Field-tuned quantum tunneling of the magnetization

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The response of the magnetization to a time-dependent applied magnetic field in single-spin models for uniaxial magnets is studied. We present staircase magnetization curves obtained from the numerically exact solution of the time-dependent Schrödinger equation. Steps are shown to correspond to field-tuned quantum tunneling between different pairs of nearly degenerate energy levels. We investigate the role played by different terms that allow for tunneling processes: transverse fields and second-order and fourth-order transverse anisotropies. Magnetization curves for nonsaturated initial states and for excited initial states showing steps when the field decreases in absolute value are also presented. These results are discussed in relation to recent experiments on high-spin compounds. © *1998 American Institute of Physics.* [S0021-8979(98)16111-X]

Magnetic molecules containing high-spin clusters[1] such as Mn_{12} or Fe_8 provide physical systems by which to study quantum tunneling of the magnetization (QTM).[2,3] Recent experiments on these systems[4,5] have reported the appearance of steps in the hysteresis loops at low temperature which have been attributed to thermally assisted resonant tunneling between quantum states. This interpretation is based on a single-spin $S=10$ model with strong uniaxial anisotropy ($\mathscr{H}=-DS_z^2-g\mu_B\mathbf{SH}$, where D is the uniaxial anisotropy energy) for which energy levels ($|Sm\rangle$ for $\mathbf{H}\|\hat{z}$, where $S_z|Sm\rangle=m|Sm\rangle$) cross at fields $g\mu_B H_n=nD$. At these fields, the relaxation time of the magnetization shows minima. For QTM to occur, this model has to be extended to include symmetry breaking terms such as those originating from dipolar interaction, interaction with nuclear spins or phonons, etc.[5–7] The detailed mechanism by means of which QTM occurs in hysteresis experiments on uniaxial magnets is investigated in this article. Previously, magnetization tunneling in mesoscopic systems has been semiclassically studied by several authors[8–10] and, more recently, quantum dynamical calculations for several models of nanomagnets such as the Heisenberg model[11] and the single-spin quantum model[12] have shown the occurrence of resonant coherent QTM at zero temperature. The staircase structure in the magnetization curves for a time-dependent field has been recently shown[13] to be well described by successive Landau–Zener (LZ) transitions.[14,15] In addition, recent theoretical works have also studied the problem of spin tunneling in a swept magnetic field.[16,17]

The most general Hamiltonian for a single quantum spin including a transverse field (which might have a hyperfine or dipolar origin), second-order and fourth-order transverse anisotropies, and a time-dependent applied magnetic field is

$$\mathscr{H}=-K_xS_x^2-K_yS_y^2-K_zS_z^2-C_xS_x^4-C_yS_y^4-C_zS_z^4-\Gamma S_x-\mathbf{H}(t)\mathbf{S}, \tag{1}$$

where K_z, K_x and K_y are the anisotropy constants along the easy, medium, and hard axes, respectively, $\mathbf{S}=(S_x,S_y,S_z)$ is the vector representing the magnetization, C_x, C_y, and C_z are the fourth-order anisotropy constants, Γ is the transverse field, and $\mathbf{H}(t)=H(t)(\sin\theta,0,\cos\theta)$ denotes the applied field.

The time evolution of the magnetization at $T=0$ is obtained from the exact numerical solution of the time-dependent Schrödinger equation (TDSE), $i\hbar\partial|\Psi(t)\rangle/\partial t=\mathscr{H}|\Psi(t)\rangle$, where $|\Psi(t)\rangle$ denotes the wave function of the spin system at time t. We study the following situation: First we set the applied magnetic field to its minimum value $H(t=0)=-H_0$ and put the system in the corresponding ground state, i.e., $|\Psi(0)\rangle=|\Phi_0(0)\rangle$ where $\mathscr{H}(-H_0)|\Phi_0(0)\rangle=E_0(-H_0)|\Phi_0(0)\rangle$. The time evolution of the wave function is then calculated by means of $|\Psi(t+\tau)\rangle=\exp(-i\tau\mathscr{H})|\Psi(t)\rangle$, where τ is the time step used to integrate the TDSE. During the integration of the TDSE, the applied field changes from $-H_0$ to H_0 with a given speed, which is defined by the field step ΔH between two consecutive field values and the amount of time τ_H the system feels each constant field. The temporal evolution of the αth ($\alpha=x,y,z$) component of the spin can be calculated from $\langle S_\alpha(t)\rangle=\langle\Psi(t)|S_\alpha|\Psi(t)\rangle$. For each constant field value we compute the expectation value of S_α averaged over time $\underline{S_\alpha}=\underline{1}/\tau_H\int_0^{\tau_H}dt\langle S_\alpha(t)\rangle$. In the following we will refer to $M=\underline{S_z}/S$ as the magnetization. The energy of the system is given by $E[H(t)]=\langle\Psi(t)|\mathscr{H}|\Psi(t)\rangle$.

In order to understand the origin of the steps in the magnetization curves, we first consider the simplest case of (1), namely, a single spin 1/2 system described by the Hamiltonian $\mathscr{H}=-\Gamma\sigma_x-H(t)\sigma_z$, where σ_x and σ_z are the Pauli-spin matrices, and we study the response of the magnetization to the time-dependent applied field $H(t)$. Γ sets the scale of the splitting at $H=0$ between the two energy levels (see inset of Fig. 1). Figure 1 presents the magnetization curves for several field sweep rates for the ground state as the initial state, showing steps of different sizes at $H=0$.

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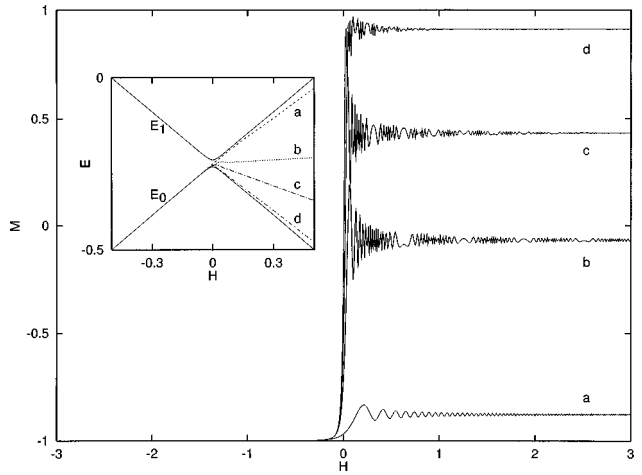

FIG. 1. M vs H for model (1) with $S=1/2$, $K_z=1.0$, and $\Gamma=0.02$ for several field sweep rates $\Delta H/\tau_H$: $\Delta H=0.001$ and (a) $\tau_H=0.1$, (b) $\tau_H=1$, (c) $\tau_H=2$, and (d) $\tau_H=5$. Initial state: Φ_0. The inset shows the levels crossing and the system energy for cases (a)–(d).

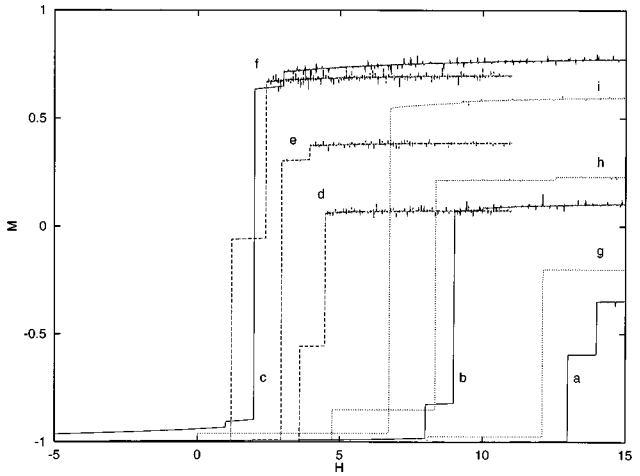

FIG. 2. M vs H for model (1) with $S=10$, $K_z=1$, and $\theta=0°$ supplemented by a transverse field term for Γ equal to (a) 0.5, (b) 2, and (c) 6.5; second-order anisotropy terms with $K_x=0.6$ and K_y equal to (d) 0.5, (e) 0.4, and (f) 0.1; and fourth-order anisotropy terms with $C=C_x=C_y=C_z$ equal to (g) 0.0005, (h) 0.0025, and (i) 0.01. Field sweep parameters for (a), (b), (c): $\Delta H=3\times10^{-5}$, $\tau_H=1200$; for (d), (e), (f): $\Delta H=2\times10^{-5}$, $\tau_H=800$; for (g), (h), (i): $\Delta H=3\times10^{-5}$, and $\tau_H=900$.

According to the adiabatic theorem, a slowly changing external perturbation will keep the system in the eigenstate it started from (Φ_0) unless this eigenstate comes closer to another eigenstate (Φ_1). Then the adiabatic approximation might break down, allowing the system to escape from Φ_0 and tunnel to Φ_1 via the Landau–Zener tunneling mechanism.[14] The probability of staying in the same eigenstate Φ_0 (which has opposite magnetization after the crossing) when the field is swept is given by $p=1-\exp[-\pi\Delta E^2/(2\Delta H/\tau_H)]$, which depends on the energy splitting and the field sweep rate $\Delta H/\tau_H$. The final state is then a linear combination of both eigenstates with weights p and $1-p$ and the size of the step at $H=0$ is proportional to p, i.e., $\Delta M=pM_0^{\text{final}}+(1-p)M_1^{\text{final}}-M_0^{\text{initial}}$, where the superscripts initial and final refer to before and after the crossing. Curve (d) is the closest to adiabatic behavior ($p\approx1$, large step); curve (a) corresponds to a fast sweep and the scattering is almost complete ($p\approx0$, small step). The appearance of steps in the magnetization curves is a general feature for many models of uniaxial magnets and follows naturally from the occurrence of field-tuned tunneling transitions between nearly degenerate eigenstates of the Hamiltonian. The size of the step depends on the energy-level splitting of the participating levels, the weight of the corresponding eigenstates in the current state of the system, the field sweep speed, and the value of the magnetization itself.

In Fig. 2 we present magnetization curves for the Hamiltonian most commonly assumed[4,5] in the attempt to explain recent experimental data ($\mathscr{H}=-K_zS_z^2-\mathbf{H}(t)\mathbf{S}$, with $\mathbf{H}\|\hat{z}$ and $S=10$), supplemented by terms that break the rotational symmetry about the z axis, i.e., those in model (1). These terms allow for the occurrence of field-tuned QTM and the corresponding steps in the magnetization. All these cases have in common that, for some specific fields H_n, pairs of energy levels become almost degenerate. If $\Phi_0(-H_0)$ is the initial state, the levels involved in the crossing at H_n are E_n and E_{n+1}.

Curves (a), (b), and (c) correspond to the case including a transverse field. Γ allows all transitions $\Delta m=\pm1$. At resonance $H_n=nK_z=n$, and the values of n for which steps appear depend on Γ. Thus, for (a) $\Gamma=0.5K_z=0.5$ we find $n=12,13,14$; for (b) $\Gamma=2$, $n=8,9$; and for (c) $\Gamma=6.5$, $n=1,2,3$.

Curves (d), (e), and (f) show that the presence of second-order transverse anisotropy terms can also induce QTM. They correspond to $K_z=1$, $K_x=0.6$, and several values of K_y. For $K_y=K_x$, the energy and S_z commute and no tunneling occurs. These transverse anisotropy terms change the spacing between resonant fields although they remain regularly spaced as in case the case of a transverse field Γ. These terms allow transitions that obey the selection rule $\Delta m=\pm2$. For (d) $K_y=0.5$, $n=8,10$; for (e) $K_y=0.4$, $n=4,6,8$; and for (f) $K_y=0.1$, $n=2,4$.

Fourth-order anisotropy terms [curves (g), (h), and (i)] allow the occurrence of field-tuned tunneling between levels satisfying $\Delta m=\pm4$. In this case, the fields at which pairs of energy levels cross are not equally spaced. Results are shown for different values of $C_x=C_y=C_z=C$. For (g) $C=0.0005K_z=0.0005$, $n=8,12$; for (h) $C=0.0025$, $n=4,8,12$; and for (i) $C=0.01$, $n=0,4,8$.

None of the curves in Fig. 2 presents steps when $|\mathbf{H}|$ decreases. This can be easily understood since the system starts from the ground state Φ_0 and the energy level scheme as a function of the field is such that E_0 only crosses another level at zero field. Another feature of these curves is that the magnetization does not reach the saturation value (unless the system stays in the ground state when crossing $H=0$ in which case there is one big step from $M=-1$ to $M=1$) even for $H\to\infty$. The explanation comes from the fact that the system can only gain or lose energy through the time-dependent field but not through interaction with the environment.

The field sweep rate ($\Delta H/\tau_H$) is a crucial paramater in this problem. As was shown for the simple case of a single

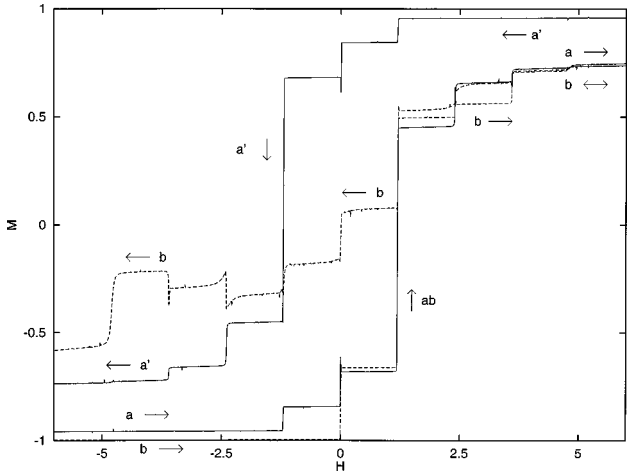

FIG. 3. M vs H for model (1) with $S=10$, $K_x=0.6$, $K_y=0.1$, $K_z=1.0$, $C=\Gamma=0$, and $\theta=0°$. Curves (a) and (a′): The field goes (a) from $-H_0$ to H_0 and (a′) from H_0 to $-H_0$ for $H_0=10.0$, starting from the initial states: $\Psi_{(a)}^{(a')}(0)=c_0\Phi_0(\mp H_0)+c_1\Phi_1(\mp H_0)+c_2\Phi_2(\mp H_0)$, respectively, where $c_0=0.7$, $c_1=0.22$, and $c_2=0.08$. Field sweep parameters: $\Delta H=0.0025$, $\tau_H=10^5$. Curve (b): The initial state is $\Phi_0(-H_0)$ and the field goes from $-H_0$ to H_0 and then, before reaching saturation, back to $-H_0$ for $H_0=10.0$. At $H=H_0$, where the field is reversed, $\Psi(H_0)=\Sigma_n c_{2n}\Phi_{2n}(H_0)$, where $c_0=0.168$, $c_2=0.653$, $c_4=0.038$, $c_6=0.111$, $c_8=0.027$, and $c_{10}=0.002$.

spin 1/2, the probability of QTM depends on it. In general, the lower the sweep rate, the larger the size of the step. However, also relevant is the smoothness of the field swept: If ΔH is too large, the size of the steps depends in a nontrivial way on ΔH, τ_H, and ΔE, and LZ theory does not apply.

In Fig. 3 we consider the case of an initial state which is not the ground state but a linear combination of several eigenstates. Unlike the ground state, the excited levels can become nearly degenerate with other levels for $\mathbf{H}\neq 0$, and therefore there is a nonzero probability of finding steps when $|\mathbf{H}|$ decreases, as illustrated by curves (a) and (a′). Moreover, if the field is reversed after one sweep from $-H_0$ to H_0 [curve (b)], the system restarts from a linear combination of several eigenstates (corresponding to a nonsaturated state in an experiment) and the situation is similar to that of curves (a) and (a′). As shown by curve (b), there is some probability of finding steps when $|\mathbf{H}|$ decreases and of getting both negative and positive steps. The same reasoning applies to QTM from thermally populated excited levels. Although the tunneling probability increases with the excitation level, and smaller off-diagonal terms are required to induce field-tuned QTM, the fact that the tunneling processes involve excited levels implies that some probability of finding steps when $|\mathbf{H}|$ decreases exists, at variance with the experimental results. Moreover, preliminary experimental results in which the field is reversed before saturation is reached show that steps can appear when $|\mathbf{H}|$ decreases,[18] in qualitative agreement with our findings.

We have shown that $T=0$ field-tuned QTM leads to staircase magnetization curves. The following might be relevant when comparing to experiments[4,5] on Mn_{12}: A transverse field Γ allows $\Delta m=\pm 1$ transitions and yields equally spaced steps, in agreement with experiments. However, the theoretical magnetization curves [with Γ as the only off-diagonal term and $\Phi_0(-H_0)$ as the initial state] look similar to the experimental ones (steps at the first energy level crossings $g\mu_B H_n=nD$, n small) for much larger values ($\Gamma\sim 1-5D\equiv 0.44-2.2T$) than those estimated for dipolar ($\sim 0.01T$) or hyperfine ($\sim 0.05T$) interactions.[19] Second-order transverse anisotropy terms are often discarded due to Mn_{12} tetragonal symmetry, although local symmetries could affect the structure of the spectrum. These terms are relevant for other systems such as Fe_8.[20] Fourth-order anisotropy terms cannot account for all the steps observed and they lead to nonequally spaced steps. They can be responsible for small deviations from $\Delta m=\pm 1$ transitions and equally spaced steps. However, the single-spin model proposed for the Mn_{12} molecule may be too simple to mimic the actual energy spectrum: The single-spin $S=10$ system is described by 21 eigenstates whereas a proper description of the magnetic state of the Mn_{12} molecule requires 10^8 states. A better understanding of the situation when the field is not swept smoothly enough and the Landau–Zener picture does not apply is also needed, especially since this appears to be the experimental case. Finally, further experimental work investigating the possibility of obtaining steps for decreasing $|\mathbf{H}|$ and observing negative (opposite to the field sweep) steps may clarify the effect of thermal activation, which in principle allows the appearance of these steps.

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