Quantum Dynamics of Atomic Magnets: Cotunneling and Dipolar-Biased Tunneling

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(Received 20 May 2003; published 16 December 2003)

Multispin tunneling cross relaxations in an ensemble of weakly coupled Ho^{3+} ions, mediated by weak anisotropic dipolar interactions, can be evidenced by ac-susceptibility measurements in a high temperature regime. Based on a four-body representation, including the rare-earth nuclear spin, two-ion tunneling mechanisms can be attributed to both dipolar-biased tunneling and cotunneling processes. The coreversal involving entangled pairs of magnetic moments is discussed with a particular emphasis, giving new evidence to elucidate the many-body quantum dynamics in dipolar spin glasses.

DOI: 10.1103/PhysRevLett.91.257204 PACS numbers: 75.45.+j, 71.70.–d, 75.50.Lk

Since the discovery of quantum tunneling of the magnetization in single molecule magnets (SMMs) [1–3], the effects of environmental degrees of freedom on tunneling of mesoscopic spins, especially due to other spins [4], have been investigated in detail within the single-spin framework [5,6]. Indeed, most features of the staircaselike hysteresis loops, observed in an *ensemble* of weakly interacting mesoscopic spins, were rather well understood within this simple picture of a single spin submitted to external and internal magnetic fields. In the presence of an axial anisotropy, hysteresis occurs at low temperatures due to the energy barrier E_B hindering the magnetization reversal, when thermal activation over the barrier requires a very long relaxation time $\tau = \tau_0 e^{E_B/k_B T}$. Nevertheless, nonstationary quantum mechanics allows for a faster time evolution at avoided level crossings within the single-spin Zeeman diagram (tunneling), leading to magnetization steps for well-defined values of the magnetic field applied along the easy axis (resonance conditions). Each mesoscopic spin experiences a time-dependent distribution of internal fields which is determinant for the analysis of the quantum relaxation of weakly coupled spins [4,7,8]. These fields being generated by environmental spins, coupled by dipolar and eventually exchange interactions, one should ask the question to what extent the measured tunneling rate is related to the dynamics of quasi-isolated spins or of larger entities such as two (or more) spins.

Recent magnetization measurements of mesoscopic Ho^{3+} ions, highly diluted in a $LiYF_4$ single crystal, evidenced the coherent rotation of both the electronic angular momentum and the nuclear spin of a nearly isolated Ho^{3+} ion [6]. At low temperatures, a single Ho^{3+} ion in $LiYF_4$ behaves as an *atomic magnet* due to a large axial crystal-field anisotropy along the tetragonal easy c axis, thus leading to very long spin-phonon relaxation times (the energy barrier $E_B \approx 10$ K is limited by the first excited electronic singlet). Therefore, the magnetic moment is oriented along the c axis and constitutes a two-level system (electronic doublet of Ising-type), with the moment being frozen either up or down. Nevertheless, the Zeeman diagram is strongly modified by the hyperfine interaction with the rare-earth nuclear spin $I = 7/2$, so that quantum tunneling of the magnetic moment occurs at avoided electronuclear level crossings of a single Ho^{3+} ion. In this *strong* hyperfine coupling case, decoherence is due only to nuclear spins of diamagnetic ions (that is, mainly the nuclear spins of eight fluorine ions, with $I = 1/2$). This single-ion tunneling process leads to staircaselike hysteresis loops, as observed with SMMs, but the crossing fields are related *only* to the hyperfine constant A_J. Furthermore, some additional small magnetization steps were also observed at fast field-sweep rates, and still remain ambiguous because these steps have no explanation in terms of level crossings within the single-ion model. Besides, the effect of a many-body quantum dynamics was also observed in holmium-based spin glasses [9], but the way quantum fluctuations arise in this more concentrated regime still remains unclear. In this Letter, we demonstrate that new tunneling mechanisms originate from an *unused* feature of the single-ion picture: Equally spaced energy levels allow for nondissipative spin-spin cross-relaxation tunneling processes. The ac-susceptibility measurements in a rather high temperature regime give us a unique means to assess the *various* multispin tunneling mechanisms which may affect the quantum dynamics of an assembly of mesoscopic spins. Moreover, a two-ion picture is introduced to give the first description of the tunneling of pairs of Ho^{3+} ions, hence corresponding to a *cotunneling* process.

The ac susceptibility of a 0.1 at. % holmium-doped $LiYF_4$ single crystal was studied as a function of a quasistatic field applied along the easy c axis. The measurements were performed in a high temperature regime ($T \geq 1.75$ K) with a quantum design MPMS SQUID magnetometer, using a 4 Oe-amplitude excitation field. In Fig. 1, a low-frequency measurement, as obtained with $f_m = 163$ Hz, reveals peaks (dips) in the in-phase (dissipative) response when the dc field is changed, allowing

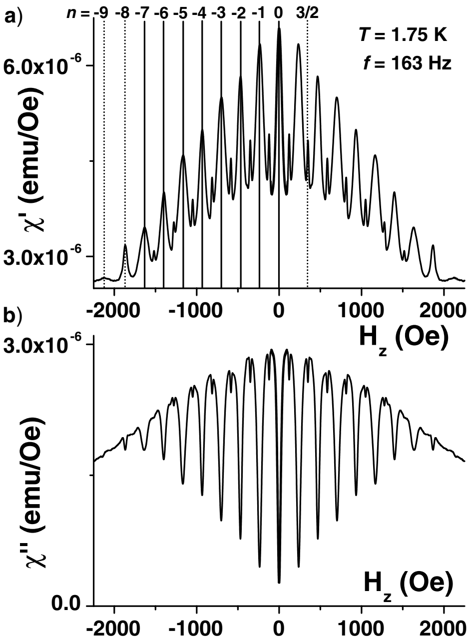

FIG. 1. (a),(b) The ac susceptibility measured at $T = 1.75$ K with a frequency $f_m = 163$ Hz. The nonmonotonous ac response, as a function of H_z, gives evidence for a faster relaxation at well-defined values $H_n = n \times 230$ Oe. Large and broad peaks or dips are clearly observed for integer n values, with $-7 \leq n \leq +7$, whereas smaller and narrower ones are measured for half-integer n values, with $-13 \leq 2n \leq +13$, as well as for $n = \pm 8$ and $n = \pm 9$. The solid lines correspond to electronuclear levels crossing fields calculated within the single-ion representation [see Fig. 4(a)], whereas the dotted lines are associated with additional crossing fields calculated within the two-ion representation [see Fig. 4(b)].

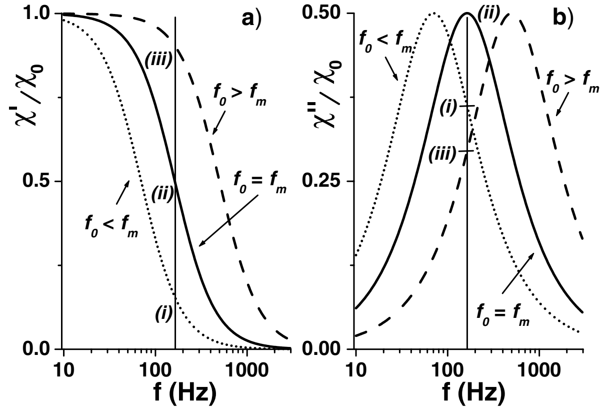

FIG. 2. Variation of the in-phase (a) and dissipative (b) responses in the ac susceptibility for three different relaxation rates f_0, described within the Debye model assuming a single (dominant) relaxation time. The constant measurement frequency f_m is suggested by the vertical solid line, and χ_0 is the static susceptibility. Depending on the value of f_m, the dissipative response can be either increased (case *i*) or decreased (case *iii*) if the dynamics gets faster. In any case, the in-phase response follows the variations of f_0.

us to investigate the role of the various quantum relaxation mechanisms. In every case, the results can be qualitatively understood when considering a field-dependent relaxation time to describe the system dynamics.

As shown in Fig. 2, if the constant frequency measurement f_m is smaller than the characteristic frequency f_0 of spin fluctuations (case *iii*), an increase in the in-phase response, or a decrease in the dissipative response, is associated with a faster relaxation rate (i.e., f_0 increases). The large deviations to the monotonous response, as observed in Fig. 1, are clear signatures of the *single-ion quantum dynamics*. Indeed, the faster relaxation of the magnetization observed for all the resonant fields H_n, with $H_n = n \times [A_J/(2g_J\mu_B)] = n \times 230$ Oe (with $-7 \leq n \leq +7$, n being an integer, and $A_J/k_B \approx 38.6$ mK) is in agreement with the crossing fields of the electronuclear Zeeman diagram calculated within the single-ion picture [see solid lines in Fig. 1 and in Fig. 4(a) (below)]. As the single-ion tunneling dynamics occurs in a thermally activated regime, the width of these anomalies is temperature dependent. Besides, similarly to unexpected magnetization steps observed in hysteresis loops at very low temperatures, additional peaks and/or dips are also evidenced for integer values of $|n|$ larger than 7, as well as for half-integer n values with $-13 \leq 2n \leq +13$, which do not correspond to any level crossing in Fig. 4(a) (below). These new features strongly suggest that *two* new tunneling mechanisms occur.

Because of the dipolar nature of the intra-atomic hyperfine coupling, all these fields involve a unique property within the single-ion representation: Some energy levels are equally separated, so that simultaneous multispin transitions may conserve the total energy. This allows for a *multi-ion quantum dynamics*. Furthermore, part of these cross-spin relaxation (CSR) processes may *not* conserve the total magnetization of the system, some electronuclear states being associated with opposite directions of the magnetic moment. Among these transitions, we can clearly distinguish between the cotunneling and the biased tunneling processes. In particular, we discuss the role of cotunneling transitions for the first time in mesoscopic magnetism. Here, we focus on the tunneling of pairs of Ho^{3+} ions, weakly coupled by anisotropic dipolar interactions, which leads to new resonance conditions that are an intrinsic property of the two-ion picture (no matter is the coupling strength), and show that pairs of Ho^{3+} ions may cotunnel with interactions as weak as a few mK. This suggests that, under these specific field conditions, any environmental Ho^{3+} ion may cotunnel with a "central" spin, making the quantum spin dynamics much more collective than expected before.

As discussed below, ac-susceptibility anomalies for half-integer n are *only* related to cotunneling events involving a two-ion process. These occur only within the dipolar window, their width thus being temperature independent. In addition, this width is smaller than the one related to thermally activated single-ion processes, because at $T \geq 1.75$ K the homogeneous broadening due to spin-phonon couplings is larger than the inhomogeneous dipolar broadening. Note that thermal activation over the energy barrier still requires longer times than the CSR *tunneling* events; the spin-phonon relaxation time can be measured at applied fields located out of any resonance [10]. In this strongly diluted limit, N-ion cotunneling transitions with $N > 2$ are less probable. If not, $N = 3$ transitions should be observed, the first resonance condition $H_{(n=1)}/3$ being out of the dipolar width of the zero-field resonance. Finally, to clearly distinguish between every tunneling mechanism, we used a higher measurement frequency f_m to evidence the role of dipolar-biased tunneling processes. Indeed, these lead to additional anomalies in the dissipative response. At $f_m = 800$ Hz and $T = 1.75$ K, the relaxation rate associated with a thermally activated single-ion tunneling process is smaller than f_m (case *i* in Fig. 2), whereas it is larger for the dipolar-biased tunneling process (case *iii*). Both rates increase being closer to resonance conditions with integer n values and $|n| \leq 7$. However, the dissipative response can either increase or decrease close to a resonance (case *i* or *iii*, respectively). As the phonon-induced broadening is larger than the dipolar-induced one in this temperature range, the response first *increases* when the applied field gets closer to the resonance, but still being out of the dipolar window so that CSR do not occur. When this field enters the dipolar window centered around the resonance, the relaxation is quickly dominated by the CSR rate and the dissipative response now *decreases.* This feature allows us to clearly evidence, for the first time, the dipolar-biased tunneling mechanism as the occurrence of a dip dug in the dissipative response [see Fig. 3(b)]. Again, the width of this dip corresponds to the narrow dipolar window, but it is now *temperature independent* only below $T \approx 2.2$ K. When the temperature is increased further, the thermally activated tunneling rate indeed gets faster than the measurement frequency. The large maximum envelope of the response then turns into a minimum and we cannot distinguish between these two processes anymore.

To underline the role of spin-spin interactions and discuss the physics of CSR in LiYF$_4$:Ho^{3+} in detail, we go beyond the single-ion picture and introduce a two-ion representation energy scheme. As shown in Fig. 4(b), within this four-body picture (two electronic angular momenta and two nuclear spins) the former situation of equally spaced levels now corresponds to the existence of energy-level crossings of pair states. These are associated with either a cotunneling event (that is, two spins, initially in the same electronic state, flip simultaneously to the opposite state), a biased tunneling process (that is, only one spin flips), or a flip-flop process (that is, two spins with an opposite initial state flip simultaneously).

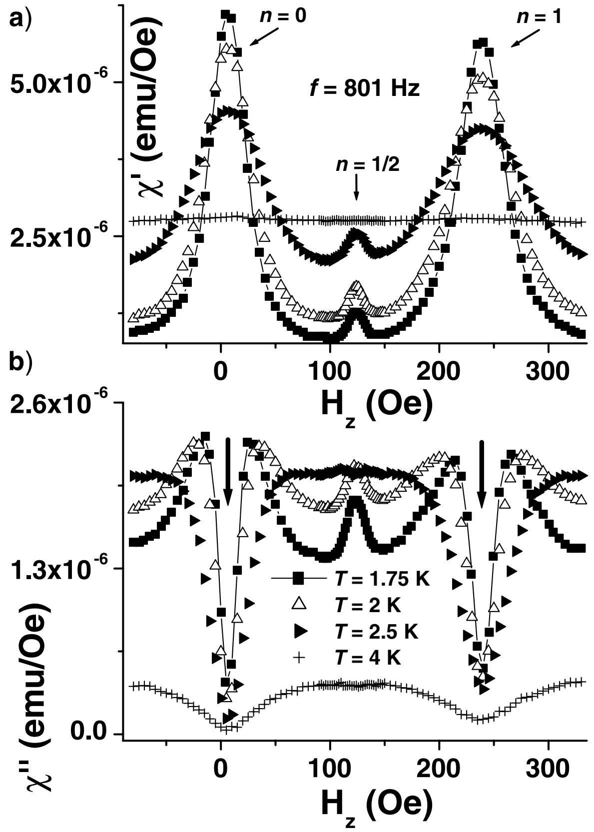

FIG. 3. (a),(b) The ac susceptibility measured at a larger frequency $f_m = 800$ Hz. Dipolar-biased tunneling is clearly evidenced, at low-enough temperatures, due to a decrease in the dissipative response for every integer n value. The large arrows in (b) show the dips observed for $n = 0$ and $n = 1$. The width of these dips is constant below $T \approx 2.2$ K and corresponds to the average amplitude of dipolar interactions.

Only the first two mechanisms contribute to the relaxation of the magnetization, the latter being associated with the so-called spin-diffusion phenomenon. The two-ion Zeeman diagram was calculated on the basis of the single-ion electronuclear states shown in Fig. 4(a). Details of the calculation will be published elsewhere. Without taking any interaction between Ho^{3+} ions into account, we emphasize in Fig. 4(b) the intrinsic new features of this four-body picture: Some additional crossing fields are related only to the energy-level separations within the single-ion picture (see dotted lines). New tunneling resonances correspond to either a coreversal of two Ho^{3+} ions ($|n| \leq 14$, integer $2n$) or to a single-spin flip ($8 \leq |n| \leq 14$, integer n). The effect of an additional *isotropic* coupling is shown in the inset of Fig. 4(b), using a large amplitude for the sake of clarity. Part of the degeneracies are removed so that, in an ensemble of weakly coupled mesoscopic spins, some crossings are shifted by a distribution of equivalent molecular fields H_{bias}, leading to biased tunneling. Nevertheless, cotunneling crossing fields are not affected. Note that only

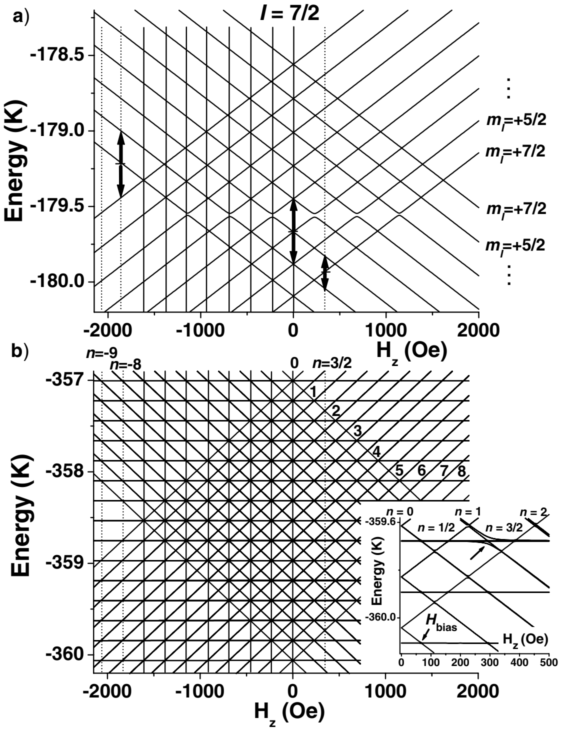

FIG. 4. (a) Electronuclear energy levels calculated within the single-ion representation. Equally spaced levels in the Zeeman diagram allow for nondissipative CSR processes in the tunneling regime. As suggested by large arrows, *three* various kinds of CSR may occur at well-defined values $H_n = n \times 230$ Oe. (b) Within the two-ion Zeeman diagram, each cross-relaxation process involving a pair of magnetic moments now corresponds to a level crossing. Note that the finite slopes are twice larger than in (a). Their crossing describes a cotunneling process (integer or half-integer n, with $|2n| \leq 14$). Other crossings involve only the flipping of one magnetic moment (integer n, with $|n| \leq 14$) or a flip-flop process. The inset shows how an isotropic interaction, with a given coupling strength, removes part of the degeneracies for integer n values, leading to biased tunneling, as well as an avoided level crossing due to both Ho^{3+} nuclear spin and first electronic singlet.

anisotropic interactions allow for CSR tunneling transitions, leading to finite tunneling gaps, such as the nonsecular part of the dipole-dipole interaction.

All the features observed in Fig. 1 now have an interpretation in terms of level crossings involving a pair of Ho^{3+} ions, that is, within the four-body picture. The same ideas can be extended to N-ion cotunneling processes with $N > 2$, which may occur at resonant fields $H_p^{(N)} = p/N \times [A_J/(2g_J\mu_B)]$ (integer p, with $|p| \leq 7N$), as well as to weakly coupled SMMs, such as the well-known molecular nanomagnets Mn_{12} and Fe_8. Indeed, cotunneling could explain specific heat anomalies observed at intermediate temperatures in Fe_8 by Gaudin and co-workers [11]. Moreover, isotropic exchange-biased tunneling was also recently observed in a molecular dimer $[Mn_4]_2$ but in a strong antiferromagnetic coupling regime [12], thus preventing cotunneling events, as well as in weakly interacting Mn_4 SMMs [13], still with a larger ferromagnetic exchange coupling than dipolar interactions.

In $LiYF_4$:Ho^{3+}, two-ion energy levels are strongly degenerate due to the high degree of symmetry of the single-ion Zeeman diagram, the strong dipolar hyperfine coupling resulting in many equally separated energy levels. This unique property makes diluted Ho^{3+} ions in $LiYF_4$ a *model system* to evidence, and describe in detail all the various CSR tunneling mechanisms that can occur in an ensemble of weakly coupled mesoscopic spins. Generally speaking, additional resonance conditions associated with the multispin tunneling dynamics can be easily deduced from energy-conserved multitransition events within the single-spin picture. In particular, cotunneling processes are a pure *intrinsic property of the many-body picture*, even for vanishing interactions, the crossing fields being independent of the coupling strength. More importantly, cotunneling events are allowed only by anisotropic interactions, which are also expected to be a key ingredient to understand quantum fluctuations at larger scales in complex systems, such as in the quantum spin glass problem.

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