Dipolar-mediated quantum spin-lattice relaxation

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The concept of thermal equilibrium relies on the ability of physical systems to exchange energy with their surroundings, usually termed as the thermal "bath". In the case of spins in solid lattices, the attainment of equilibrium is mediated by a spin-lattice interaction. Early theories [1,2,3] of the relaxation phenomenon considered this interaction to be brought about by the modulation that lattice vibrations, i.e. phonons, induce on dipole-dipole interactions (Waller's process) and the electrostatic crystal's field (Van Vleck's process). The latter is generally thought to be dominant and it accounts reasonably well for relaxation experiments performed under applied magnetic fields [4-7]. However, beginning with the first measurements obtained in Leiden [8,9], deviations from the predicted values have been found at low temperatures and under weak or no applied magnetic fields [3,8]. Deviations become most noticeable in the case of large spins, as those present in some molecular magnetic crystals [10,11], for which the calculated rates are many orders of magnitude below the observed ones. In the present work, we have studied the spin-lattice relaxation of clusters containing a single lanthanide ion. Our results are in qualitative disagreement with the classical theories. We observe that the relaxation rate is enormously enhanced by dipole-dipole

interactions between the electronic spins whereas, in contrast, it is rapidly suppressed by the application of external magnetic fields. Our results suggest that dipole-dipole interactions mediate the energy transfer between the spins and the thermal phonons. For sufficiently low magnetic fields, spins transfer their energy to the "dipolar bath" via quantum tunnelling processes. Since the spin-lattice interaction is also a source of quantum decoherence [12], our results could help to design "robust" molecular spin q-bits. The relaxation of magnetic impurities has also been proposed as the source of the low-frequency noise usually found in superconducting interference devices (SQUIDs) [13].

The molecular core of our material, hereafter referred to as ErW_{10}, is depicted in Fig. 1. It consists of a single Er^{3+} ion that is surrounded by an organic sandwich of polyoxometalate molecules [14]. The choice of this material is justified by its relative simple and well defined structure, and because it allows a direct comparison with results obtained, under larger magnetic fields, on rare-earth ionic compounds, experiments which are considered to be well understood [4-8]. In its ground state, Er^{3+} possesses a large magnetic moment, associated with the total angular momentum, which is $J = 15/2$ for the free ion. Electronic levels are split into Kramer's doublets by the action of the local crystal field. On account of the high symmetry of the molecular core, spin states can be labelled by the projections J_z of J on the molecular axis z. The $\pm J_z$ doublets are split by dipole-dipole and hyperfine interactions. We are interested in the process by which thermal equilibrium populations of these energy levels are established near zero field.

Er^3

$J = 15/2$

Crystal field

Hyperfine + dipolar interactions

$J_z = \pm\dfrac{15}{2}$

$J_z = \pm\dfrac{1}{2}$

$J_z = \pm\dfrac{13}{2}$
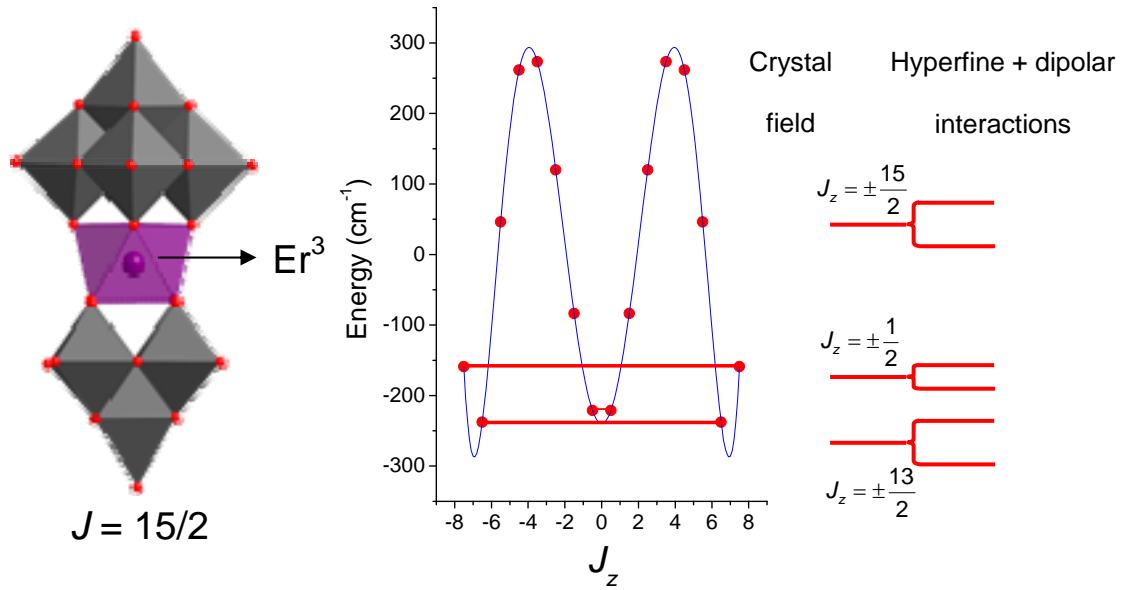
Some predictions of the early theories, regarding the qualitative dependence of the rate Γ (or $1/\tau$, where τ is a relaxation time) on temperature T and the strength H of the magnetic field, are rather insensitive to the precise nature of the spin-lattice interaction. These theories [1-3,15] predict

$$\frac{1}{\tau} = \frac{3}{2\hbar\pi\rho v^5}\left|\langle b|V|a\rangle\right|^2\left(\frac{\Delta_{ba}}{\hbar}\right)^3\coth\left(\frac{\Delta_{ba}}{2k_BT}\right) + \frac{1}{\tau_0}\exp\left(\frac{\Delta_{cb}}{k_BT}\right) \qquad (1)$$

In the limit of very low temperatures, the rate is governed chiefly by direct transitions between spin states a and b (see Fig. 1) accompanied by the absorption and emission of a single resonant phonon. At higher temperatures, two-phonon processes, which involve virtual or real intermediate transitions to some excited spin state c, play a dominant role. These processes are the Raman scattering of phonons and the Orbach process, in which a real transition to an excited intermediate state takes place. In Eq. (1), we have included only the latter processes for simplicity and because these two terms are able to account well for the experimental results obtained in the temperature range of our interest. As we are mainly interested in the relaxation in the limit of very low temperatures, we consider mainly the main aspects of direct processes.

Independently of the size of the spin-lattice interaction Hamiltonian V, which obviously sets the scale Γ, Eq. (1) predicts that Γ should level-off to a constant value (the rate of spontaneous emission of phonons) as $T \to 0$. This rate should increase rapidly with increasing magnetic field H. This is associated directly with the increase in the density of available resonant phonons. In the case of half-odd spins, as it is the case with Er^{3+}, the dependence with H is even enhanced because terms that depend linearly on H contribute to the matrix element as they lift Kramer's degeneracy. Within this picture, effects of dipolar and hyperfine interactions can be approximately taken into account as "effective magnetic fields" [3,16]. This approximation is justified for spins with very high anisotropy [16], as it is the case for ErW_{10}.

The spin-lattice relaxation times of ErW_{10} were determined by means of frequency-dependent linear response experiments. The linear susceptibility data measured between 1.8 K and 6 K are displayed in Fig. 2 (left plot). These data show a drop in the real component χ' accompanied by a maximum in the imaginary component χ''. The frequency ν of the susceptibility drop approximately fulfils the relationship $\omega = 2\pi\nu = 1$, which therefore enables extracting the relaxation time at each temperature. In our analysis, we actually fitted the data with a Cole-Cole function

$$\chi' = \chi_S + (\chi_T - \chi_S)\frac{1 + (\omega\tau)^\alpha \sin(\alpha\pi/2)}{\left[1 + (\omega\tau)^\alpha \cos(\alpha\pi/2)\right]^2 + \left[(\omega\tau)^\alpha \sin(\alpha\pi/2)\right]^2}$$

$$\chi'' = (\chi_T - \chi_S)\frac{(\omega\tau)^\alpha \cos(\alpha\pi/2)}{\left[1 + (\omega\tau)^\alpha \cos(\alpha\pi/2)\right]^2 + \left[(\omega\tau)^\alpha \sin(\alpha\pi/2)\right]^2}$$

$$(2)$$

enabling us to obtain also information on the distribution of relaxation times via the exponent α ($\alpha = 1$ for a single τ). The fact that the low-frequency susceptibility, as well as the susceptibility jump ($\chi_T - \chi_S$), follow Curie-Weiss' law evidences that the rates measured correspond to relaxation of the spins to

thermal equilibrium, and not to internal relaxation processes within the lattice (or bath) of spins (or spin-spin relaxation). For sufficiently low frequencies, spins are in fact observed to "feel" and follow the temperature of the thermal bath down to $T = 80$ mK.

The rate $1/\tau$, shown in Fig. 2 (right hand plot), follows well the qualitative behaviour predicted by Eq. (1): a thermally activated process dominates at high temperatures with a cross-over to a nearly temperature independent regime at low T. Remarkably enough, the values we find for the parameters τ_0 and Δ_{cb} are of the same order as those found, for $H \approx 750$ Oe, for Er^{3+} ions diluted in a host crystal of $La(C_2H_5SO_4)_3.9H_2O$ [5]. In contrast, and most surprisingly from the perspective of standard models, the rate we find at zero field for the direct process $\Gamma_{dir} \approx 1.2 \times 10^3$ s^{-1} is 100 times faster than what is reported in [5].
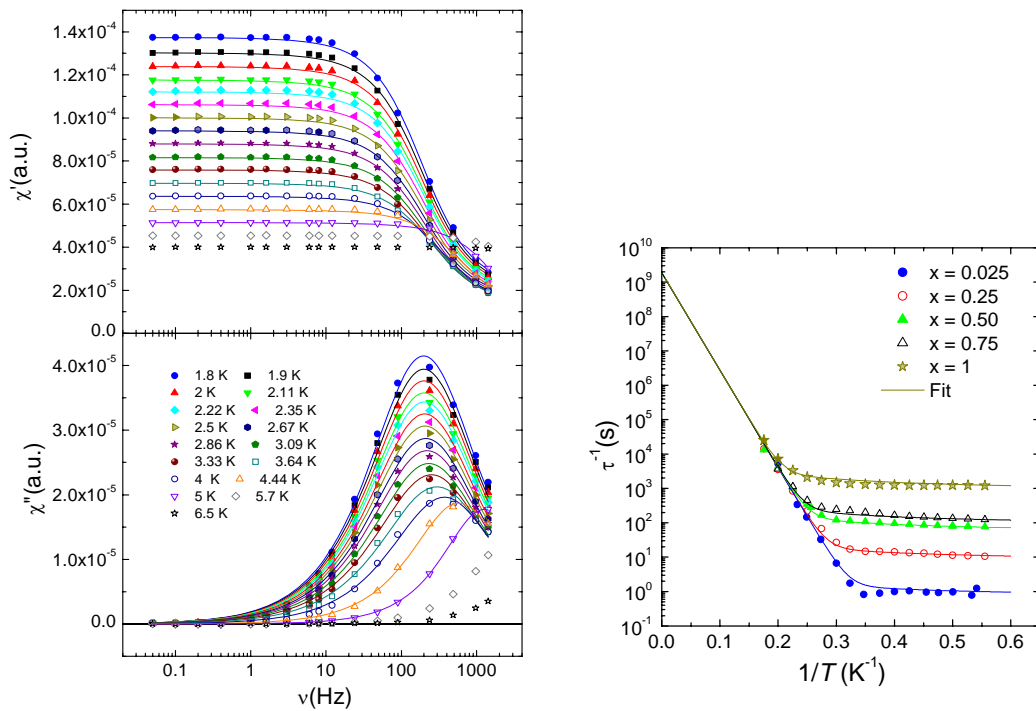

The same plot in the right hand side of Fig. 2 shows data obtained on samples of diluted spins, for which a fraction $(1 - x)$ of the Er-containing molecules have

been replaced, within the same crystal structure, by nearly identical clusters made of nonmagnetic Y^{3+}. The concentration of Er^{3+} ions was estimated by scaling the Curie constant to the value found for the pure compound. Interestingly, the rate of direct processes decreases by three orders of magnitude as x decreases from 100% to 5 % (see also Fig. 3). Qualitatively, this might be understood on basis of Eq. (1), if we consider that diluting the spins reduces the effective magnetic fields associated with dipole-dipole interactions between them. Our data for the most diluted sample are also in better agreement with results obtained for dilute Er in inorganic crystals.

These ideas can be tested by measuring the susceptibility under external magnetic fields. The results are shown in the right hand side of Fig. 3 and show that χ' deviates from equilibrium with increasing H. In other words, the spin-lattice relaxation rate not only does not increase, but it actually decreases, just the opposite as predicted by Eq. (1). Estimating directly τ from the frequency-dependent susceptibility, as it is done at zero field, can unfortunately not be done in this case because the samples are in powder form. The random orientation of the magnetic field with respect to the crystal's axes broadens considerably the distribution of relaxation times and therefore precludes a reliable fit of the data with Eq. (2). However, it is still possible to get an average relaxation time by using the definition $\omega\tau_{av} = \lim_{\omega\to 0}\left(\dfrac{\chi''}{\chi'}\right)$ that is often used in random magnetic materials and even in spin glasses [17]. As we anticipated, τ_{av}^{-1} decreases very rapidly upon the application of magnetic fields: for x = 1, τ_{av}^{-1} drops by a factor of 100 between H = 0 and 300 Oe. The sharp contrast between the field and concentration dependences of τ shows that dipole-dipole interactions are actually playing a very different role from that of an effective field. At high magnetic fields, the rates measured for different concentrations

merge, thus the influence of interactions vanishes. We conclude that the mechanism that controls the thermalization of spins near zero field is qualitatively different from those that operate at high fields. This mechanism is, as yet, unknown. We next discuss its possible nature on the basis of our experimental evidence.
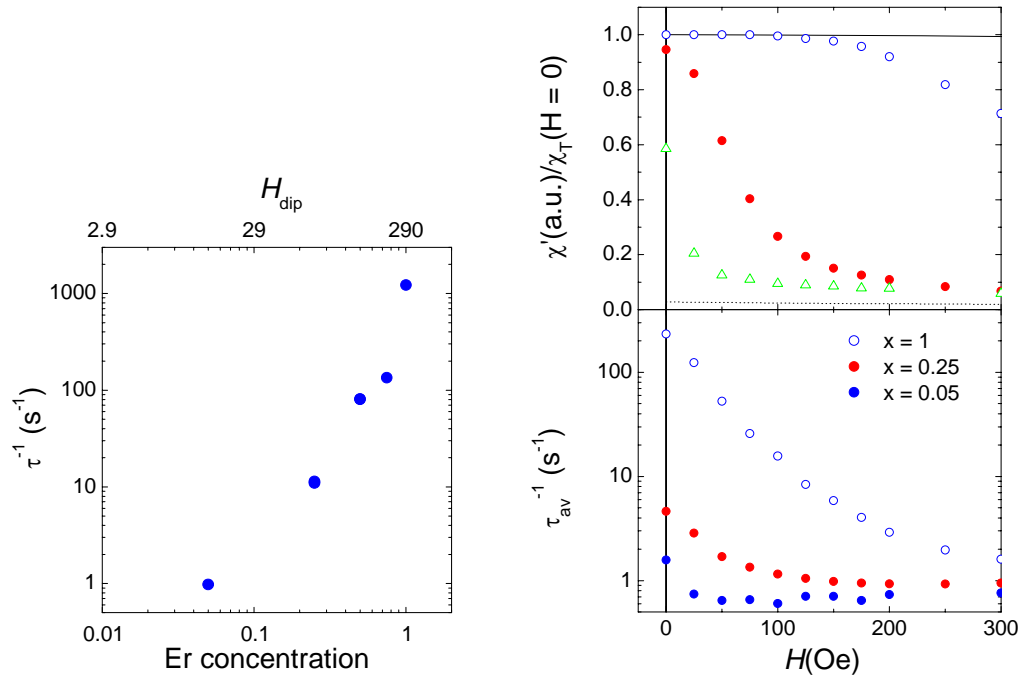
Experiments suggest that dipole-dipole interactions act as a kind of mediator of energy between single spins and the lattice. How this transfer might take place via quantum tunnelling of spins is schematically shown in Fig. 4. Consider first an ion that, with respect to single ion interactions like the crystal's field and the hyperfine interaction, occupies an excited state. The electronic spin can flip, by tunnelling, provided that the dipolar bias generated by other spins nearly compensates, up to the width of the two levels, the hyperfine splitting. Evidences of this "nuclear mediated tunnelling" have been found in adiabatic magnetic relaxation and hysteresis experiments performed in many molecular nanomagnets. From the point of view of the energy balance, the flip involves a

transfer of a quantum of energy Δ_{ba} from the given ion to the lattice of interacting spins, or as it is sometimes called, to the "dipolar bath". The process is in this respect analogous to a spin cross-cross relaxation [18-20], by which electronic spins exchange energy between themselves by co-flipping simultaneously. Cross-cross relaxation processes between different ions might speed up the attainment of thermal equilibrium of one species provided that the other possesses a faster relaxation rate than the former [19]. By analogy, tunnelling events of the type just described will contribute to enhance the thermalization of Er^{3+} spins if the energy transfer between the dipolar bath and the phonon bath, by which the distribution of dipolar fields returns to equilibrium from the small distortion associated to the single spin tunnelling, occurs more efficiently than the direct process of a single spin.
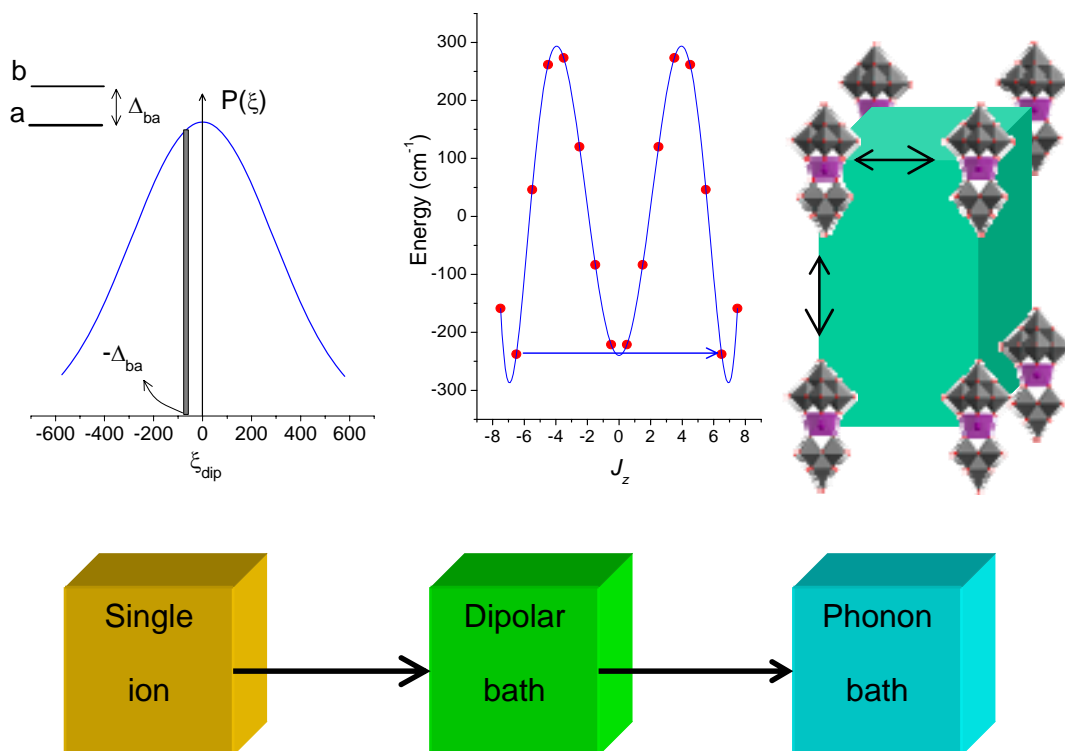
The model, despite its qualitative nature, explains a number of experimental facts. The tunnelling rate of each spin will be approximately be given by

$$\Gamma \propto \frac{\Delta^2}{\hbar \xi_0} \exp\left(-\frac{\xi_{hyp}^2}{2\sigma^2} \right) \qquad\qquad (3)$$

where Δ is the tunnel splitting of a single ion, ξ_{hyp} its hyperfine splitting and σ the width of the distribution of dipolar bias. If, by diluting, the dipolar interactions become weaker, the dipolar bath might be unable to take the energy required to flip a spin, thus some spins are effectively disconnected from this bath. On the other hand, the process is resonant: the application of a uniform external magnetic field takes electronic spins out of the tunnelling conditions as soon as the Zeeman splitting it generates becomes comparable to σ. This occurs when $H \approx 300$ Oe for the concentrated sample and correspondingly lower fields for the dilute samples, in agreement with the experiments. Finally, the amplitude h_{ac} of the oscillating magnetic field used to measure the susceptibility can become comparable to the width of the spin levels, and therefore contribute to create an effective "tunnel window" $\xi_0(ac) \approx 4$ mK. We have checked that the rate t-1 depends indeed on the amplitude of the ac field for fields larger than 0.5 Oe.

Methods.

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Competing interests statement The authors declare that they have no competing financial interests.