Spin-lattice relaxation via quantum tunneling in diluted crystals of Fe₄ single-molecule magnetsA. Repollés,^{1,2} A. Cornia,^{3,*} and F. Luis^{1,2,†}¹*Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain*²*Departamento de Física de la Materia Condensada, Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain*³*Dipartimento di Scienze Chimiche e Geologiche and UdR INSTM, Università di Modena e Reggio Emilia, via G. Campi 183, 41125 Modena, Italy*

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We investigate the dynamic susceptibility of Fe₄ single-molecule magnets with integer spin ($S = 5$) in the form of pure crystals as well as diluted in crystals of isostructural, but nonmagnetic, Ga₄ clusters. Below approximately 1 K, the spin-lattice relaxation becomes dominated by a temperature-independent process. The spin-lattice relaxation time τ measured in this “quantum regime” is 12 orders of magnitude shorter than the characteristic time scale of direct phonon-induced processes but agrees with the relaxation times of pure (i.e., not assisted by phonons) spin tunneling events. The present results show that the latter phenomenon, despite conserving the energy of the ensemble of electronic and nuclear spins, drives the thermalization of electronic spins at very low temperatures. The spin-lattice relaxation time scales with the concentration of Fe₄, thus suggesting that the main effect of dipolar interactions is to block tunneling. The data show therefore no evidence for the contribution of collective phonon emission processes, such as phonon superradiance, to the spin-lattice relaxation.

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Single molecule magnets (SMMs) [1] are high-spin magnetic molecules comprising one or more metal centers encapsulated in a shell of organic ligands. They provide a very attractive workbench for research on quantum phenomena in magnetism, such as magnetization tunneling [2–4], Berry phase interferences [5], quantum spin coherence [6–8], and quantum phase transitions [9]. Although the underlying physics governing such phenomena is fairly well understood, some fundamental questions still remain open.

A particularly intriguing puzzle concerns the nature of spin-lattice relaxation (SLR) mechanisms that bring spins to thermal equilibrium at very low temperatures, typically for $T \lesssim 1$ K, when thermally activated processes [10–12] die out. Under these conditions and near zero magnetic field, spins predominantly flip by tunneling across the anisotropy energy barrier. Hyperfine interactions with environmental nuclear spins (e.g., those of the metal centers themselves and of other atoms present in the outer ligand shell) can compensate for the magnetic bias associated with intercluster dipolar interactions, thus bringing some molecular spins close to resonance conditions and enabling them to tunnel [13–15]. Tunneling modifies the magnetization but conserves the energy of the ensemble of nuclear and electronic spins. By contrast, SLR requires that magnetic energy is either released or absorbed from the lattice, e.g., via the direct emission or absorption of a phonon [16]. Since the latter events can be extremely slow at low magnetic fields, it can be expected that magnetization dynamics and SLR take place at very different time scales [17].

Yet, experiments performed on different SMMs [18–20] give SLR times that are close to the expected tunneling times, thus suggesting that the thermalization of electronic spins is dictated by tunneling fluctuations. A plausible, yet *qualitative* interpretation of the existing experimental evidences is that

SLR takes place via phonon superradiance [21] from particular spin configurations, which the spin ensemble “visits” via tunneling processes [22]. This phenomenon has been investigated on lanthanide ions diluted in diamagnetic crystals [22,23]. Unfortunately, the results are obscured by either the dependence of the quantum tunnel splitting Δ on concentration (for Kramer’s ions) or the existence of large hyperfine splittings, which dominate the physics at very low T . These effects prevent any simple, quantitative comparison of SLR experiments with theoretical predictions for spin tunneling.

Crystals of *polynuclear* SMMs can provide a valuable alternative. However, synthesizing crystalline solid solutions of intact polynuclear species and their diamagnetic analogues is a very challenging task. First, preparing isostructural but diamagnetic variants of known SMMs may be difficult or impossible, especially for mixed-valent species. Second, the solid solution must crystallize without metal scrambling, i.e., without any exchange of metals that produces mixed-metal species. The first successful synthesis of diluted polynuclear SMMs in crystalline form was achieved [24] with tetra-iron molecular clusters (see Fig. 1), which are known to be highly stable and robust [25–27]. A fraction of Fe₄ clusters ($S = 5$) is replaced with nonmagnetic but structurally equivalent Ga₄ clusters, thereby providing a means of controlling the characteristic energy scale of dipolar couplings. In addition, the vast majority (98%) of Fe atoms carry no nuclear spin. These crystals are therefore model systems to study the relationship between SLR and tunneling, and to elucidate the role played by dipolar interactions. In this paper, we study the SLR times of pure as well as diluted Fe₄ crystals and compare the results with existing theories for SLR and spin tunneling.

Single-crystalline samples of $[(\text{Fe}_4)_x(\text{Ga}_4)_{1-x}(\text{L})_2(\text{dpm})_6] \cdot \text{C}_6\text{H}_6$, hereafter referred to as $(\text{Fe}_4)_x(\text{Ga}_4)_{1-x}$ with $x = 1.00$ and 0.05 , were prepared as described in Ref. [24]. Compounds of the series $(\text{Fe}_4)_x(\text{Ga}_4)_{1-x}$ are isomorphous and crystallize in the monoclinic space group $C2/c$ with four equivalent molecules per unit cell. Only minor variations

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FIG. 1. (Color online) (a) Molecular structure of Fe_4 viewed along the normal to the metal plane, which is taken to coincide with the easy magnetic axis (Z). (b) Magnetic energy level scheme of Fe_4 (dotted horizontal lines). Levels are labeled by the m quantum number associated with the Z component of the spin in the absence of tunneling effects. The solid line is the classical double-well potential as a function of m . (c) Crystal structure of Fe_4 SMMs diluted in a diamagnetic crystal of Ga_4 clusters. Color code: Fe, light orange; Ga, dark blue; O, red; C, gray. Hydrogen atoms and benzene lattice molecules have been omitted for clarity. The normal to the metal plane (Z) forms an angle of 1.44° with a^* .

of unit cell parameters are observed in the series, with a 1% contraction of unit cell volume from $x = 1.00$ to $x = 0$ at 120 K. Magnetic measurements in the region of $1.8 \text{ K} \leq T \leq 300 \text{ K}$ were performed on powder specimens using a commercial SQUID magnetometer. Ac susceptibility measurements have been extended down to 13 mK using a μ -SQUID susceptometer installed inside the mixing chamber of a ^3He - ^4He dilution refrigerator [28,29]. In these experiments, $\sim 800 \times 400 \times 200 \mu\text{m}^3$ single crystals were directly placed on top of one of the two μ -SQUID loops. The easy magnetic axis made an angle $\psi \simeq 56^\circ$ with respect to the ac excitation magnetic field ($h_{\text{ac}} < 1 \text{ mOe}$). The frequency of the latter was varied between $\omega/2\pi = 0.01 \text{ Hz}$ and $2 \times 10^5 \text{ Hz}$.

Representative examples of the in-phase χ' and out-of-phase χ'' magnetic susceptibilities of Fe_4 and $(\text{Fe}_4)_{0.05}(\text{Ga}_4)_{0.95}$, measured as a function of frequency at fixed temperatures, are shown in Fig. 2. They show the typical behavior of a SMM, with a well defined transition from equilibrium conditions, at sufficiently low frequencies, to adiabatic conditions, in the opposite frequency limit. The

FIG. 2. (Color online) Frequency dependent susceptibility isotherms of pure Fe_4 (left) and of $(\text{Fe}_4)_{0.05}(\text{Ga}_4)_{0.95}$ (right) at several temperatures. Solid lines are least-square Cole-Cole fits [cf. Eqs. (1) and (2)]. The insets show the temperature dependence of the reciprocal in-phase susceptibility jump $1/\Delta\chi$. Solid lines are least-square Curie-Weiss fits, with the parameters shown in each graph.

transition takes place approximately when $\omega\tau \simeq 1$, where τ is the SLR relaxation time, and coincides with the maximum of χ'' . We find (see the insets of Fig. 2) that the in-phase susceptibility “jump” $\Delta\chi$ (i.e., the net variation between its high and low frequency limits) follows Curie-Weiss law $\Delta\chi \simeq C/(T - \theta)$, where C is the Curie constant and θ is the Weiss temperature that depends on the average strength of intermolecular magnetic interactions. This shows that linear susceptibility experiments measure SLR to *thermal equilibrium* and not spin-spin relaxation within the “spin-bath.” This experimental situation contrasts sharply with that met in spin tunneling experiments, be it magnetization hysteresis or Landau-Zener relaxation measurements. In the latter case, magnetization jumps that occur at tunneling resonances (level crossings) link two nonequilibrium spin configurations. As expected, C scales with x since it is proportional to the number of spins per unit of sample mass. In addition, θ of Fe_4 is about six times larger than that of $(\text{Fe}_4)_{0.05}(\text{Ga}_4)_{0.95}$, thus showing that interactions become significantly reduced by dilution.

Above $T \simeq 1 \text{ K}$, SLR times were obtained by fitting susceptibility isotherms with Cole-Cole functions [30]

$$\chi' = \chi_S + \frac{(\chi_T - \chi_S) \{1 + (\omega\tau)^\beta \cos(\beta\pi/2)\}}{1 + 2(\omega\tau)^\beta \cos(\beta\pi/2) + (\omega\tau)^{2\beta}} \quad (1)$$

$$\chi'' = \frac{(\chi_T - \chi_S) (\omega\tau)^\beta \sin(\beta\pi/2)}{1 + 2(\omega\tau)^\beta \cos(\beta\pi/2) + (\omega\tau)^{2\beta}}, \quad (2)$$

where χ_T and χ_S are the equilibrium and adiabatic susceptibilities, respectively, and β gives information on the width of the distribution of relaxation times. We find that β ranges from 0.85 at $T = 2.1 \text{ K}$ to 0.79 at $T = 1.2 \text{ K}$ for pure Fe_4 and from 0.82 at $T = 2.1 \text{ K}$ to 0.72 at $T = 1.2 \text{ K}$ for $(\text{Fe}_4)_{0.05}(\text{Ga}_4)_{0.95}$. For temperatures below 1 K, the maxima of χ'' occur at frequencies lower than our minimum experimental limit

(0.01 Hz). Even so, SLR times can be approximately estimated using the relation $\tau \simeq [r/(\sin \beta \pi/2 - r \cos \beta \pi/2)]^{(1/\beta)}/\omega$, which follows from Eqs. (1) and (2). Here, $r = \chi''/(\chi' - \chi_S)$, and β and χ_S have been fixed to their respective values found at $T = 1.2$ K, as they are expected to vary only weakly with T .

The results are shown in Fig. 3. SLR relaxation times of both samples follow a thermally activated behavior above approximately 1.2 K, where $\tau \simeq \tau_0 \exp(U/k_B T)$, gradually approaching a nearly constant value below 1 K. However, some differences are seen between the two samples. The activation energy U is largest for the pure Fe_4 crystal, which also has the shortest prefactor τ_0 . The same trend was found by in-field (0.1 T) ac measurements on powder samples [24]. In the temperature-independent, or quantum, regime, the relaxation of the pure Fe_4 compound is about 10 times slower than that of the diluted sample.

We next compare these results with predictions for the characteristic time scales of phonon-induced relaxation and pure tunneling processes. Let us first consider the spin Hamiltonian of an isolated Fe_4 cluster. Magnetic interactions between the four Fe^{3+} ions within the cluster core, shown in Fig. 1, give rise to a ground state with a net spin $S = 5$ and a gyromagnetic ratio $g = 2.005(4)$. Interactions with the crystal field and with magnetic fields split this multiplet. These effects can be described by the following spin Hamiltonian:

$$\mathcal{H} = B_2^0 O_2^0 + B_2^0 O_2^2 + B_4^0 O_4^0 - g\mu_B \vec{S} \cdot \vec{H} + \mathcal{H}', \quad (3)$$

where $B_2^0/k_B = 0.200(2)$ K, $B_2^2/k_B = 0.023(1)$ K, and $B_4^0/k_B = 9(4) \times 10^{-6}$ K are magnetic anisotropy parameters,

FIG. 3. (Color online) Spin-lattice relaxation times of pure Fe_4 (top) and $(\text{Fe}_4)_{0.05}(\text{Ga}_4)_{0.95}$ (bottom). Solid symbols were obtained from Cole-Cole fits [Eqs. (1) and (2)] of isothermal susceptibility vs frequency measurements. Open symbols were obtained from the ratio $\chi''/(\chi' - \chi_S)$, as described in the text. Solid lines are phonon-induced relaxation times calculated by solving a Pauli master equation for the population of magnetic energy levels. The dotted lines are spin tunneling times predicted by Eq. (4).

determined from the fit of spectroscopic data, and $\mathcal{H}'$ is an effective term arising from interactions that mix states from different multiplets [24]. The ensuing energy level scheme is shown in Fig. 1. The population of the ground state level doublet, associated with the maximum projections $m = \pm S$ of the spin along the anisotropy axis Z , becomes larger than 99% for $T \lesssim 1$ K. Under these conditions, each Fe_4 cluster behaves effectively as a two level system, with an energy splitting $\Delta E = (\Delta^2 + \xi^2)^{1/2}$, where Δ is the quantum tunnel splitting induced by off-diagonal terms in Eq. (3) and $\xi \simeq 2g\mu_B S H_z$ is the energy bias associated with longitudinal magnetic fields. In Ref. [24], it was reported that $\Delta/k_B \simeq 9 \times 10^{-7}$ K and that it depends only weakly on transverse magnetic fields.

In order to realistically account for the influence of intermolecular magnetic interactions, we have also evaluated the distributions of internal dipolar fields in concentrated and diluted samples. Two model crystal samples were tested: (i) a spherical portion of crystal lattice with radius 300 Å and (ii) a model crystal mimicking the typical crystal shape bound by faces (001), (111), and (111) (and their equivalents) at distances of 20, 16, and 8 interplanar spacings, respectively, from the origin. The two models comprised comparable numbers of complete molecules ($\sim 4.3 - 4.5 \times 10^4$). To describe magnetically-diluted samples, a fraction $1 - x$ of molecules was randomly chosen and removed from the ensemble. Molecular spins were randomly assigned to be either in the $m = +5$ or in the $m = -5$ states, with equal probability. The dipolar field $\vec{H}_d = (H_{d,x}, H_{d,y}, H_{d,z})$ acting on each molecule was computed from the dipolar fields experienced by its constituent ions. The longitudinal component $H_{d,z}$ was evaluated as the weighted average over the four ions, whereas for the transverse (XY) component an unweighted average was used [24,31]. Owing to the zero magnetization, the demagnetizing field vanishes, and calculations made on the spherical and nonspherical model samples give virtually identical results (see Fig. 4). For the pure Fe_4 sample, the bias field distribution is Gaussian with FWHM of approximately 20 mT, while for the diluted sample it is non-Gaussian and much narrower (FWHM ~ 2 mT). The transverse fields distribution for $x = 1$ is rather broad and extends up to 30 mT with a peak at ca. 10 mT. By contrast, the diluted sample features a more structured distribution extending up to about 10 mT, with a main peak at 0.5 mT and secondary maxima at higher field values. These arise from pairs of neighboring Fe_4 complexes in the lattice.

SLR times have been numerically computed by applying a Pauli master equation to calculate the time-dependent populations of the magnetic energy levels of Eq. (3) and, from them, the frequency-dependent susceptibility [10,32]. The spin-phonon interaction Hamiltonian was $3B_{20}\{(\epsilon_{xz} + \omega_{xz}) \otimes [S_x S_z + S_z S_x] + (\epsilon_{yz} + \omega_{yz}) \otimes [S_y S_z + S_z S_y]\}$, where ϵ_{iz} and ω_{iz} represent phonon-induced strains and rotations, respectively. The overall scale of all relaxation rates is fixed by a constant parameter $q \propto n_{\text{ph}}/c_s^5$, where n_{ph} is the number of relevant low-energy phonon modes and c_s is the speed of sound that describes, in the simplest manner, the dispersion relation $\omega = c_s k$ of phonon modes. This parameter was determined by fitting τ measured at $T = 2$ K on pure Fe_4 . The speed of sound derived from this fit ranges then from $c_s = 5 \times 10^4$ cm/s (for

FIG. 4. (Color online) (a) Shaded areas, distribution of dipolar bias fields $H_{d,z}$ calculated for magnetically unpolarized crystals of Fe_4 (light red) and $(\text{Fe}_4)_{0.05}(\text{Ga}_4)_{0.95}$ (dark blue); lines, least-squares fits of these distributions using either a Gaussian ($x = 1$) or a Lorentzian ($x = 0.05$) function. (b) Distributions of transverse dipolar magnetic fields calculated for the same model samples.

$n_{\text{ph}} = 3$ acoustic modes) to 1.5×10^5 cm/s (if all 768 acoustic and optical modes contribute). These values are comparable to those previously found for other SMMs [18,20,32]. In order to “tune” the ground state tunnel splitting to its actual value while keeping the numerical calculations tractable, we simulated the effect of $\mathcal{H}'$ by introducing an off-diagonal $B_6^5 O_6^5$ term into the giant spin Hamiltonian of the $S = 5$ multiplet, with $B_6^5/k_B = 1.05 \times 10^{-6}$ K. The susceptibility has been averaged over the bias field distribution $P(H_{d,z})$ shown in Fig. 4. For simplicity, transverse dipolar interactions have been taken into account by introducing an average transverse magnetic field $H_{d,\perp}(1/\sqrt{2}, 1/\sqrt{2}, 0)$, with $H_{d,\perp} = 10$ mT and 0.5 mT for the concentrated and diluted samples, respectively.

The results of these calculations are shown in Fig. 3. Above 1 K, they account well for the experimental data: At any temperature, thermally activated relaxation becomes faster as the magnetic concentration x decreases. In particular, the effective activation energies (obtained from fits for $T > 1$ K) are $U/k_B \simeq 12.9$ K for $x = 1$ and $U/k_B \simeq 12$ K for $x = 0.05$. Both values are smaller than the “classical” activation energy $U_{\text{cl}}/k_B = 15.0$ K extracted from spectroscopic data

through Eq. (3) [24], thus showing that tunneling via thermally activated spin states strongly influences τ in this regime. By contrast, the same model completely fails to account for the SLR observed below 1 K. It predicts a monotonic increase of τ with decreasing temperature down to approximately 0.1 K, where it tends to saturate to an astronomically long ($\gtrsim 10^{13}$ s) value, associated with direct phonon-induced processes. Clearly, a different process drives SLR below 1 K.

At very low temperatures, spin dynamics is fully dominated by pure quantum spin tunneling events. According to the Prokof'ev and Stamp model [13], the average tunneling rate is approximately given by

$$\Gamma = \frac{\Delta^2}{\hbar} P(\xi_d), \quad (4)$$

where $P(\xi_d) = P(H_{d,z})/(2g\mu_B S)$ is the distribution of dipolar energy bias. Tunneling times Γ^{-1} obtained from Eq. (4) for pure and diluted samples agree very well with the SLR times measured below 1 K. In particular, at zero applied field, Eq. (4) predicts (dotted lines in Fig. 3) that Γ^{-1} approximately scales with the width of $P(\xi_d)$, i.e., with x , as the SLR time indeed does. This result contrasts with the decrease of τ with increasing Er^{3+} concentration observed in crystals of $\text{Na}_9[\text{Er}_x\text{Y}_{1-x}(\text{W}_5\text{O}_{18})_2] \cdot y\text{H}_2\text{O}$ [22]. Yet, the markedly different behavior of these materials can also be reconciled with the above interpretation, on the basis of Eq. (4). While Δ of Fe_4 is approximately independent of $H_{d,\perp}$, Δ of Er^{3+} , a Kramer's ion with $J = 15/2$, vanishes unless the local $H_{d,\perp} \neq 0$, thus it is expected to *increase* with concentration. Also, the slight temperature dependence of τ in the quantum regime can be associated with gradual changes in the distribution of dipolar bias.

The thermalization of spins plays a crucial role in fundamental phenomena, such as the attainment of magnetically ordered states, as well as in their application as magnetic refrigerants or thermometers, thus its relevance can hardly be overestimated. Our experiments show that spin-lattice relaxation of anisotropic spins takes place, at very low temperatures, at rates that quantitatively match predictions for spin tunneling processes, thus much faster than those of direct spin-phonon processes. However, the precise mechanism by which the spins that flip by tunneling exchange energy with the lattice remains obscure. For a fixed tunneling rate, such as that of Fe_4 , dipolar interactions mainly slow down the relaxation process by taking most spins off-resonance. Therefore, experiments provide no evidence supporting the contribution of collective emission of phonons to spin-lattice relaxation. The last piece of the puzzle thus remains to be found.

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