m=\pm10\rangle$. As H_z increases, the energy of one of the wells decreases with respect to the other (see Fig. 12) and, as a result, the barrier U decreases according to Eq. (3). Consequently, a monotonic decrease of τ_1 as H_z increases follows in this model [see Eq. (2)], in contradiction with the two experimentally observed dips exhibited in Fig. 4.

A magnetization quantum tunneling relaxation mechanism has been proposed recently by Politi *et al.*[19] for the $\mathrm{Mn_{12}Ac}$ molecules. The unperturbed Hamiltonian given by Eq. (5) commutes with S_z for $\theta=0$ and quantum transitions between different orientations of the magnetic moment along the easy axis are then forbidden. The perturbation $\mathcal{H}'$ proposed in Ref. 18 follows from a fourth-order distortion of the uniaxial anisotropy; it induces tunneling between the $|m=-10\rangle$ unperturbed state, which is assumed to be the initial state of the molecule, and a final $|+m\rangle$ unperturbed state. However, this term only allows tunneling between unperturbed spin states $|m'\rangle$ and $|m''\rangle$ which satisfy $m'-m''=4N$, where N is an integer. From the field dependence of the unperturbed Hamiltonian eigenvalues (see Fig. 12), crossing of such levels would occur only at fields H_n with n=even. In contradiction with this prediction, we observe susceptibility maxima at all the integer multiples of H_1 $(n=0,1,2)$. The prediction of Ref. 8 that the relaxation time decreases monotonically as H_z increases is in marked contrast with our observation of minima at all $H=H_n$.

From the above discussion we may conclude that the relaxation mechanism underlying our experimental results performed on $\mathrm{Mn_{12}Ac}$ molecules appears to be neither a classical thermally activated process nor tunneling through the lowest-lying states. We propose a relaxation mechanism which involves three steps: (1) thermal population of an excited state $|+m'\rangle$ from the initial $|+10\rangle$ unperturbed state, (2) tunneling through the anisotropy barrier through some excited levels, and (3) decay to the ground state $|-10\rangle$. This process is represented schematically in Fig. 11. Then, the maxima observed in $\chi'(H)$ at $H_z=0$, 4.1, and 8.4 kOe would be related to the existence of resonant tunneling between nearly degenerate unperturbed states at these fields, which leads to local minima of the relaxation time τ_1 [see Fig. (4)].

The tunneling effects we have observed require thermal activation. This is so because tunneling through the lowest-lying energy states is suppressed by fields as small as the ac field amplitude $h_0(\sim 4\ \mathrm{Oe})$ we have applied in our experiments. The corresponding Zeeman energy is much larger than the relevant energy splittings, ΔE_T, that one expects to be generated by $\mathcal{H}'$.[19–21] Detuning therefore takes place even if the dc field satisfies $H_z=nH_1$. However, ΔE_T increases sharply [exponentially fast in $|m|$ (Ref. 20)] as one moves up the energy barrier. It is therefore not surprising to find a pair of states $|m\rangle$ and $|-m+n\rangle$, for $|m|$ sufficiently small, for which $\Delta E_T\sim g\mu_B h_0$ is fulfilled. Now, consider temperatures that are not too low, such that the dominant mechanism off resonance (that is, for H_z away from nH_1) is thermal activation over the energy barrier. Then tunneling through states $|m\rangle$ and $|m'=-m+n\rangle$ that lie below the energy barrier is to be expected when $H_z=nH_1$, $n=0,1,2,\ldots$. The relaxation time follows an Arrhenius law with an effective activation energy U_{eff}, which is the energy difference between the metastable state $|+10\rangle$ and the energy of the tunneling states. We infer this from our experimental results, independently of whether tunneling is phonon assisted or not.

It is worth pointing out that small stray external fields (Earth's magnetic field, for instance) would not suppress tunneling between these excited states because their tunneling splitting ΔE_T is large (see Ref. 20). The inhibiting field H_D large enough to switch tunneling off is $H_D\approx\Delta E_T/g\mu_B(m-m')$. If $|H-H_n|>H_D$ for all levels below the energy barrier top, the magnetic moments relax by thermal activation over the classical energy barrier U. Since $U>U_{\mathrm{eff}}$, ''Zeeman detuning'' leads to the increase of the relaxation time that we have observed experimentally. The interaction of the molecule with a thermal bath as well as hyperfine field effects [$H_{\mathrm{hyp}}\approx250$ Oe (Ref. 22)] broaden the unperturbed energy levels. In addition, the local field which is seen by the magnetic moment fluctuates due to thermal modulation of the dipolar interaction with neighboring molecules, leading to homogeneous broadening of the susceptibility peaks. All these effects enlarge the value of H_D and, consequently, the experimental halfwidth Δ_n. The susceptibility peaks are also broadened (about 30 Oe) by any slight misalignment of the crystallites' c axis from the z axis of the sample.

In the following discussion, we try to find the most effective relaxation channel. The relaxation time τ_1 is expected to follow approximately Arrhenius' law for thermally activated tunneling (for $|H-H_n|<H_D$) as well as for classical over-barrier (for $|H-H_n|>H_D$) relaxation. Moreover, the effective energy barrier U_{eff} for tunneling through excited states is smaller than the classical value U for thermally activated overbarrier transitions. At the $H_0=0$ in-tune condition, the difference between the calculated classical barrier height $U=73$ K and the measured value $U_{\mathrm{eff}}=61$ K, scaled by D yields $\Delta U/D=16.4$, very close to the value $\Delta U/D=16$ of the $|m=+4\rangle$ and $|m=-4\rangle$ tunneling states (Fig. 12). At $H_1=4.1$ kOe and $H_x=0$, the calculation of the barrier height yields $U=66$ K, while the measurement yields $U_{\mathrm{eff}}=57$ K, thus the difference is $\Delta U/D=12.3$, close to the value $\Delta U/D=11$ which corresponds to the $|m=-3\rangle$, $|m=+4\rangle$ tunneling doublet. We can conclude from these estimations that in the temperature region we are exploring, the doublets involved in tunneling lie about $U-U_{\mathrm{eff}}\approx9$–12 K below the top of the barrier. This estimation is corroborated by the measurements performed at $\theta=25°$, where the values $U_{\mathrm{eff}}=51$ K for the in-tune field $H_1=4.5$ kOe, and $U_{\mathrm{eff}}=60$ K for the off-tune field $H=5$ kOe were obtained. That is, the difference $\Delta U=9$ K is identical to the estimated difference at $\theta=0$.

From the values of τ_0 obtained from the Arrhenius law fits of the data for τ_1 obtained at fixed field and varying temperature, collected in Table I, we can conclude that they do not vary too strongly for the different applied fields. If, consequently, we assume the approximation that τ_0 may be considered as constant we may obtain the field dependence of U_{eff} on H_z from the $\tau_1(T=5\ \mathrm{K},H_z)$ data plotted in Fig. 4 using the expression $U_{\mathrm{eff}}(H_z)=kT\ln[\tau_1(H_z)/\tau_0]$. With $\tau_0=6\times10^{-8}$ s, the value for $H_z=0$, the resulting

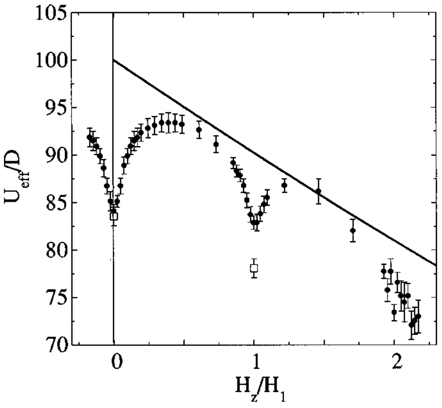

FIG. 13. Activation energies U_{eff} (scaled to D) versus applied field H_z (scaled to H_1) ($H_x=0$); □, Data obtained from Arrhenius law fits (Table I); ●, Points derived from $\tau_1(H_z)$ data, with $\tau_0=6\times10^{-8}$ s; (−), Classical overbarrier activation energy. The experimental points have been scaled with the parameters $D=0.73$ K and $H_1=4.1$ kOe.

$U_{\mathrm{eff}}(H_z)/D$ values show sharp minima at the tuning fields and maxima corresponding to overbarrier process (Fig. 13). In the same figure we have plotted the values of U_{eff}/D obtained from the Arrhenius law fits of the data taken at fixed field and varying temperature (Table I), observing a reasonable agreement, a proof of the soundness of the $\tau_0=$constant approximation. The field dependence of the activation energy $U(H_z)$ for classical overbarrier process has also been plotted in the same figure (scaled to D and H_1). This line coincides nicely with the $U_{\mathrm{eff}}(H_z)/D$ points at the off-tune field values $H_z/H_1=0.6$ and at $H_z/H_1=1.5$. Thus the maximum values decrease as H_z increases because the barrier height decreases, and the dominant process for these off-tune field values is overbarrier hopping.

Consider the parallel and transverse components, H_z and H_x, respectively, of the field that is applied at an angle θ from the anisotropy axis. We now discuss the observed dependence of the relaxation time as a function of H_x, keeping $H_z=(H_1)_z=$const. The magnetic interaction term, $g\mu_B H_x S_x$, has two effects: the classical barrier height $U(H_z,H_x)$ decreases as H_x increases, and energy levels as well as energy splittings change with H_x. Now, which is the most effective channel for tunneling depends on how the Boltzmann factor and the energy splitting change from one energy level to the next one. Furthermore, energy-level spacings *at a given energy below the barrier* top depend weakly on H_x, while the energy splitting of a level with energy E_n depends *exponentially* on $U-E_n$, but more weakly on H_x.[20] Consequently, the energy difference between the doublet or doublets which contribute most to magnetic tunneling at $H_z=H_1$ and the lower state of the metastable well is roughly given by $U_{\mathrm{eff}}=U(H_x)-$const. As mentioned above the most effective tunneling doublet for $H_z=(H_1)_z=4.1$ kOe and $H_x=0$ is about 9 K below the barrier, for temperatures near 5 K. We therefore estimate the value of τ_1 versus the transverse component H_x at $H_z=H_1$ with Arrhenius' law with $\tau_0=1.1\times10^{-7}$ s, the value obtained from the fit of the $\tau_1(T)$ data measured at $\theta=0°$. The resulting $\tau_1(H_x)$ curve, shown in Fig. 10, fits the experimental data points reasonably close. Thus, the data we have obtained with fields applied at a nonzero angle to the anisotropy (i.e., for $H_x\neq0$) axis fit well with the tunneling process that we infer above for $H_x=0$.

Attempts to explain the observed effects by processes taking place near the top of the barrier fail for the reasons that follow. All unperturbed energy levels lie below the top of the barrier for any field H applied along the z direction. These levels lie on a pattern that is repeated when H changes by *twice* the value of H_1. If such a process would induce resonances in τ_1 versus H, they would be spaced at *twice* the observed amount. Moreover, if the process involves the first one or two levels below the top of the barrier the difference in activation energy ΔU would amount to an order of magnitude less than observed.

V. CONCLUSIONS

We have performed a detailed ac susceptibility study of the magnetic relaxation of $\mathrm{Mn_{12}Ac}$ molecules at temperatures above 1.8 K. A possible relaxation mechanism, the tunneling between thermally excited spin states explains qualitatively the experimental results. When the field is applied parallel to the anisotropy axis of the sample we observe sharp susceptibility maxima at the field values H_n, with $n=0$, 1, and 2 that correspond to the crossing of the Zeeman splitted spin levels. The most striking result is that the relaxation time exhibits minima as a function of magnetic field at the crossing field values. The temperature dependence of the relaxation time follows an Arrhenius law. The corresponding activation energy U depends on H, with a value which is lower at $H=H_n$ than at any other field of similar magnitude but off-tune condition. At any of the crossing fields, pairs of levels with opposite spin orientation are tuned in energy so that a non-negligible tunneling probability exists for pairs lying not far below the top of the barrier. The pair with the largest value of tunneling rate times the relevant Boltzmann factor dominates the relaxation process and determines an effective activation energy U_{eff} of the Arrhenius law. This energy is lower than the classical overbarrier flipping process activation energy U, determined at off-tuning field condition. From the difference between both activation energies the level pairs involved in the tunneling have been deduced.

A transverse field hardly modifies the crossing field value $(H_1)_z$, while it does reduce the relaxation time. This reduction can be explained as due to a lowering of the effective activation energy of the tunneling process due to the decrease in the height of the barrier caused by the transverse field.

We think that the main questions left to be answered are, (1) the nature of the perturbing Hamiltonian $\mathcal{H}'$, even in the absence of any applied field, (2) how tunneling takes place, and (3) how to predict what energy levels contribute most to relaxation as a function of temperature. We believe that the perturbing Hamiltonian $\mathcal{H}'$ must be linear in spins (such as random dipolar or applied magnetic fields, or hyperfine interaction) but not of fourth order in transverse spins, as proposed by Politi *et al.*,[19] since then the peaks at $H=nH_1$, with $n=$odd, would not be observed.

Note added in proof. Magnetization measurements performed on a single crystal have corroborated the presence of hysteresis jumps.[23]

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[1] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature **365**, 141 (1993).

[2] C. Paulsen, J.-G. Park, B. Barbara, R. Sessoli, and A. Caneschi, J. Magn. Magn. Mater. **140-144**, 379 (1995).

[3] C. Paulsen, J. G. Park, B. Barbara, R. Sessoli, and A. Caneschi, J. Magn. Magn. Mater. **140-144**, 1891 (1995).

[4] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1995).

[5] J. M. Hernández, X. X. Zhang, F. Luis, J. Tejada, J. R. Friedman, M. Sarachik, and R. Ziolo, Phys. Rev. B **55**, 5858 (1997).

[6] J. M. Hernández, X. X. Zhang, F. Luis, J. Bartolomé, J. Tejada, and R. Ziolo, Europhys. Lett. **35**, 301 (1996).

[7] M. A. Novak, R. Sessoli, A. Caneschi, and D. Gatteschi, J. Magn. Magn. Mater. **146**, 211 (1995).

[8] M. A. Novak and R. Sessoli, in *Quantum Tunneling of the Magnetization*, edited by L. Gunther and B. Barbara, NATO ASI Series, Series E: Applied Sciences (Kluwer, Dordrecht, 1995), Vol. 301, p. 171.

[9] A. Caneschi, D. Gatteschi, R. Sessoli, A. L. Barra, L. C. Brunel, and M. Guillot, J. Am. Chem. Soc. **113**, 5873 (1991).

[10] T. Lis, Acta Crystallogr. B **36**, 2042 (1980).

[11] M. I. Shliomis and V. I. Stepanov, J. Magn. Magn. Mater. **122**,176 (1993).

[12] L. Néel, Ann. Géophys. **5**, 99 (1949).

[13] W. F. Brown, Jr., J. Appl. Phys. **30**, 130S (1959).

[14] H. Pfeiffer, Phys. Status Solidi A **122**, 377 (1990).

[15] W. T. Coffey, D. S. F. Crothers, J. L. Dormann, L. J. Geoghean, Yu. P. Kalmykov, J. T. Waldron, and A. W. Wickstead, Phys. Rev. B **52**, 15 951 (1995).

[16] C. Paulsen and J.-G. Park, in *Quantum Tunneling of the Magnetization* (Ref. 8), p. 171.

[17] A. Chaneschi, D. Gatteschi, R. Sessoli, A. L. Barra, L. C. Brunel, and M. Guillot, J. Am. Chem. Soc. **113**, 5875 (1991).

[18] J. Villain, F. Hartmann-Boutron, R. Sessoli, and A. Rettori, Europhys. Lett. **27**, 159 (1994).

[19] P. Politi, A. Rettori, F. Hartmann-Boutron, and J. Villain, Phys. Rev. Lett. **75**, 537 (1995).

[20] D. A. Garanin, J. Phys. A **24**, L61 (1991).

[21] E. Chudnovsky, Phys. Rev. Lett. **72**, 3433 (1994).

[22] F. Hartmann-Boutron, P. Politi, and J. Villain, Int. J. Mod. Phys. B (to be published).

[23] L. Thomas, F. Lionki, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature **383**, 145 (1996).