PHYSICAL REVIEW B **82**, 060403(R) (2010)

Spin-lattice relaxation via quantum tunneling in an Er^{3+}-polyoxometalate molecular magnet

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(Received 10 June 2010; revised manuscript received 27 July 2010; published 18 August 2010)

We investigate the mechanism of spin-lattice relaxation of Er ions encapsulated in polyoxometalate clusters, which below 4 K can only reverse its spin via quantum tunneling processes. The temperature-independent rate τ^{-1} is, at zero field, ten orders of magnitude larger than the rates predicted for direct phonon-induced processes. In addition, we observe that τ^{-1} is suppressed by external magnetic bias and hyperfine interactions but enhanced by increasing the concentration of Er ions. The observed relaxation agrees with predictions for pure quantum tunneling, showing that this phenomenon drives the thermalization of electronic spins. A possible link between these two phenomena is discussed, involving the collective emission of phonons from particular spin configurations attained via quantum tunneling.

DOI: 10.1103/PhysRevB.82.060403 PACS number(s): 75.50.Xx, 75.45.+j, 76.30.Kg, 75.40.Gb

The fundamental equations of magnetism, including Curie's law, rely on the ability of magnetic moments to attain thermal equilibrium with the solid lattice. In spite of the progress achieved in studying and manipulating individual spins in solids,[1] the spin-lattice relaxation (SLR) mechanisms are not well understood yet. An intriguing situation arises, near zero field, for strongly anisotropic spins, e.g., magnetic molecular clusters or rare-earth ions. When thermally activated tunneling processes[2] die out, at sufficiently low temperatures (typically $T \lesssim 1$ K), spins can only flip by pure quantum tunneling (QT) across the anisotropy energy barrier. Theoretical descriptions[3–5] of QT in the presence of hyperfine couplings and dipolar spin-spin interactions account well for experiments that measure the time-dependent magnetization under such conditions.[6–8] Concerning SLR, a major difficulty arises. It stems from the fact that QT modifies the magnetization but conserves the energy of the ensemble of nuclear and electronic spins. Therefore, equilibrium states might well be reached long after the characteristic time scales of QT.[9]

However, a few experiments suggest otherwise. Specific-heat studies[10] indicate that Mn_4 and Fe_8 single-molecule magnets (SMM) attain thermal equilibrium at rates comparable to those found in magnetization relaxation experiments. In addition, NMR experiments on Mn_{12} clusters[11] show that the nuclear spin and bath temperatures remain the same down to the neighborhood of absolute zero.

In order to elucidate the nature of the SLR mechanism and its relationship with QT, direct measurements of the SLR rates as a function of temperature, magnetic field, concentration of spins, etc., are clearly desirable. Studying the SLR of molecular nanomagnets at very low temperatures and under weak magnetic fields is, however, a demanding experimental task because tunneling time scales are on the order of days even for clusters made of a few atoms. In order to overcome this difficulty, simpler molecules need to be studied. In the present work, we report the SLR rates of polyoxometalate (POM) clusters containing individual lanthanide ions. The results evidence that the thermalization of electronic spins is dictated by tunneling fluctuations.

We have chosen as molecular nanomagnet the POM cluster of the salt $Na_9[Er(W_5O_{18})_2]\cdot yH_2O$, hereafter referred to as ErW_{10}, which behaves as a SMM at low T.[12] It consists of a single Er^{3+} ion sandwiched between two POM moieties [see Fig. 1(a)] with a D_{4d} local symmetry. ErW_{10} crystallizes in a triclinic structure with $Z=2$ molecules per unit cell. Spin-spin interactions are expected to be very weak, even in the pure compound, because nearest-neighbor distances are $\simeq 13$ Å. Solid solutions $Er_xY_{1-x}W_{10}$ were synthesized as well, by dissolving together the corresponding amounts of ErW_{10} and YW_{10}.[13] The magnetic susceptibility of single crystals was measured, above 1.8 K, using a commercial superconducting quantum interference device (SQUID) magnetometer that enables rotating the sample *in situ*. The ac magnetic field amplitude was $h_{ac}=4$ Oe. Experiments in the region of very low temperatures ($T \geq 13$ mK) were performed with a homemade SQUID microsuceptometer[14] operating in the frequency region $0.01 < \nu < 1$ MHz. The sample was an $800 \times 400 \times 200$ μm^3 ErW_{10} single crystal, whose anisotropy axis made approximately 42° with respect to the ac magnetic field ($h_{ac} < 1$ mOe). Experiments on diluted compounds were performed on powdered specimens.

The susceptibility of ErW_{10} is shown in Fig. 2. The very large ratio between the susceptibilities measured along the

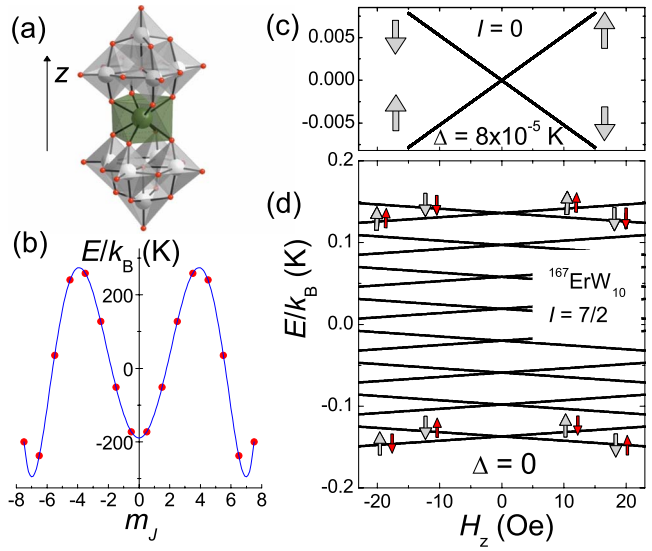

FIG. 1. (Color online) (a) Molecular structure or ErW_{10} with the Er^{3+} ion at its center. (b) Magnetic energy levels of ErW_{10} at zero field. The solid line represents the classical potential energy. (c) and (d) represent the energies of lowest electronic energy states ($m_J = \pm 13/2$) of $I=0$ isotopes and $^{167}ErW_{10}$ ($I=7/2$), respectively. Calculations are made for $B_{\mathrm{dip},\perp}=80$ Oe$\simeq\sigma_{\mathrm{dip}}$. Gray and solid (red) arrows indicate the electronic- and nuclear-spin orientations, respectively.

molecular axis (χ_z) and perpendicular to it ($\chi_\perp$) confirms the strong uniaxial character of the magnetic anisotropy.[12] The spin Hamiltonian can be written, in terms of Steven's operators O_n^m, as follows:

$$\mathcal{H} = B_{20}O_2^0 + B_{40}O_4^0 + B_{60}O_6^0 + B_{44}O_4^4 + g\mu_B\mathbf{HJ} + A_J\mathbf{IJ}, \tag{1}$$

where the first four terms account for the magnetic anisotropy and the last two describe the interactions of the $J=15/2$ electronic angular momentum with the magnetic field H and with the Er nuclear spin I (only for the ^{167}Er isotope), respectively. The gyromagnetic factor $g=6/5$ and the hyperfine coupling constant $A_J/k_B=-6\times10^{-3}$ K. The diagonal parameters $B_{20}/k_B=-1.35$ K, $B_{40}/k_B=-1.07\times10^{-2}$ K, and $B_{60}/k_B=1.07\times10^{-4}$ K have been determined by the simultaneous fit of the equilibrium susceptibility, the specific-heat, and electron-spin-resonance data.[12] The off-diagonal parameter $B_{44}/k_B=1.8(5)\times10^{-2}$ K has been determined by fitting the SLR rate in the thermally activated regime (see below). Erbium being a Kramers ion, electronic $\pm m_J$ states of $I=0$ isotopes (77% in natural Er) are degenerate at zero field. Below 4 K, the population of excited states above the ground state $m_J=\pm13/2$ doublet becomes smaller than one in 10^4. This cluster represents therefore a model two-level system.

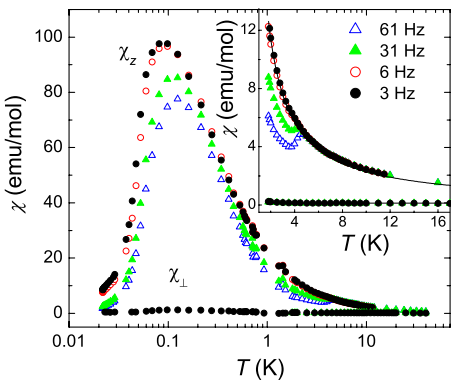

FIG. 2. (Color online) Longitudinal and transverse ac susceptibilities of ErW_{10}. The inset shows a magnification of the region above 2 K in linear scale. The lines represent the equilibrium susceptibilities calculated from the energy-level structure shown in Fig. 1.

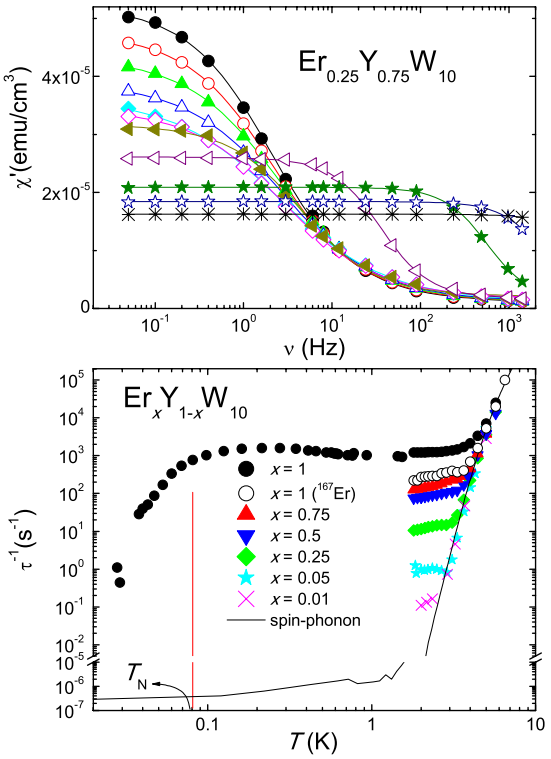

FIG. 3. (Color online) Top: frequency-dependent susceptibility of $Er_{0.25}Y_{0.75}W_{10}$ measured at $T=$ (from top to bottom) 1.8, 2, 2.22, 2.5, 2.86, 3.09, 3.33, 4, 5, 5.7, and 6.5 K. Solid lines are least-squares Cole-Cole fits (Ref. 15). Bottom: SLR rates. The solid line shows the prediction of standard theories (Refs. 17 and 18) of SLR. The vertical line marks the magnetic ordering temperature $T_N=81$ mK of ErW_{10}.

χ_z of ErW_{10} depends on frequency below ~5 K, signaling the "freezing" of the spins by the anisotropy barriers. The blocking is however not complete and not even observable at all for $\nu<10$ Hz. This behavior indicates that the thermally activated spin reversal is gradually replaced, below 4 K, by a temperature-independent relaxation mechanism, as will be confirmed below. To determine, at each temperature, the SLR rate τ^{-1} we fit the in-phase χ' and out-of-phase χ'' susceptibility data using a Cole-Cole function[15] (an illustrative example is shown in Fig. 3). The susceptibility provides the full picture of the magnetic relaxation, from the adiabatic limit χ_S, at $1/\nu\ll\tau$, to the isothermal or equilibrium response χ_T, for $1/\nu\gg\tau$.

Above 100 mK, χ_T follows the Curie-Weiss' law, χ_T

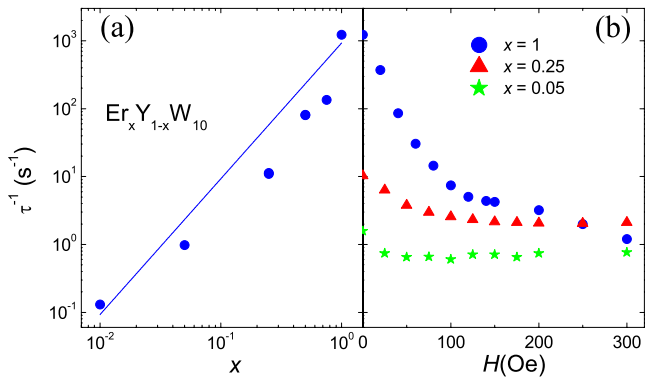

FIG. 4. (Color online) SLR rate of $Er_xY_{1-x}W_{10}$ at 2 K as a function of (a) concentration x at $H=0$ and (b) the applied magnetic field. The line in (a) is a quadratic fit.

$=C(T-\theta)$ with $\theta=-88$ mK, showing that these linear-response experiments measure SLR to *thermal equilibrium*, and not the spin-spin relaxation within the "spin bath." The low-frequency χ' of ErW_{10} attains a maximum at $T_N=81$ mK (Fig. 2), which marks the onset of long-range magnetic order. The maximum χ' is three times lower than the ferromagnetic limit $1/N$, where $N=4\pi$ is the demagnetizing factor of a flat single crystal, suggesting that the order is antiferromagnetic (AF). Above T_N, spin-spin interactions give rise to distributions $P(H_{\mathrm{dip},z})$ and $P(H_{\mathrm{dip},\perp})$ of, respectively, longitudinal and transverse dipolar fields. The width σ_{dip} can be estimated roughly from the condition $2g\mu_B J\sigma_{\mathrm{dip}}\sim k_B T_N$, which gives $\sigma_{\mathrm{dip}}\simeq 70$ Oe. Dipolar fields split the ground-state doublet by the amount $\Delta E=(\Delta^2+\xi_{\mathrm{dip}}^2)^{1/2}$, where $\Delta\equiv g_\perp\mu_B H_{\mathrm{dip},\perp}$, is the quantum tunnel splitting, $\xi_{\mathrm{dip}}\equiv g_z\mu_B H_{\mathrm{dip},z}$ is the dipolar bias, and g_z and $g_\perp$ are the longitudinal and transverse effective gyromagnetic ratios, respectively. Notice that $g_\perp$ reflects the combined action of the off-diagonal anisotropy terms and the transverse dipolar fields, as follows from arguments based on stationary perturbation theory.[16] Typical values (for $H_{\mathrm{dip}}\simeq\sigma_{\mathrm{dip}}$) are $\Delta/k_B\sim 8\times 10^{-5}$ K and $\xi_{\mathrm{dip}}/k_B\sim 0.08$ K.

Figure 3 shows the SLR rates of the $Er_xY_{1-x}W_{10}$ ($0.01\leqslant x\leqslant 1$) samples. A thermally activated process, with activation energy $U/k_B=63(1)$ K, dominates at high T. This high-temperature behavior is independent of x and, as shown in Fig. 3, it is well described by calculations made for conventional phonon-induced SLR processes.[17,18] The saturation of τ^{-1} observed below 4 K in ErW_{10}, defines the crossover to a pure quantum regime. In this regime, the observed relaxation is no longer compatible with simple SLR models:[17] the rate measured on ErW_{10} is ten(!) orders of magnitude faster than the rate of direct phonon-induced transitions. Further, it strongly depends on Er concentration, decreasing by nearly four orders of magnitude between $x=1$ and $x=0.01$ [see also Fig. 4(a)]. Another intriguing phenomenon is the abrupt drop of τ^{-1} near T_N. The unconventional character of the SLR mechanism is confirmed by the dependence of τ^{-1} on the external magnetic field H, shown in Fig. 4(b). It does not increase with H, as is expected for a direct phonon-induced process,[17] but instead decreases.

As we argue next, the observed SLR agrees with predictions for the tunneling rate Γ,[3–5] thereby showing that a direct link exists between these two phenomena. At zero field, only the small fraction of clusters fulfilling the condition $\Delta\gtrsim\xi_{\mathrm{dip}}$ can reverse its magnetic moment at any given time.[19] The net Γ is then approximately described by[3–5]

$$\Gamma=\frac{\Delta^2}{\hbar}P(\xi_{\mathrm{dip}}=0), \tag{2}$$

where $P(\xi_{\mathrm{dip}})\equiv P(H_{\mathrm{dip},z})/g_z\mu_B$. For a Gaussian distribution of bias, $P(\xi_{\mathrm{dip}}=0)=1/\sqrt{(2\pi)}g_z\mu_B\sigma_{\mathrm{dip}}$, which gives $\Gamma\sim 3\times 10^3$ s^{-1}. Γ is independent of T and, more importantly, ten orders of magnitude larger than the rate of direct phonon-induced transitions, in fair agreement with $\tau^{-1}\simeq 1.2\times 10^3$ s^{-1}. The opposite effects caused by external and dipolar magnetic fields (see Fig. 4) can also be accounted for as follows. The external bias H_z blocks tunneling by energetically detuning spin-up and spin-down states [notice that $P(\xi_{\mathrm{dip}}=-g\mu_B JH_z)<P(\xi_{\mathrm{dip}}=0)$]. By contrast, diluting the spins reduces σ_{dip}, which affects both Δ and ξ_{dip}. Taking, as a first approximation, $\sigma_{\mathrm{dip}}\propto x$ leads to and *increase* in $\Gamma(H=0)\propto x$, in qualitative agreement with the concentration dependence of τ^{-1} [although experimentally we find $\tau^{-1}(H=0)\propto x^2$]. Finally, we consider the slowing down observed near T_N. In the AF phase, the distribution $P(\xi_{\mathrm{dip}})$ becomes narrower and its maximum shifts from $\xi_{\mathrm{dip}}=0$ toward $\xi_{\mathrm{dip}}\sim k_B T_N$,[20] generating a net bias. A curious competition arises: the onset of magnetic order, via QT, turns tunneling itself, as well as relaxation toward the ordered state, progressively slower.

The last ingredient we have investigated is the effect of hyperfine interactions. We have repeated the same experiments on a sample, $^{167}ErW_{10}$, enriched with a 95.3% of the ^{167}Er isotope ($I=7/2$). Frequency-dependent χ' and χ'' broaden considerably. The broadening reveals the coexistence of multiple SLR processes associated with the splitting of the ground-state electronic doublet into an electronuclear multiplet [see Fig. 1(c)]. As shown in Fig. 3, the (average) zero-field τ^{-1} of $^{167}ErW_{10}$ is about 4.5 times smaller than the rate measured for ErW_{10}. The drastic slowing down of SLR by hyperfine interactions contrasts sharply with the enhancement predicted for spin-phonon processes.[17,21] It shows also that the fast SLR of the nonenriched sample cannot be originated by cross relaxation[22] with ^{167}Er spins but must be attributed to QT of ions with $I=0$. The isotopic effect can, in fact, be easily reconciled with the idea of SLR via QT [cf. Eq. (2)]. On the one hand, the hyperfine splitting detunes energetically states related by the flip of the electronic spin (see Fig. 1). On the other, the tunnel splitting associated with the simultaneous reversal of the electronic and nuclear spins is $\Delta\sim 0$.

Summarizing, the present results show that QT provides a very efficient mechanism for SLR and underline a strong discrepancy between accepted theories and experiments on a fundamental problem (at the basis of Curie's law). Particularly puzzling is the question of how energy flows from the spins to the lattice. This question was considered in Ref. 9 by assuming that detailed balance holds in QT processes. But even under these conditions, the predicted SLR rate is much

longer than Γ. We speculate that a prominent role can be played by the collective emission of a single phonon by many spins. This possibility had been considered by the early theories of SLR (Refs. 17 and 23) and recently associated with the "phonon super-radiance" and "phonon-laser" phenomena.[24] Some support for this proposal can be found in the strong dependence of τ^{-1} on x [Fig. 4(a)]. The maximum phonon-laser rate is $\tau_{\mathrm{L,max}}^{-1}=J(\Delta E/8\hbar M c_s^2)^{1/2}$, where $c_s=2.3\times10^5$ cm/s is the speed of sound and $M=\rho V$, with $\rho=3.411$ g/cm^3 the density and $V=3260.8$ Å^3 the unit-cell volume. We find $\tau_{\mathrm{L,max}}^{-1}\simeq10^4$ s^{-1}, a very large rate. QT would enable spins to "visit" energetically equivalent configurations, at a rate of order Γ. Configurations whose characteristic wave vector q is close to that of the emitted phonon might have sizeable τ_{L}^{-1},[24] thus enabling the spins to exchange energy with the lattice.

Mononuclear lanthanide-based POM clusters are also promising candidates to act as the hardware for quantum information.[12] Our work shows that off-equilibrium conditions, as required for the realization of quantum operations, can be stabilized by diluting the spins or by applying magnetic fields of moderate amplitude.

We acknowledge fruitful discussions with L. J. de Jongh, J. F. Fernández, D. Garanin, and E. M. Chudnovsky. The present work has been partly funded by grant MOLSpinQIP from the EU, grants Molecular Nanoscience (Consolider Ingenio 2010 Program), MOLCHIP, M3EM and NANOMOL from the Spanish MICINN, grant NABISUP from DGA, and the PROMETEO Program from the Generalidad Valenciana. Funding from the European Research Council Advanced Grant SPINMOL (to E.C.) is also acknowledged.

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[1] S. Ghosh, R. Parthasarathy, T. F. Rosenbaum, and G. Aeppli, Science **296**, 2195 (2002); S. Bertaina *et al.*, Nat. Nanotechnol. **2**, 39 (2007); S. Bertaina *et al.*, Nature (London) **453**, 203 (2008).

[2] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996); J. M. Hernández *et al.*, Europhys. Lett. **35**, 301 (1996); L. Thomas *et al.*, Nature (London) **383**, 145 (1996).

[3] N. V. Prokof'ev and P. C. E. Stamp, Rep. Prog. Phys. **63**, 669 (2000).

[4] N. V. Prokof'ev and P. C. E. Stamp, Phys. Rev. Lett. **80**, 5794 (1998).

[5] J. F. Fernández and J. J. Alonso, Phys. Rev. Lett. **91**, 047202 (2003).

[6] W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, and C. Paulsen, Phys. Rev. Lett. **82**, 3903 (1999); W. Wernsdorfer, A. Caneschi, R. Sessoli, D. Gatteschi, A. Cornia, V. Villar, and C. Paulsen, *ibid.* **84**, 2965 (2000).

[7] R. Giraud, W. Wernsdorfer, A. M. Tkachuk, D. Mailly, and B. Barbara, Phys. Rev. Lett. **87**, 057203 (2001).

[8] N. Ishikawa, M. Sugita, and W. Wernsdorfer, Angew. Chem., Int. Ed. **44**, 2931 (2005).

[9] J. F. Fernández, Phys. Rev. B **66**, 064423 (2002).

[10] M. Evangelisti, F. Luis, F. L. Mettes, N. Aliaga, G. Aromi, J. J. Alonso, G. Christou, and L. J. de Jongh, Phys. Rev. Lett. **93**, 117202 (2004); M. Evangelisti, F. Luis, F. L. Mettes, R. Sessoli, and L. J. de Jongh, *ibid.* **95**, 227206 (2005).

[11] A. Morello, O. N. Bakharev, H. B. Brom, R. Sessoli, and L. J. de Jongh, Phys. Rev. Lett. **93**, 197202 (2004).

[12] M. A. AlDamen, J. M. Clemente-Juan, E. Coronado, C. Martí-Gastaldo, and A. Gaita-Ariño, J. Am. Chem. Soc. **130**, 8874 (2008); M. A. AlDamen *et al.*, Inorg. Chem. **48**, 3467 (2009).

[13] M. Barsukova, M. H. Dickman, E. Visser, S. S. Mal, and U. Kortz, Z. Anorg. Allg. Chem. **634**, 2423 (2008).

[14] M. J. Martínez-Pérez, J. Sesé, F. Luis, D. Drung, and T. Schurig, Rev. Sci. Instrum. **81**, 016108 (2010).

[15] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

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

[17] R. de L. Kronig, Physica **6**, 240 (1939); J. H. Van Vleck, Phys. Rev. **57**, 426 (1940); R. Orbach, Proc. R. Soc., London **A264**, 458 (1961); **A264**, 485 (1961).

[18] The SLR rate shown in Fig. 3 was calculated numerically, solving a quantum master equation including phonon-induced transitions between energy eigenstates. The spin-phonon interaction Hamiltonian was $3B_{20}\{(\epsilon_{xz}+\omega_{xz})\otimes[S_xS_z+S_zS_x]+(\epsilon_{yz}+\omega_{yz})\otimes[S_yS_z+S_zS_y]\}$, where ϵ_{iz} and ω_{iz} represent phonon-induced strains and rotations, respectively. The speed of sound $c_s=2.3\times10^5$ cm/s was determined from the Debye temperature $\theta_D=57$ K extracted from heat-capacity experiments (Ref. 12).

[19] Dipolar couplings to ^{23}Na (100%, $I=3/2$) and ^{183}W (14%, $I=1/2$) nuclear spins of the molecule can broaden the "energy window" for QT (Refs. 3–5). The estimated hyperfine bias $\xi_0/k_B\sim2\times10^{-4}$ K is, however, of the same order as Δ/k_B.

[20] M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946).

[21] The enhancement of direct phonon-induced relaxation rates by hyperfine interactions was observed in ESR experiments performed on $Er_xY_{1-x}(C_2H_5SO_4)_3\cdot9H_2O$ by G. H. Larson and C. D. Jeffries, Phys. Rev. B **145**, 311 (1966).

[22] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. B **114**, 445 (1959).

[23] H. N. V. Temperley, Proc. Cambridge Philos. Soc. **35**, 256 (1939).

[24] E. M. Chudnovsky and D. A. Garanin, Phys. Rev. Lett. **93**, 257205 (2004).