Dynamics and thermalization of the nuclear spin bath in the single-molecule magnet Mn$_{12}$-ac: test for the theory of spin tunneling.

Andrea Morello
Kamerlingh Onnes Laboratory, Leiden University,
P.O. Box 9504, 2300 RA Leiden, The Netherlands

L. J. de Jongh
Kamerlingh Onnes Laboratory, Leiden University,
P.O. Box 9504, 2300 RA Leiden, The Netherlands.

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The description of the tunneling of a macroscopic variable in the presence of a bath of localized spins is a subject of great fundamental and practical interest, and is relevant for many solid-state qubit designs. Most of the attention is usually given to the dynamics of the “central spin” (i.e., the qubit), while little is known about the spin bath itself. Here we present a detailed study of the dynamics of the nuclear spin bath in the Mn$_{12}$-ac single-molecule magnet, probed by NMR experiments down to very low temperatures ($T \approx 20 \text{ mK}$). The results are critically analyzed in the framework of the Prokof’ev-Stamp theory of nuclear-spin mediated quantum tunneling. We find that the longitudinal relaxation rate of the $^{55}$Mn nuclei in Mn$_{12}$-ac becomes roughly $T$-independent below $T \approx 0.8 \text{ K}$, and can be strongly suppressed with a longitudinal magnetic field. This is consistent with the nuclear relaxation being caused by quantum tunneling of the molecular spin, and we attribute the tunneling fluctuations to the minority of fast-relaxing molecules present in the sample. The transverse nuclear relaxation is also $T$-independent for $T < 0.8 \text{ K}$, and can be explained qualitatively and quantitatively by the dipolar coupling between like nuclei in neighboring molecules. This intercluster nuclear spin diffusion mechanism is an essential ingredient for the global relaxation of the nuclear spin bath. We also show that the isotopic substitution of $^1\text{H}$ by $^2\text{H}$ leads to a slower nuclear longitudinal relaxation, consistent with the decreased tunneling probability of the molecular spin. Finally, we demonstrate that, even at the lowest temperatures - where only $T$-independent quantum tunneling fluctuations are present - the nuclear spins remain in thermal equilibrium with the lattice phonons, and we investigate the timescale for their thermal equilibration. After a review of the theory of macroscopic spin tunneling in the presence of a spin bath, we argue that most of our experimental results are consistent with that theory, but the thermalization of the nuclear spins is not. This calls for an extension of the spin bath theory to include the effect of spin-phonon couplings in the nuclear-spin mediated tunneling process.

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I. INTRODUCTION

The understanding of quantum tunneling in mesoscopic systems has made huge progress in the past decades, to the point that nano-fabricated devices are now being exploited as coherently tunneling two-level systems (TLSs) for quantum information purposes. Conceptually, a first breakthrough was the proper description of the coupling of an effective TLS to an environment described by an oscillator bath. Whether the system is an intrinsic TLS (e.g. a spin $s = 1/2$) or the low-energy truncation of a more complicated entity (e.g. the flux state of a SQUID), one can generally apply the oscillator bath theory when the environment is described by localized modes (conduction electrons, phonons, photons, etc.) and the couplings of the TLS to each oscillator are weak. In many solid-state systems, however, it can be necessary to account for localized environmental excitations whose couplings to the TLS are not weak. This type of environment is called “spin bath” and cannot be mapped onto an oscillator bath. Importantly, a spin bath environment can cause decoherence even at $T = 0$ and is therefore of great relevance for quantum systems that are designed to show coherent dynamics, like qubits for quantum computation. The prototypical realization of a tunneling TLS coupled to a spin bath is the giant spin of a single-molecule magnet (SMM). These molecular systems consist of a core of strongly interacting transition metal ions, surrounded by organic ligands. At sufficiently low temperatures the core of the molecule behaves effectively like a single large spin $\mathbf{S}$. When uniaxial magnetic anisotropy is present, the reversal of the spin direction requires - classically - a large energy, so that the spin direction can be frozen at very low $T$. However, in the presence of a transverse magnetic field or a biaxial anisotropy, the spin direction can be reversed by tunneling through the anisotropy barrier. The electronic spins that form
the SMM are magnetically coupled to the nuclear spins that either belong to the magnetic ions themselves ($^{55}$Mn, $^{56}$Fe, . . . ) or to the surrounding ligand molecules ($^1$H, $^{13}$C, . . . ). As a consequence of these couplings, the observation of macroscopic quantum tunneling of magnetization in SMMs cannot be understood without invoking the dynamics of the nuclear spins themselves. The theoretical predictions for the role of nuclear spins in the magnetization tunneling of SMMs have been verified by a series of experiments on the Fe$_8$ compound. Most remarkably, this material allows to change the isotopic composition of the sample, both by strengthening ($^{56}$Fe → $^{57}$Fe substitution) and weakening ($^1$H → $^2$H substitution) the hyperfine couplings, while leaving the electronic structure of the SMMs unaffected. As predicted, the role of quantum relaxation of the magnetization was found to be directly related to the nuclear isotopic composition of the sample. More recently, the effect of isotopic substitution has been observed in the low-$T$ electronic specific heat of Fe$_8$ (Ref. 19) and in the dephasing time of coherent electron spin precession in Cr$_2$Ni. Nuclear spin effects were also invoked in the interpretation of $\mu$SR data in isotropic molecules and in an alternative description of the short-term magnetic relaxation in SMMs. All these works have analyzed the effect of the nuclei on the dynamics of the “central spin”, but a crucial aspect of the theory of the spin bath is that the tunneling of the central system has repercussion on the dynamics of the bath itself, so that the latter cannot be simply regarded as an independent source of “noise”. Until now, the experiments to probe the electron spin dynamics have not been able to test this delicate aspect of the theory. To understand the details of the nuclear spin fluctuations, one should then look directly at the nuclear spins by means of low-temperature NMR experiments, performed under different regimes for the quantum dynamics of the electron spin. These experiments have been carried out by several groups, but an accurate analysis of their implications for the more general theory of nuclear-spin mediated quantum tunneling is still lacking.

In this work, we present a comprehensive set of experiments on the dynamics of $^{55}$Mn nuclear spins in the Mn$_{12}$-ac SMM, and we use our results for a critical assessment of the theory of the spin bath. Our data provide definitive proof that the nuclear spin dynamics is strongly correlated with that of the central spin, that is, it cannot be treated as an independent source of noise. Indeed, we find that the nuclear spin fluctuations change dramatically when the tunneling dynamics of the central spin is modified, e.g. by an external magnetic field. In addition, we shall demonstrate that the nuclear spins remain in thermal equilibrium with the phonon bath down to the lowest temperatures ($T \sim 20$ mK) accessible to our experiment, where the thermal fluctuations of the electron spins are entirely frozen out. This implies that there is a mechanism for exchanging energy between nuclei, electrons and phonons through the nuclear-spin mediated quantum tunneling of the central spin. This is the point where the current theoretical description of macroscopic quantum tunneling in the presence of a spin bath needs to be improved.

As regards the “macroscopicness” of the quantum effects observed in SMMs, we adopt Leggett’s view that the most stringent criterion is the “disconnectivity” $D$, which roughly speaking is the number of particles that behave differently in the two branches of a quantum superposition. For instance, while a Cooper pair box is a relatively large, lithographically fabricated device, the quantum superposition of its charge states involves in fact only one Cooper pair, i.e. two electrons, and its disconnectivity is only $D = 2$. The matter-wave interference in fullerene molecules for instance, is a much more “quantum macroscopic” phenomenon, since it means that $60 \times (12$ nucleons + 6 electrons) = 1080 particles are superimposed between different paths through a diffraction grating. For the spin tunneling in Mn$_{12}$-ac SMMs discussed here, we have 44 electron spins simultaneously tunneling between opposite directions, which places this system logarithmically halfway between single particles and fullerenes on a macroscopicness scale.

The paper is organized as follows. Section II describes the physical properties of the sample used in the experiments, the design and performance of our measurement apparatus, and the methods of data analysis. Section III presents the experimental results on the nuclear spin dynamics, starting with the NMR spectra, the longitudinal and transverse relaxation rates in zero field, and their dependence on a longitudinal external field. We also study the nuclear relaxation in different Mn sites within the cluster, and the effect of isotopic substitution in the ligand molecules. In Section IV we discuss the thermal equilibrium between nuclear spins and phonon bath, the experimental challenges in optimizing it, and the indirect observation of magnetic avalanches during field sweeps. In Section V we give an introductory review of the theory of the spin bath, and apply its predictions to the calculation of the nuclear relaxation rate as observed in our experiments. Together with the information on the thermal equilibrium of the nuclear spins, this will allow us to draw clear-cut conclusions on the status of our current theoretical understanding of quantum tunneling of magnetization. We conclude with a summary and implications of the results in Section VI.

II. EXPERIMENT

A. Sample properties

We chose to focus our study on the well-known $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (Mn$_{12}$-ac) compound, which belongs to the family of SMMs with the highest anisotropy barrier. As we shall see below, the rationale for choosing a SMM with high anisotropy barrier is that the electron spin fluctuations become slow
on the NMR timescale already at temperatures of a few kelvin. The structure of the cluster \(^{(2)}\) (Fig. 1(a)) consists of a core of 4 Mn\(^{3+}\) ions with electron spin \(s = 3/2\), which we shall denote as Mn\(^{(1)}\), and 8 Mn\(^{3+}\) ions \((s = 2)\) on two inequivalent crystallographic sites, Mn\(^{(2)}\) and Mn\(^{(3)}\) (Ref. 32). The molecules crystallize in a tetragonal structure with lattice parameters \(a = b = 17.319\) Å and \(c = 12.388\) Å. The ground state of the molecule has a total electron spin \(S = 10\) and, for the temperature range of interest in the present work (\(T < 2\) K), we may describe the electron spin of the cluster by means of the effective spin Hamiltonian:

\[
H = -DS^2_z - BS^4_z + E(S^2_y - S^2_y) - C(S^4_z + S^4_z) + +\mu_B\mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}. \tag{1}
\]

Commonly adopted parameter values are \(D = 0.548\) K, \(B = 1.17\) mK and \(C = 22\) \(\mu\)K as obtained by neutron scattering data and for the \(g\) tensor the values \(g_{||} = 1.93\) and \(g_{\perp} = 1.96\) from high-frequency EPR.\(^{34,35,36}\) The uniaxial anisotropy terms \(-DS^2_z\) and \(-BS^4_z\) can be attributed to the single-ion anisotropy of the Mn\(^{3+}\) ions\(^{31}\) which is due to the crystal field effects resulting in the Jahn-Teller distortions of the coordination octahedra, where the elongation axes are approximately parallel to the \(c\)-axis of the crystal. Considering only the diagonal terms, the energy levels scheme would be a series of doublets of degenerate states, \(|\pm m\rangle\), separated by a barrier with a total height \(DS^2 + BS^4 \simeq 66.6\) K [Fig. 1(b)]. The transverse anisotropy terms, \(E(S^2_y - S^2_y) - C(S^4_z + S^4_z)\), lift the degeneracy of the \(|\pm m\rangle\) states and allow quantum tunneling of the giant spin through the anisotropy barrier. We call \(\Delta_m\) the matrix element for the tunneling of the giant spin through the \(m\)-th doublet, and \(2\Delta_m\) the corresponding tunneling splitting. The \(C(S^4_z + S^4_z)\) term arises from the fourfold \(S_z\) point symmetry of the molecule, but there is now solid experimental evidence\(^{37,38}\) for the prediction\(^{39}\) that a disorder in the acetic acid of crystallization is present and gives rise to six different isomers of Mn\(_{12}\) cluster, four of which have symmetry lower than tetragonal and therefore have nonzero rhombic term \(E(S^2_z - S^2_y)\). EPR experiments give an upper bound \(E \leq 14\) mK.\(^{40}\) For the purpose of NMR experiments, such isomerism may cause slight variations in the local hyperfine couplings, causing extra broadening in the MnN resonance lines. Very recently, a new family of Mn\(_{12}\) clusters has been synthesized, which does not suffer from the solvent disorder mentioned above, and yields indeed more sharply defined Mn NMR spectra.\(^{41}\)

When adding spin-phonon interactions,\(^{41,42}\) the possible transitions between the energy levels of \(|\pm m\rangle\) are sketched in Fig. 1(b). We distinguish between intrawell spin-phonon excitations, where the spin state remains inside the same energy potential well, and the interwell transitions, which involve spin reversal by quantum tunneling through the barrier, allowed by the terms in \(|\pm m\rangle\) that do not commute with \(S_z\). Thermally-assisted tunneling involves both these types of transitions.

The above discussion refers to the majority of the molecules in a real sample, but for our experiments the crucial feature of Mn\(_{12}\)-ac is the presence of fast-relaxing molecules (FRMs),\(^{43}\) i.e. clusters characterized by a lower anisotropy barrier and a much faster relaxation rate, as observed for instance by ac-susceptibility and magnetization measurements.\(^{44}\) It has been recognized that such FRMs originate from Jahn-Teller isomerism.\(^{45}\)
i.e. the presence in the molecule of one or two Mn$^{3+}$ sites where the elongated Jahn-Teller axis points in a direction roughly perpendicular instead of parallel to the crystalline $\hat{c}$-axis. This results in the reduction of the anisotropy barrier to 35 or 15 K in the case of one or two flipped Jahn-Teller axes, respectively, and presumably in an increased strength of the non-diagonal terms in the spin Hamiltonian as well. Furthermore, the anisotropy axis $z$ of the whole molecule no longer coincides with the crystallographic $\hat{c}$-axis, but deviates e.g. by $\sim 10^\circ$ in the molecules with 35 K barrier. The Jahn-Teller isomerism is very different from the above-mentioned effect of disorder in solvent molecules, and produces much more important effects for the present study. As will be argued below, the presence of the FRMs is essential for the interpretation of our results and, to some extent, may be regarded as a fortunate feature for this specific experiment.

The sample used in the experiment consisted of about 60 mg of polycrystalline Mn$_{12}$-ac, with typical crystallite volume $\sim 0.1 \, \text{mm}^3$. The crystallites were used as-grown (i.e., not crushed), mixed with Stycast 1266 epoxy, inserted in a $\varnothing 6$ mm capsule and allowed to set for 24 hours in the room temperature bore of a 9.4 T superconducting magnet. With this procedure, the magnetic easy axis of the molecules (which coincides with the long axis of the needle-like crystallites) ends up being aligned along the field within a few degrees. In addition, we shall report NMR spectra taken on a small single crystal (mass $\sim 1 \, \text{mg}$).

### B. Low-temperature pulse NMR setup

Our experimental setup is based on a Leiden Cryogenics MNK126-400ROF dilution refrigerator, fitted with a plastic mixing chamber that allows the sample to be thermalized directly by the $^3$He flow. A scheme of the low-temperature part of the refrigerator is shown in Fig. 2, together with the NMR circuitry. The mixing chamber consists of two concentric tubes, obtained by rolling a Kapton foil coated with Stycast 1266 epoxy. The tops of each tube are glued into concentric Araldite pots: the inner pot receives the downwards flow of condensed $^3$He and, a few millimeters below the inlet, the phase separation between the pure $^3$He phase and the dilute $^3$He/$^4$He phase takes place. The circulation of $^3$He is then forced downwards along the inner Kapton tube, which has openings at the bottom side to allow the return of the $^3$He stream through the thin space in between the tubes. Both the bottom of the Kapton tail and the outer pot are closed by conical Araldite plugs smeared with Apiezon N grease.

A 2-turns copper coil is wound around the capsule containing the sample, mounted on top of the lower conical plug and inserted in the $^3$He/$^4$He mixture at the bottom of the mixing chamber tail, which coincides with the center of a 9 T superconducting magnet. The coil is then connected by a thin brass coaxial cable (length $\approx 0.5 \, \text{m}$) to two tunable cylindrical teflon capacitors, mounted at the still (see Fig. 2). At the frequency where the cable connecting capacitors and coil is precisely one wavelength, the circuit is equivalent to a standard lumped LC-resonator. However, since the L-cable is a low-conductivity coax for low-$T$ applications, the quality factor of the resonator (which includes the cable) is drastically reduced. Although this affects the sensitivity of the circuit, it also broadens the accessible frequency range without the need to retune the capacitors. Cutting the cable for one wavelength at $\sim 280 \, \text{MHz}$, the circuit is usable between (at least) 220 and 320 MHz. As for the room-temperature NMR electronics, details can be found in Ref. [48].

The temperature inside the mixing chamber is monitored by two simultaneously calibrated Speer carbon thermometers, one in the outer top Araldite pot, and the other at the bottom of the Kapton tail, next to the sample. At steady state and in the absence of NMR pulses, the temperature along the mixing chamber is uniform within $\lesssim 0.5 \, \text{mK}$. The effect of applying high-power ($\sim 100 \, \text{W}$) NMR pulses is shown in Fig. 2(a) and (b). A sudden increase in the measured temperature is seen both at the bottom and the top thermometer, and can be attributed to the short electromagnetic pulse. The temperature at the lower thermometer, i.e. next to the sample and the NMR coil, quickly recovers its unperturbed value, whereas the upper thermometer begins to sense the “heat wave” carried by the $^3$He stream with a delay of about 3 minutes. This has the important consequence that we can use the upper thermometer to distinguish the effect of sudden electromagnetic radiation bursts from the simple heating of the $^3$He/$^4$He mixture, as will be shown in IV B below.

The sample temperature is regulated by applying current to a manganin wire, anti-inductively wound around a copper joint just above the $^3$He inlet in the mixing chamber. In this way we can heat the incoming $^3$He stream and uniformly increase the mixing chamber temperature.

For the $^3$He circulation we employ an oil-free pumping system, consisting of a 500 m$^3$/h Roots booster pump, backed by two 10 m$^3$/h dry scroll pumps. The system reaches a base temperature of 9 mK, and the practical operating temperature while applying rf-pulses is as low as 15 - 20 mK.

### C. Measurements and data analysis

The $^{55}$Mn nuclear precession was detected by the spin-echo technique. A typical pulse sequence includes a first $\pi/2$-pulse with duration $t_{\pi/2} = 12 \, \mu\text{s}$, a waiting interval of 45 $\mu\text{s}$, and a 24 $\mu\text{s}$ $\pi$-pulse for refocusing. Given the heating effects shown in Fig. 2, a waiting time of 600 s between subsequent pulse trains easily allows to keep the operating temperature around 15 – 20 mK. Moreover, at such low temperature the signal intensity is so high that...
we could obtain an excellent signal-to-noise ratio without need of averaging, so that a typical measurement sequence took less than 12 hours. Above 100 mK it proved convenient to take a few averages, but there the heating due to the rf-pulses became negligible, and the waiting time could be reduced to ∼100 s.

The longitudinal spin relaxation (LSR) was studied by measuring the recovery of the longitudinal nuclear magnetization after an inversion pulse. We preferred this technique to the more widely used saturation recovery because it avoids the heating effects of the saturation pulse train, but we checked at intermediate temperatures that the two methods indeed lead to the same value of LSR rate. An example of echo signals obtained as a function of the waiting time after the inversion pulse is shown in Fig. 3(a). By integrating the echo intensity we obtain the time-dependence of the nuclear magnetization, $M(t)$, as shown in Fig. 3(b).

For the ease of comparison between different curves, we renormalize the vertical scale such that $M(0)/M(\infty) = -1$ and $M(t \gg T_1)/M(\infty) = 1$, even though usually $|M(0)| < |M(\infty)|$, as could be deduced from Fig. 3(a). This is just an artifact that occurs when the NMR line is much broader than the spectrum of the inversion pulse, and does not mean that the length of the π-pulse is incorrect. Since the $^{55}$Mn nuclei have spin $I = 5/2$, we fitted the recovery of the nuclear magnetization with

$$\frac{M(t)}{M(\infty)} = 1 - \left[ \frac{100}{63} e^{-30Wt} + \frac{16}{45} e^{-12Wt} + \frac{2}{35} e^{-2Wt} \right]$$

where $W$ is the longitudinal spin relaxation rate. Note that, in the simple case of a spin 1/2, $W$ is related to the relaxation time $T_1$ by $2W = T_1^{-1}$. The above multi-exponential expression and its numerical coefficients are derived under the assumption that the $I = 5/2$ multiplet is split by quadrupolar interactions, and it is possible to resolve the central transition within that multiplet. While earlier work indicated that all three manganese NMR lines are quadrupolar-split, more recent experiments on single crystal samples have questioned that conclusion and thereby the applicability of Eq. (2) to the present experiments. Even if other sources of line broadening hinder the visibility of the quadrupolar contribution, the condition for the absence of quadrupolar splitting is an exactly cubic environment for the nuclear site, which is not satisfied here. For this reason, and for the ease of comparison with our and other groups’ earlier results, we choose to retain Eq. (2) for the analysis of the inversion recovery data.

The transverse spin relaxation (TSR) rate $T_2^{-1}$ was obtained by measuring the decay of echo intensity upon increasing the waiting time $\tau$ between the π/2- and the π-pulses. The decay of transverse magnetization $M_\perp(\tau)$
changing the temperature

monitoring the echo intensity at regular intervals while

spin temperature, the measurements were performed by

magnetization is related to the nuclear spin temperature

also a gaussian component

\[ W(2) \text{ (solid line)} \] to yield the LSR rate

(normalized) integral of the echoes (open dots) is fitted to Eq. (5)

taken at

In particular, these are single-shot (no averaging) raw data

taken during an inversion recovery, i.e. measuring

signals recorded during an inversion pulse, i.e. measuring

\[ T \] except at the lowest temperatures (\( T \lesssim 0.2 \) K), where

also a gaussian component \( T_{2G} \) needs to be included:

\[ \frac{M_\perp(2\tau)}{M_\perp(0)} = \exp \left( -\frac{2\tau}{T_2} \right) \exp \left( -\frac{(2\tau)^2}{2T_{2G}^2} \right) \] (4)

As regards the experiments to determine the nuclear spin temperature, the measurements were performed by monitoring the echo intensity at regular intervals while changing the temperature \( T_{\text{bath}} \) of the \(^3\)He/\(^4\)He bath in which the sample is immersed. Recalling that the nuclear magnetization is related to the nuclear spin temperature

\[ T_{\text{nucl}} \] by the Curie law:

\[ M(T_{\text{nucl}}) = N\mu_0 \frac{\hbar^2\gamma^2}{3k_B} \frac{I(I+1)}{T_{\text{nucl}}} \] (5)

and assuming that \( T_{\text{bath}} = T_{\text{nucl}} \) at a certain temperature \( T_0 \) (e.g. 0.8 K), we can define a calibration factor \( K \) such that \( M(T_0) = K/T_{\text{nucl}}(T_0) \) and use that definition to derive the time evolution of the nuclear spin temperature as \( T_{\text{nucl}}(t) = K/M(t) \) while the bath temperature is changed.

Due to the strong magnetic hysteresis of Mn\(_{12}\)-ac, it is important to specify the magnetization state of the sample since, as will be shown below, this parameter can influence the observed nuclear spin dynamics. Therefore we carried out experiments under both zero-field cooled (ZFC) and field-cooled (FC) conditions, which correspond to zero and saturated magnetization along the easy axis, respectively. Heating the sample up to \( T \approx 4 \) K is sufficient to wash out any memory of the previous magnetic state. When the sample is already at \( T \ll 1 \) K, the field-cooling procedure can be replaced by the application of a longitudinal field large enough to destroy the anisotropy barrier, e.g. \( B_z = 8 \) T. Importantly, the shift of the \(^{55}\)Mn NMR frequency with external field depends on the magnetization state of the sample in a ZFC sample each resonance line splits in two, one line moving to \( \omega_0 + \gamma N B_z \) and the other to \( \omega_0 - \gamma N B_z \). Conversely, in a FC sample only one line is observed, shifting to higher or lower frequency depending on the direction of \( B_z \) relative to the magnetization direction. Therefore, by measuring the intensity of the shifted lines in a moderate longitudinal field, typically \( T \approx 0.5 \) T, we can check the magnetization of the sample as seen by the nuclei that contribute to the NMR signal.

III. NUCLEAR SPIN DYNAMICS

A. NMR spectra

The basic feature of the \(^{55}\)Mn NMR spectra in Mn\(_{12}\)-ac is the presence of three well-separated lines, that can be ascribed to three crystallographically inequivalent Mn sites in the molecule. The Mn\(^{1}\) line, centered around \( \nu_1 \approx 230 \) MHz, originates from the nuclei that belong to the central core of Mn\(^{4+}\) ions, whereas the Mn\(^{2}\) and Mn\(^{3}\) lines, centered at \( \nu_2 \approx 280 \) and \( \nu_3 \approx 365 \) MHz, respectively, have been assigned to the nuclei in the outer crown of Mn\(^{3+}\) ions. In Fig. 4 we show the Mn\(^{1}\) and Mn\(^{2}\) spectra at \( T = 20 \) mK, both in the oriented powder and in the single crystal, in a FC sample. Note that, whereas single-crystal spectra of Mn\(_{12}\)-ac have been recently published, the present spectra are the only ones measured at subkelvin temperatures so far. As argued already in Ref. 40, the single-crystal spectra indicate that the width of the Mn\(^{1}\) line may not originate from a small quadrupolar splitting. Instead, at least two inequivalent Mn\(^{4+}\) sites may exist, supporting the growing
amount of evidence about the lack of symmetry of the Mn\textsubscript{12}-ac compound.

We also note that the highest peak in the Mn\textsuperscript{(2)} line at $T \approx 20$ mK is found at a frequency $v_2 \approx 287$ MHz about 8 MHz higher than most of the previously reported spectra at $T > 1$ K, 49,50 with the exception of Ref. 54, whereas the position of the Mn\textsuperscript{(1)} line is consistent with all the previous reports.

B. Longitudinal spin relaxation in zero field

The LSR rate as a function of temperature for the Mn\textsuperscript{(1)} line, in zero field and zero-field cooled (ZFC) sample, is shown in Fig. 4. The most prominent feature in these data is a sharp crossover at $T \approx 0.8$ K between a roughly exponential $T$-dependence and an almost $T$-independent plateau. We have previously attributed the $T$-dependent nuclear relaxation to the effect of tunneling fluctuations within the ground doublet of the cluster spins 23 and we shall dedicate most of the present paper to discuss our further results supporting this statement. Here we shall also argue that, even in the high-temperature regime, thermally assisted quantum tunneling plays an essential role, and the experimental results cannot be understood simply in terms of LSR driven by intrawell electronic transitions. 49,50 It should be noted that the crossover from thermally activated to ground-state tunneling has also been observed by analyzing the $T$-dependence of the steps in the magnetization hysteresis loops. 55,56 The important advantage of our NMR measurements is that the nuclear dynamics is sensitive to fluctuations of the cluster electron spins without even requiring a change in the macroscopic magnetization of the sample. Clearly, no macroscopic probe (except perhaps an extremely sensitive magnetic noise detector) would be able to detect the presence of tunneling fluctuations in a zero-field cooled sample in zero external field, since the total magnetization is zero and remains so. Below $T \sim 1.5$ K the steps in the hysteresis loops of Mn\textsubscript{12}-ac can be observed only at relatively high values of external field 55,56 which means that the spin Hamiltonian under those conditions is radically different from the zero-field case. Therefore, that both our data and the previous magnetization measurements show a crossover around $T \approx 0.8$ K should be considered as a coincidence.

The roughly $T$-independent plateau in the LSR rate below $T \approx 0.8$ K is characterized by a value of $W \approx 0.03$ s$^{-1}$ which is surprisingly high, which at first sight may appear like an argument against the interpretation in terms of tunneling fluctuations of the electron spin. Experimentally it is indeed well known 57 that the relaxation of the magnetization in Mn\textsubscript{12}-ac in zero field may take years at low $T$, which means that the tunneling events are in fact extremely rare. Based on this, we are forced to assume that tunneling takes place only in a small minority of the clusters, and that some additional mechanism takes care of the relaxation of the nuclei in molecules that do not tunnel. This is a very realistic assumption, since all samples of Mn\textsubscript{12}-ac are reported to contain a fraction of FRMs 45,46 as mentioned in Sect. II A. Moreover, since we are also able to monitor the sample magnetization, we verified that e.g. a FC sample maintains indeed its saturation magnetization for several weeks while nuclear relaxation experiments are being performed (at zero field).

FIG. 4: (Color online) $^{55}$Mn NMR spectra of the (a) Mn\textsuperscript{(1)} and (b) Mn\textsuperscript{(2)} lines in Mn\textsubscript{12}-ac, at $T = 20$ mK. Open circles: oriented powder. Solid squares: single crystal. The Mn sites corresponding to each line are shown in the central drawing of the molecular structure. All the spectra are measured in a field-cooled sample.

FIG. 5: (Color online) Temperature-dependence of the nuclear spin-lattice relaxation rate $W$ of the Mn\textsuperscript{(1)} line, in zero external field and ZFC sample. The inset shows some examples of recovery of the nuclear magnetization after a time $t$ from an inversion pulse, at the indicated temperatures. These curves have been fitted to Eq. (2) to extract $W$. 

\begin{equation}
W = \frac{1}{T} \ln \left( 1 + \frac{T}{T_0} \right)
\end{equation}
This confirms that any relevant tunneling dynamics must originate from a small minority of molecules. On the other hand, it also means that the observed NMR signal comes mainly from nuclei belonging to frozen molecules, thus there must be some way for the fluctuations in FRMs to influence the nuclear dynamics in the majority of slow molecules as well. One possibility is to ascribe it to the fluctuating dipolar field produced by a tunneling FRM at the nuclear sites of neighboring frozen molecules. In that case we may give an estimate of $W$ using an expression of the form:

$$W \approx \frac{\gamma^2}{4} \frac{\tau_T}{1 + \omega_N^2 \tau_T^2} \approx \frac{b_{dip}^2}{4B_{tot}} \tau_T^{-1},$$

where $b_{dip}$ is the perpendicular component of the fluctuating dipolar field produced by a tunneling molecule on its neighbors and $\tau_T^{-1}$ is the tunneling rate. The highest value that $b_{dip}$ may take is $\sim 3$ mT in the case of nearest neighbors, which leads to the condition $\tau_T^{-1} \approx 10^6$ s$^{-1}$. Such a high rate is of course completely unrealistic. We must therefore consider the effect of a tunneling molecule on the nuclei that belong to the molecule itself, and look for some additional mechanism that links nuclei in FRMs with equivalent nuclei in frozen clusters. It is natural to seek the origin of such a mechanism in the intercluster nuclear spin diffusion, and in the next section we shall provide strong experimental evidences to support this interpretation.

C. Transverse spin relaxation

The $T$-dependence of the TSR rate $T_2^{-1}(T)$ is shown in Fig. 6. One may observe that below 0.8 K the TSR, just like the LSR, saturates to a nearly $T$-independent plateau. In particular, $T_2^{-1}(T < 0.8 \text{ K}) \approx 100$ s$^{-1}$, which is a factor $\sim 3000$ larger than the low-$T$ limit of the LSR rate $W$. The values plotted in Fig. 6 are all obtained by fitting the decay of the transverse magnetization with Eq. (7), i.e. with a single exponential. While this is very accurate at high $T$, we found that for $T \lesssim 0.2$ K a better fit is obtained by including a Gaussian component, as in Eq. (6). In any case, the single-exponential fit does capture the relevant value for $T_2^{-1}$ at all temperatures.

A point of great interest is the measurement of the TSR at $T = 20$ mK in a FC and a ZFC sample, as shown in the inset of Fig. 6. The decay of the transverse magnetization is best fitted by Eq. (6), whereby the Gaussian component, $T_{2G}^{-1}$, is separated from the Lorentzian one, $T_{2L}^{-1}$. From the Gaussian component of the decay we can extract directly the effect of the nuclear dipole-dipole interaction, whereas the other mechanisms of dephasing (e.g. random changes in the local field due to tunneling molecules) contribute mainly to the Lorentzian part. The fit yields $T_{2G}^{-1}(\text{FC}) = 104 \pm 3$ s$^{-1}$ and $T_{2G}^{-1}(\text{ZFC}) = 77 \pm 3$ s$^{-1}$. These results can be understood by assuming that, at very low $T$, the main source of TSR is the dipole-dipole coupling of like nuclei in neighboring molecules.

Then we can estimate $T_2^{-1}$ from the Van Vleck formula for the second moment $M_2 = \langle \Delta \omega^2 \rangle$ of the absorption line in dipolarly-coupled spins:

$$M_2 = \left(\frac{1}{4\pi} \frac{3}{4} \gamma^2 I(I + 1) \sum_{i \neq j} \frac{(1 - 3 \cos^2 \theta_{ij})^2}{r_{ij}^6} \right),$$

yielding $T_2^{-1} = 131$ s$^{-1}$ if we take for $r_{ij}$ the distance between centers of neighboring molecules. The estimated $T_2^{-1}$ would obviously be much larger if one would consider the coupling between nuclei within the same cluster. As we argued when discussing the $^{55}$Mn spectra, it is possible that the cluster symmetry is low enough to prevent intrachannel nuclear spin flip-flops. This may explain why Eq. (6) yields the right order of magnitude when only coupling between nuclei in neighboring molecules is considered. An alternative argument is that, given the small number (4 at best) of like $^{55}$Mn spins within one cluster, the dipolar coupling between them does not yield a genuine decay of the transverse magnetization for the entire sample. The macroscopic $T_2$ decay measured in the experiment reflects therefore the slower, but global, intercluster spin diffusion rate. A similar observation was recently made also in a different molecular compound, $\text{Al}_{50}\text{C}_{120}\text{H}_{180}$ (Ref. 59).

We also note that, in the case of a ZFC sample, the sum in Eq. (6) should be restricted to only half of the

![Image](image_url)
neighboring molecules, since on average half of the spins have resonance frequency $+\omega_N$ and the other half $-\omega_N$, and no flip-flops can occur between nuclei experiencing opposite hyperfine fields. This is equivalent to diluting the sample by a factor 2, which reduces the expected $T_2^{-1}$ in ZFC sample by a factor $\sqrt{2}$. Indeed, we find in the experiment $T_2^{-1}({\text{FC}})/T_2^{-1}({\text{ZFC}}) = 1.35 \simeq \sqrt{2}$ which, together with the good quantitative agreement with the prediction of Eq. (7), constitutes solid evidence for the presence of intercluster nuclear spin diffusion. This is precisely the mechanism required to explain why the tunneling in a minority of FRMs can relax the whole nuclear spin system. The need for intercluster nuclear spin diffusion could already have been postulated by analyzing the LSR rate, and the magnetization dependence of the TSR rate gives an independent confirmation.

For comparison, in a recent study of the $^{57}$Fe NMR in Fe$_8$, Baek et al.\cite{Baek} attributed the observed TSR rate to the dipolar interaction between $^{57}$Fe and $^1$H nuclei. They analyzed their data with the expression $T_2^{-1} \simeq (M_2^2)/(12\tau_c)^{1/3}$, where $\tau_c$ is the proton TSR time due to their mutual dipolar coupling and $M_2^2$ is the second moment of the $^{57}$Fe - $^1$H coupling. However, the same model\cite{Baek} predicts the echo intensity to decay as $M_z(t)/M_z(0) \simeq \exp(-2M_2^2t^3/3)$. This function fails completely in fitting our echo decays, therefore we do not consider the $^{55}$Mn - $^1$H dipolar coupling as an alternative explanation for the TSR we observe.

Finally we stress that, in our view, the fact that the LSR and the TSR are both roughly $T$-independent below 0.8 K does not find its origin in the same mechanism. Rather, we attribute them to two different mechanisms, both $T$-independent: the quantum tunneling of the electron spin (for the LSR) and the nuclear spin diffusion (for the TSR).

Having argued that the LSR in Mn$_{12}$-ac in driven by tunneling fluctuations of the FRMs, which are peculiar of the acetate compound, it’s interesting to note that other varieties of Mn$_{12}$ molecules have meanwhile become available. In particular the Mn$_{12}$-tBuAc\cite{Dykstra,Hucht} is a truly axially symmetric variety that does not contain any FRMs, and could provide an interesting counterexample for our results if studied by low-$T$ NMR. The Mn$_{12}$BrAc molecule is also thought to be free of FRMs\cite{Dykstra,Hucht} and some low-$T$ NMR experiments have been performed on it\cite{Dykstra,Hucht} that show indeed very different results from what we report here. However, as we shall argue in \cite{Dykstra,Hucht}, a definite conclusion on the meaning of NMR experiments at very low $T$ should only be drawn when the analysis of the nuclear spin thermalization is included.

D. Field dependence of the longitudinal spin relaxation rate

Further insight in the interplay between the quantum tunneling fluctuations and the nuclear spin dynamics is provided by the study of the dependence of the LSR rate $W$ in the ZFC (solid dots) and FC (open dots) sample at $T = 20$ mK. The measuring frequencies are $\nu(B_z) = 230 + \gamma_N B_z$ MHz. The solid line is a Lorentzian fit with HWHM $\Delta B_z \simeq 60$ mT. The dotted line through the FC data is a guide for the eye.

FIG. 7: (Color online) Longitudinal field dependence of the LSR rate $W$ in the ZFC (solid dots) and FC (open dots) sample at $T = 20$ mK. The measuring frequencies are $\nu(B_z) = 230 + \gamma_N B_z$ MHz. The solid line is a Lorentzian fit with HWHM $\Delta B_z \simeq 60$ mT. The dotted line through the FC data is a guide for the eye.
for both positive and negative fields, while the value at zero field is less than half that for the ZFC sample. We therefore observe that in zero field the recovery of longitudinal magnetization in the FC sample is faster than in the ZFC, whereas the opposite is true for the decay of transverse magnetization (inset Fig. 8).

If the LSR rate $W(B_z)$ is to be interpreted as a signature of quantum tunneling, its HWHM is clearly larger than expected. Part of the reason may be the fact that the width of the Mn$^{(1)}$ line is already intrinsically larger than both $\Delta B_z$ and the distribution of dipolar fields created by the molecules. Indeed, the width of the Mn$^{(1)}$ line, $\sigma_\nu \simeq 1.2$ MHz, translates into a local field distribution of width $\sigma_B \simeq 115$ mT for $^{55}$Mn. The observed HWHM does depend, for instance, on the choice of $\nu(0)$. As soon as $B_z \neq 0$ the presence of slightly misaligned crystallites in our sample may also contribute to the width of the resonance. In any case, all of the mechanisms mentioned above (distribution of internal dipolar fields, width of the NMR line, distribution of crystallite orientations in the sample) would yield a $T$-independent linewidth for $W(B_z)$. Fig. 8 shows $W(B_z)$ in ZFC sample at three different temperatures, $T = 0.02, 0.72, 1.13$ K, covering the pure quantum regime, the thermally-activated regime, and the crossover temperature. The NMR frequency in these datasets is $\nu(B_z) = 231 + \gamma_N B_z$. The data have been fitted by Lorentzian lines yielding a HWHM $\Delta B_z = 16, 85, 118$ increasing with temperature. We note immediately that the HWHM at $T = 20$ mK is much smaller than the one obtained from the data in Fig. 7, the only difference between the two sets being $\nu(0)$ and, subsequently, all other measurement frequencies at $B_z \neq 0$. Indeed, we found that already in zero field the LSR rate does depend on $\nu$, reaching the highest values at the center of the line and falling off (up to a factor 5) on the sides. This dependence, however, becomes much weaker at high temperatures. It is therefore rather difficult to make strong statements about the meaning of the observed increase in $\Delta B_z$ with temperature. At any rate, however, the field dependencies observed here at low-$T$ are much stronger than those previously reported in the high-$T$ regime. Goto al. also reported $W(B_z)$ for the “lower branch” of the Mn$^{(1)}$ line, viz. for the nuclei whose local hyperfine field is opposite to the external field (Ref. 24, Fig. 6, closed squares). That situation is equivalent to our FC data (Fig. 7 open dots) for $B_z < 0$. At large fields an overall increase of $W$ with $B_z$ is observed in Ref. 24, but for $B_z < 1$ T the LSR rate does decrease, in agreement with our results.

We also noted, both in Fig. 8 and in the FC data in Fig. 7, that a small increase in $W(B_z)$ occurs at $|B_z| \simeq 0.5$ T, which is approximately the field value at which the $|+9\rangle$ and $|-10\rangle$ electron spin states come into resonance. This feature is barely observable, but nevertheless well reproducible. As a counterexample, in another dataset (not shown) we investigated $W(B_z)$ more carefully in the FC sample at $T = 20$ mK for positive values of $B_z$, and found no increase around $B_z \simeq 0.5$ T, as one would expect since the fully populated state, $|-10\rangle$, is pushed far from all other energy levels. A similarly small peak in $W(B_z)$ at the first levels crossing has been recently observed in Fe$_8$ as well.

**E. Deuterated sample**

The role of the fluctuating hyperfine bias on the incoherent tunneling dynamics of SMMs, predicted by Prokof’ev and Stamp$^{2}$ has been clearly demonstrated by measuring the quantum relaxation of the magnetization in Fe$_8$ crystals in which the hyperfine couplings had been artificially modified by substituting $^{56}$Fe by $^{57}$Fe or $^1$H by $^2$H (Ref. 18). For instance, the time necessary to relax 1% of the saturation magnetization below 0.2 K was found to increase from 800 s to 4000 s by substituting protons by deuterium, whereas it decreased to 300 s in the $^{57}$Fe enriched sample. More recently, Evangelisti et al. showed that the $^{57}$Fe isotopic enrichment of Fe$_8$ causes the magnetic specific heat to approach its equilibrium value within accessible timescales ($\sim 100$ s).

Since in Mn$_{12}$-ac the only possible isotope substitution is $^1$H $\rightarrow$ $^2$H, we performed a short set of measurements on a deuterated sample. The sample consists of much smaller crystallites than the “natural” ones used in all other experiments reported here. Although a field-alignment was attempted following the same procedure as described in $^{11}$C the orientation of the deuterated sample turned out to have remained almost completely random, probably due to the too small shape anisotropy of the crystallites. We therefore report only experiments in zero external field, where the orientation is in principle...
irrelevant.

The results are shown in Fig. 9: the $^{55}$Mn LSR rate at $T = 20$ mK in zero field and ZFC sample is indeed reduced to $W_\text{deut} \simeq 0.0035$ s$^{-1}$, i.e. 6.5 times lower than in the “natural” sample. This factor is the same as the reduction of the electron spin relaxation rate seen in deuterated Fe$_8$ (Ref. 18), and it coincides with the ratio of the gyromagnetic ratios of $^1$H and $^2$H. This finding unequivocally proves that the proton spins are very effective in provoking the tunneling events via the Prokof’ev-Stamp mechanism, and confirms that the LSR rate of the $^{55}$Mn nuclei is a direct probe of the electron spin tunneling rate.

As regards the TSR, the result is quite intriguing: slow but rather ample oscillations are superimposed to the decay of transverse magnetization, and the overall decay rate appears slower than in the natural sample. This behavior is reminiscent of the change in TSR rate upon application of a small longitudinal magnetic field in the natural sample. The latter has a rather complicated physical origin and is still under investigation.

F. Comparison with a Mn$^{3+}$ site

Some rather interesting results emerge from the analysis of extra measurements performed on the NMR line of the Mn$^{(2)}$ site, i.e. a Mn$^{3+}$ ion. Fig. 10 shows a comparison between the recovery of the longitudinal magnetization and the decay of the transverse magnetization in Mn$^{(1)}$ and Mn$^{(2)}$ sites, at $T = 20$ mK in the FC sample and zero external field, at a frequency $\nu^{(2)} = 283.7$ MHz. The TSR is very similar in both sites, although a closer inspection evidences that the Gaussian nature of the decay is less pronounced in the Mn$^{(2)}$ sites, which leads to $T_{\text{or}}^{-1} = 83$ s$^{-1}$ instead of the $T_{\text{or}}^{-1} = 104$ s$^{-1}$ found in Mn$^{(1)}$. More importantly, the LSR is three times slower in the Mn$^{(2)}$ site, as seen in Fig. 10(b). This is opposite to the high-$T$ regime, where the Mn$^{3+}$ sites were found to have much faster relaxation. Furthermore, the field dependence of the LSR rate appears sharper in the Mn$^{(2)}$ site, as shown in Fig. 11. The asymmetry in $W(B_z)$ for a FC sample is still present, but less evident than in the Mn$^{(1)}$ site due to the more pronounced decrease of $W$ already for small applied fields.

The similarity between the TSR rates in the Mn$^{(1)}$ and the Mn$^{(2)}$ sites is indeed expected if $T_2$ is determined by intercluster nuclear spin diffusion. Conversely, the difference in LSR is more difficult to understand if one assumes that the process that induces longitudinal spin relaxation is the tunneling of the molecular spin. However, one clear difference between Mn$^{(1)}$ and Mn$^{(2)}$ is the width of the NMR line, much larger in Mn$^{(2)}$. Since the integrated intensity of both lines is identical, the Mn$^{(2)}$ has an accordingly lower maximum intensity. We have verified for both sites that the LSR rate is the fastest when measuring at the highest intensity along each line. Thus, the factor 3 slower LSR in Mn$^{(2)}$ could simply be another manifestation of the apparent dependence of the measured $W$ on the NMR intensity along each line. We point out, however, that the measured LSR rate is independent of the $\pi/2$ pulse length, which determines the spectral width of the pulse and thereby the fraction of spins being manipulated and observed. This means that the difference in $W$ for the two sites cannot be simply attributed to a difference in the number of spins excited during a pulse of given length but that other (more complex) factors must play a role.

IV. THERMALIZATION OF THE NUCLEAR SPINS

Having demonstrated that the $^{55}$Mn longitudinal spin relaxation below 0.8 K is driven by $T$-independent quantum tunneling fluctuations, a natural question to ask is whether or not the nuclear spins are in thermal contact with the lattice at these low temperatures. Let us recall that any direct coupling between phonons and nu-
clear spins is expected to be exceedingly weak, due to the very small density of phonons at the nuclear Larmor frequency. Relaxation through electric quadrupole effects, if present, would show a temperature dependence $\propto (T/\Theta_D)$ for direct process or $\propto (T/\Theta_D)^2$ for Raman process ($\Theta_D$ is the Debye temperature), which is not consistent with our observations. Therefore the thermalization of the nuclei will have to take place via the electron spin - lattice channel. Since in the quantum regime the only electron spin fluctuations are due to tunneling, the question whether the nuclear spins will still be in equilibrium with the lattice temperature is of the utmost importance.

We have addressed this problem by cooling down the refrigerator from 800 to 20 mK while monitoring simultaneously the temperature $T_{\text{bath}}$ of the $^3\text{He}/^4\text{He}$ bath in the mixing chamber (just next to the sample) and the NMR signal intensity of the Mn$^{(1)}$ line, in zero external field and on a ZFC sample. The signal intensity was measured by spin echo with repetition time $t_{\text{rep}} = 60$ s. The nuclear spin temperature $T_{\text{nucl}}$ is obtained as described in §II C, and plotted in Fig. 12 together with $T_{\text{bath}}$. We find that the nuclear spin temperature strictly follows the bath temperature, with small deviations starting only

![FIG. 10: (Color online) Comparison between (a) the recovery of longitudinal magnetization and (b) the decay of transverse magnetization in Mn$^{(1)}$ (circles) and Mn$^{(2)}$ (diamonds) sites, at $T = 20$ mK in FC sample and zero external field. The solid (Mn$^{(2)}$) and dashed (Mn$^{(1)}$) lines are fits to Eq. (2) in panel (a) and Eq. (4) in panel (b).](image)

![FIG. 11: (Color online) Longitudinal field dependencies of the LSR rates in Mn$^{(1)}$ (circles) and Mn$^{(2)}$ (diamonds) sites, normalized at the zero-field value. The data are taken at $T = 20$ mK in FC sample with central measuring frequencies $\nu^{(1)}(0) = 230$ MHz and $\nu^{(2)}(0) = 283.7$ MHz.](image)

![FIG. 12: (Color online) Comparison between bath temperature $T_{\text{bath}}$ (solid lines) and nuclear spin temperature $T_{\text{nucl}}$ (circles), while cooling down the system (main panel) and while applying step-like heat loads (inset). The waiting time between NMR pulses was 60 s in the main panel and 180 s in the inset. Both datasets are at zero field in ZFC sample.](image)


below $\sim 200$ mK. This result is crucial but rather paradoxical, and we shall discuss its implications in detail in §V.D Experimentally, however, it certifies the effectiveness of our cryogenic design in achieving the best possible thermalization of the sample, since the nuclear spins are the last link in the chain going from the $^3$He/$^4$He bath via the phonons in the sample to the electron spins and finally to the nuclei.

The lowest spin temperature that can be measured appears to depend on the pulse repetition time $t_{\text{rep}}$. To measure $T_{\text{nuc}}$ with the pulse NMR method we need a $\pi/2$ pulse to create a transverse nuclear magnetization, and after a time $T_2$ the spins are effectively at infinite $T$ so enough time must elapse before taking the next $T_{\text{nuc}}$ measurement. For the data in Fig. 12 $t_{\text{rep}} = 60$ s was barely longer than the observed time for inversion recovery [see Fig. 3b], and the lowest observed spin temperature is $T_{\text{min}}\text{nuc} \sim 80$ mK. This improved when using longer waiting times between pulses, e.g. $T_{\text{min}}\text{nuc} \sim 35$ mK with $t_{\text{rep}} = 180$ s, as shown in the inset of Fig. 12. However, no matter how long the waiting time, we never observed a $T_{\text{nuc}}$ lower than $\sim 30$ mK.

Next we study the time constant $\tau_{\text{th}}$ for the thermalization of the nuclear spin system with the helium bath, by applying step-like heat loads and following the time evolution of $T_{\text{nuc}}$. In particular, we are interested in the relationship between $\tau_{\text{th}}$, the LSR time $T_1 = 1/2W$ as obtained from the inversion recovery technique, and the $^3$He circulation rate $\dot{n}$, which is proportional to the refrigerator’s cooling power, $Q$. $T_1$ is easily tuned by measuring at different longitudinal fields and Mn sites, while $\dot{n}$ is changed by applying extra heat to the refrigerator still. Since also the NMR signal intensity changes under different fields and Mn sites, we must redefine every time the conversion factor $K$ between signal intensity and $T_{\text{nuc}}$. In the following we choose $K$ such that the asymptotic value of $T_{\text{nuc}}$ for $t \to \infty$ matches the measured $T_{\text{bath}}$ at the end of the heat step. This implies that the measuring pulses do not saturate, i.e. “heat up”, the nuclear spins, and requires $t_{\text{rep}} > T_1$. Fig. 13 shows four examples of the time evolution of $T_{\text{nuc}}$ under the application of a heat load for $\sim 2$ hours, in Mn$^{(1)}$ and Mn$^{(2)}$ sites, with or without an applied field, and with an increased $^3$He flow rate. We fitted the data to the phenomenological function:

$$T_{\text{nuc}}(t) = T_{\text{nuc}}(0) + (T_{\text{nuc}}(\infty) - T_{\text{nuc}}(0)) \left[1 - \exp\left(-\frac{t - t_0}{\tau_{\text{th}}}\right)\right],$$

where $T_{\text{nuc}}(\infty)$ is set by definition equal to $T_{\text{bath}}$ at the end of the step, $T_{\text{nuc}}(0)$ follows automatically from the above constraint, and $t_0$ is the time at which the heat pulse is started. We find that $\tau_{\text{th}}$ is always much longer than the nuclear LSR time $T_1$, and that larger $T_1$ corresponds to larger $\tau_{\text{th}}$. However, the dependence of $\tau_{\text{th}}$ on Mn site and applied field is not as strong as for $T_1$, i.e. $\tau_{\text{th}}$ and $T_1$ are not strictly proportional to each other. Conversely, by changing the $^3$He flow rate we observe that, within the errors, the ratio of heat transfer from the $^3$He stream to the nuclear spins is proportional to $\dot{n}$, given the same conditions of nuclear site and external field.

We should stress that, when measuring $T_1$ by inversion recovery, we effectively “heat up” only a small fraction of the nuclear spins, namely those whose resonance frequencies are within a range, $\delta \nu$, proportional to the inverse of the duration, $t_\pi$, of the $\pi$-pulse. With $t_\pi \simeq 20 \mu$s we get $\delta \nu = 1/2t_\pi \simeq 8$ KHz, which is less than 0.2% of the width of the Mn$^{(1)}$ line. Conversely, by increasing the bath temperature we heat up the entire spin system, thereby requiring a much larger heat flow to occur between the $^3$He stream and the nuclear spins. Therefore, these results show that the thermal equilibrium between nuclear spins and lattice phonons does occur on a timescale of the order of $T_1$ as obtained from inversion recovery, since the main bottleneck appears to be between lattice phonons and $^3$He stream, as demonstrated by the dependence of $\tau_{\text{th}}$ on $\dot{n}$. In a later set of experiments (not shown here) using a small single crystal instead of a large amount of oriented powder, we have indeed observed an even shorter $\tau_{\text{th}}$, which indicates that $\tau_{\text{th}}$ should ultimately tend to $T_1$ for small sample size and strong thermal contact between lattice phonons and helium bath.

### B. Longitudinal field sweeps and magnetic avalanches

To conclude our study on the nuclear spin thermalization, we attempted to measure $T_{\text{nuc}}$ in the presence of large longitudinal magnetic field sweeps, motivated by the fact that much of the experiments on spin tunneling in SMMs are based on the measurement of magnetic hysteresis loops. Under those conditions, the electron spins are flipped at abnormally large rates, and one may ask whether or not the nuclear spins are still able to remain in thermal equilibrium. Unfortunately, monitoring $T_{\text{nuc}}$ while $B_z$ is being swept means that one should continuously change the NMR probe frequency, and synchronize that change with the field sweep. This being technically cumbersome, we could only measure $T_{\text{nuc}}$ at zero field.

### TABLE I: Experimental conditions and relaxation rates for the nuclear spin temperature experiments in Fig. 13

| Panel | Mn site | $B_z$ (T) | $\dot{n}$ (μmol/s) | $\dot{Q}$ (mW) | $t_{\text{rep}}$ (s) | $T_1$ (s) | $\tau_{\text{th}}$ (min) |
|-------|---------|-----------|--------------------|----------------|--------------------|----------|------------------|
| a     | 1       | 0         | 330                | 0.63           | 120                | 41.3     | 58 ± 5           |
| b     | 2       | 0         | 330                | 0.63           | 120                | 122      | 83 ± 13          |
| c     | 1       | 0         | 430                | 0.78           | 120                | 41.3     | 37 ± 3           |
| d     | 2       | 0.2       | 330                | 0.63           | 300                | 355      | 92 ± 33          |
at the beginning and at the end of a $B_z$ sweep. The results are somewhat inconclusive and shall not be discussed here, but more details can be found in section 4.4.2 of Ref. 48.

We do mention, however, that during the $B_z$-sweep experiments we always encountered magnetic avalanches, i.e., abrupt reversal of the electronic magnetization of the whole sample. This phenomenon has been first reported already some time ago but is only recently being studied in more detail. Importantly, the magnetization reversal is expected to be accompanied by the emission of electromagnetic radiation, which is in fact what we observed in our experiments, since we were not equipped to measure the electronic magnetization directly on short time scales. Fig. 14 shows the temperature recorded by the upper thermometer in the mixing chamber (see Fig. 2), while the longitudinal field is being swept at a rate $dB_z/dt = 0.5$ T/min. The sweeping field gives a heat load that raises the observed temperature to $\approx 30$ mK, but the most striking feature of the data is the sudden jump of $T_{\text{upper}}$ to above 100 mK, whenever the applied field reaches $|B_z| \approx 1.9$ T and its direction is opposite to the instantaneous magnetization. We note that the timescale for the apparent temperature jump is essentially identical to what we observe immediately after the application of a rf-pulse for NMR measurements, as shown in Fig. 2(b). In the same figure it is seen that a heat pulse applied at the sample location shows its effect at the upper thermometer with a delay of about 3 minutes (due to the $^3$He drift velocity) in the form of a broad temperature “bump”. We therefore conclude that the sudden jumps in $T_{\text{upper}}$ shown in Fig. 14(b) must be of electromagnetic rather than thermal origin, and may be attributed to the radiation produced by the sudden reversal of the entire electronic magnetization of the sample by the magnetic avalanche. The radiation bursts reported in Ref. 68 at a temperature $T = 1.8$ K occurred at $|B_z^{(\text{av})}| \approx 1.4$ T, which corresponds to the third level crossing field for spin tunneling, i.e., the value of field at which the resonance between $m = \pm 10$ and $m = \mp 7$ states is obtained. We found instead the avalanches at $|B_z^{(\text{av})}| \approx 1.9$ T, i.e., the fourth level crossing, $m = \pm 10 \leftrightarrow \mp 6$, but our measurements are done at $T \approx 30$ mK. Goto et al. also reported the observation of magnetic avalanches in Mn$_{12}$-ac, and studied the temperature dependence of the avalanche field $B_z^{(\text{av})}$. Their finding that $B_z^{(\text{av})}$ increases with temperature was interpreted as a sign that the avalanches occur more easily when the thermal contact to the bath is weaker. Indeed, whereas they would observe avalanches even at fields as low as $B_z^{(\text{av})} \approx 0.5$ T (the first level crossing) with the sample loosely anchored to the mixing chamber of a dilution re-
FIG. 14: (Color online) (a) Longitudinal magnetic field and (b) temperature of the upper thermometer (see Fig. 2) during a field sweep at $dB_z/dt = 0.5$ T/min. The sample was initially field-cooled with $B_z > 0$. The sharp jumps in $T_{upper}$ occur when $|B_z| \simeq 1.9$ T, i.e. at the fourth level crossing field, and are attributed to the radiation produced by a magnetic avalanche.

frigeparator at $T = 0.15$ K, they never saw avalanches when the same sample was placed directly in a liquid helium bath at $T = 1.4$ K. In this sense, our observation of a high $B_z^{(av)} \simeq 1.9$ T confirms once more that our strategy for the sample thermalization is very effective. Suzuki et al. found even higher values of $B_z^{(av)}$ at subkelvin temperatures when measuring the local magnetization of a small Mn$_{12}$-ac crystal immersed in liquid $^3$He. However, their observations differ markedly from ours in that they found avalanches occurring in a wide range of (not necessarily resonant) fields, whereas we saw avalanches always and only at the fourth level-crossing field.

V. ANALYSIS OF THE NUCLEAR SPIN DYNAMICS AND THEORETICAL IMPLICATIONS

In this section we attempt a quantitative analysis of our experimental results, particularly the observed values of LSR rate. To this end, we shall apply the Prokof’ev-Stamp (PS) theory of the spin bath, which describes the dynamics of a “central spin” $S$ (here the giant electronic spin of a Mn$_{12}$-ac cluster) coupled to a bath of environmental (in this case, nuclear) spins. In view of the complexity of the model we provide here an introductory overview of some essential elements of the PS theory needed for our analysis, referring the reader to the original papers for more details. For comparison, we also calculate the LSR rate assuming that the electron spin tunneling is driven by spin-phonon coupling. We anticipate that the result of this effort will be that the existing theory is not sufficient to properly describe these and other related experiments. We shall carry out the analysis in detail in order to emphasize at every step what assumptions are being made, what is their actual validity, and why the known theories cannot explaining the data.

The goal of our analysis is to link the electron spin tunneling rate, $\Gamma = \tau^{-1}$, to the observed LSR rate, $W$, based on the following assumptions, justified by the experiments presented in the previous sections: (i) The nuclear relaxation is driven by tunneling fluctuations in a minority of fast-relaxing molecules. We shall assume the fraction of FRMs to be 5% of the total. The neighboring slow molecules can be safely considered as frozen during the timescale of interest and serve simply as a “reservoir of nuclear polarization”. (ii) The dipole-dipole coupling between $^{55}$Mn nuclei in equivalent sites of neighboring molecules allows intercluster nuclear spin diffusion, at a rate $T_2^{-1}$ much faster than the LSR rate. (iii) The nuclear spin system is in thermal equilibrium with the phonon bath.

Before we start, it is of interest to point out some rather striking peculiarities of the problem at hand. First and most importantly, one cannot use any result from perturbation theory here, because the nuclear Zeeman splittings arise uniquely from hyperfine fields, which themselves jump between two different directions each time the electron spin of a molecule tunnels, so there is no static part of the nuclear Hamiltonian. Perhaps the only situation that resembles this is the nuclear quadrupolar relaxation in systems with molecular rotations. Conversely, in the overwhelming majority of NMR experiments one has a static external field (produced by an actual magnet) and some local fluctuating fields arising from the magnetic environment of the nuclei, which can be treated as small perturbations. Then the LSR rate is easily related to the spectral density of the local magnetic fluctuations, calculated at the NMR frequency determined by the external field. Also curious is the way nuclear spin diffusion proceeds in our system. The well-known treatment of nuclear relaxation by coupling to paramagnetic impurities plus nuclear spin diffusion shows that there is a “spin diffusion barrier radius” below which neighboring nuclear spins cannot exchange energy because the large dipolar field from the impurity brings them out of resonance. Here, instead, there is no such minimum radius for spin diffusion because nuclei at equivalent sites of different molecules are also magnetically equivalent (provided both molecules have the same electron spin orientation).
A. Spin-bath analysis and tunneling rate

To apply the spin bath theory to the $^{55}\text{Mn}$ NMR in Mn$_{12}$-ac, we begin by truncating the giant spin Hamiltonian of the cluster to its tunneling-split ground doublet, and by taking as a basis for its subspace the $m = \pm \mathcal{S}$ projections of $\mathcal{S}$ along the $z$-axis, denoted by $| \uparrow \rangle, | \downarrow \rangle$. This restriction will be relaxed to consider higher excited electron spin doublets when discussing thermally-assisted tunneling. Further, we assume that each central spin is coupled to $N$ nuclear spins $\{I_k\}, k = 1 \ldots N$. The strength of each coupling is given by the quantities $h \omega_{k}^\parallel$ and $h \omega_{k}^\perp$, which represent the part of the hyperfine coupling that does or does not change upon flipping the central spin, respectively (Fig. 15). For nuclei in Mn$^{(1)}$ sites of Mn$_{12}$-ac the hyperfine field $\mathbf{B}_{\text{hyp},k}$ is exactly parallel or antiparallel to the direction of the cluster’s $z$ axis, so $\omega_{k}^\parallel = 0$ and $\omega_{k}^\perp = \gamma_{N} B_{\text{hyp},k}$. In Mn$^{(2)}$ and Mn$^{(3)}$ sites there’s a small nonzero value of $\omega_{k}^\perp$ due to the orbital contribution to the hyperfine field. Conversely, for nuclei such as $^1\text{H}$, which are subject to the vector sum of hyperfine fields from several surrounding clusters, we may expect $\omega_{k}^\parallel$ and $\omega_{k}^\perp$ to have comparable values. Let us define for each nuclear spin a number $m_k$ representing the spin projection of $I_k$ along the direction of the local hyperfine field $\mathbf{B}_{\text{hyp},k}$. For $^1\text{H}$ nuclei $m_k = \pm 1/2$, while for $^{55}\text{Mn}$ $m_k = -5/2 \ldots +5/2$. Then the total hyperfine bias on the cluster is $\xi_{N} = -2h \sum_{k=1}^{N} m_k \omega_{k}^\parallel$. With this definition, $\xi_{N} < 0$ when the majority of nuclear spins is parallel to the local $\mathbf{B}_{\text{hyp},k}$, thereby lowering the total energy of the system. Notice that, for a given orientation of the nuclear spins, $\xi_{N}$ changes sign whenever the electron spin flips, since the direction of $\mathbf{B}_{\text{hyp}}$ does. Thus we define an absolute index of nuclear polarization in each cluster as $P = C_S \sum_{k} m_k$, with $C_S = +1$ when $\mathbf{S}$ is in the $| \uparrow \rangle$ state, and $C_S = -1$ otherwise. Each possible value of $P$ defines a “polarization group”, and is independent of the electron spin state. Since the individual hyperfine couplings vary over a broad range (from ~ 1 MHz for distant protons to 365 MHz in Mn$^{(3)}$), the possible values of the bias $\xi_{N}$ for each $P$ are also widely spread, yielding a set of largely overlapping polarization groups. Globally, we may describe the coupled “central spin + spin bath” system by two manifolds of states, one for each electron spin state $| \uparrow \rangle, | \downarrow \rangle$, split by hyperfine interactions into a dense band of states indexed by the nuclear polarization $P$, as shown in Fig. 15. Calling $P_{\text{max}}$ the maximum value assumed by $P$, $P_{\text{max}} = N$ if $I_k = 1/2 \forall k$. The profile of the hyperfine bias distribution can be calculated with the knowledge of the individual couplings, and is well described by a Gaussian with half-width $E_0 = \sum_{k} \frac{(I_k + 1)/3}{(\omega_{k}^\parallel)^2} \approx 0.082 \text{ K}_{\text{PS}}$.

In addition to the hyperfine couplings, the $\mathbf{S}$ spins are also mutually coupled by dipolar interactions, which yield an additional bias $\xi_{D} = 2 g_{\mu_B} \mathbf{S} \cdot \mathbf{B}_{\text{dip}}$. The dipolar bias can be considered quasi-static in the sense that it remains essentially constant over time intervals that are long compared to the typical timescale for the hyperfine bias fluctuations. The distribution of dipolar biases depends on the total magnetization of the sample and, in general, on its shape. For a demagnetized, ZFC sample of Mn$_{12}$-ac, the dipolar bias distribution is described by a Gaussian with half-width $E_D \approx 0.32 \text{ K}_{\text{PS}}$ Finally, one may in general apply a static external field, $B_z$, along the $z$-axis, which produces an additional bias $\xi_{B} = 2 g_{\mu_B} S_z B_z$. For zero external field and some typical nonzero value of $\xi_{D}$, the energy level scheme of a Mn$_{12}$-ac cluster coupled to its nuclear spins would resemble the sketch shown in Fig. 16.

To analyze the behavior of this system with respect to incoherent tunneling of the electron spin, the crucial question to be answered is what happens to the nuclear spins when $\mathbf{S}$ suddenly changes direction. How many of the $\{I_k\}$ coflip with $\mathbf{S}$? As extensively discussed in the PS literature, there are two mechanisms by which nuclear spins may be flipped by a tunneling event. First, a nuclear spin may coflip with $\mathbf{S}$ if the local hyperfine field does not exactly reverse its direction after $\mathbf{S}$ has tunneled, since it would then start to precess around a different axis, hence the name “orthogonality blocking” or “precessional decoherence” for this mechanism. The number of spins collapsed this way is $\kappa$, defined as (see Fig. 15 for $\beta_h$):

$$e^{-\kappa} = \prod_{k} \cos \beta_h \approx e^{-\frac{1}{2} \sum_{k} \beta_h^2}$$

(9a)

$$\cos(2\beta_h) = -\frac{B_{\text{hyp},k}^{(1)} \cdot B_{\text{hyp},k}^{(2)}}{|B_{\text{hyp},k}^{(1)}||B_{\text{hyp},k}^{(2)}|}$$

(9b)

The cosine factors in Eq. (9a), which are multiplied over all the bath spins, are the overlap matrix elements between the initial and final bath states, i.e. $\langle i | U_k | f \rangle$, where $U_k$ is the rotation operator of the $k$-th bath spin (Ref. 7, Appendix A.2). Clearly, $\kappa$ depends only on the direction of the hyperfine fields, and not on the timescale of the electron spin flip. The nuclei in Mn$^{(1)}$ sites do not
\[ P = -P_{\text{max}} (\downarrow \uparrow \downarrow \downarrow \downarrow) \]

\[ P_{\text{max}} (\downarrow \uparrow \downarrow \downarrow \downarrow) \]

\[ P_{\text{max}}^{-1} (\uparrow \uparrow \downarrow \uparrow \uparrow) \]

\[ P_{\text{max}} (\uparrow \uparrow \downarrow \uparrow \uparrow) \]

“high” nuclear energy

“low” dipolar energy

\[ |\psi\rangle \]

\[ W \]

\[ \xi \]

FIG. 16: (Color online) Sketch of the hyperfine-split manifolds representing the energy of the \( m = \pm S \) electron spin levels coupled to the nuclear spin bath.

The other possibility is that the nuclear spins follow adiabatically the rotation of \( S \). For this to happen, the “bounce frequency” of \( S, \Omega_0 \), has to be small or comparable with the nuclear Larmor frequencies. \( \Omega_0 \) is given here by the energy difference between the \( |m| = S \) and \( |m| = S - 1 \) cluster spin states: since we are interested in FRMs, knowing that the resonance between \( m = -S \) and \( m = S - 1 \) states occurs at \( B_2 \approx 0.39 \) T (Ref. [45]) yields \( \hbar \Omega_0 \approx 10 \) K, i.e., several orders of magnitude larger than \( \{\omega_k\} \). Therefore, the nuclei cannot adiabatically follow the dynamics of \( S \) and the number of spins coflipped by this mechanism, \( \lambda \), is essentially zero. As a matter of nomenclature, this mechanism leads to what is called “topological decoherence” because the topological phase of the \( \{I_k\} \) becomes entangled with that of \( S \).

Combining the two flipping mechanisms defines a parameter \( \xi_0 \propto \lambda + \kappa \), which expresses how much the nuclear polarizations before and after the electron spin flip may differ for the flip to be likely to occur. Two opposite situations are sketched in Fig. 17 where we call \( P^{(1)} \) and \( P^{(2)} \) the nuclear polarizations before and after the electron spin flip, respectively. In any case the system has to tunnel between states at the exact resonance, but in case (a) the electron flip does not require any nuclear coflip \( (P^{(1)} = P^{(2)}) \), while case (b) requires all nuclei to coflip \( (P^{(1)} = -P^{(2)}) \), which is extremely unlikely. As a result, the expression for the tunneling rate contains a factor \( \exp(-\xi/\xi_0) \) that describes precisely this restriction. From the above discussion it is clear that - at least in the absence of external transverse fields - the main contribution to \( \xi_0 \) comes from \( ^1H \) nuclei, and that

\[ \xi_0 \ll \{E_0, E_D\} \]

In the presence of a dipolar bias, the tunneling transition with highest probability, i.e. no coflipping nuclei, occurs when \( \xi_D = \xi_N \) (Fig. 16). This means that a tunneling event effectively entails an exchange of dipolar and hyperfine energy. We may then distinguish between transitions that increase the hyperfine energy (“left to right” in Fig. 16), occurring at a rate \( w_1 \), and transitions that decrease it (“right to left ” in Fig. 16) at a rate \( w_1 \). The total tunneling rate is \( \Gamma^N = (w_1 + w_1)/2 \).
the ground doublet, are

\[ \Gamma_m^N(\xi) \approx \frac{2\Delta^2}{\sqrt{\pi}hE_0^{(m)}} \exp(-\xi^2/\xi_0), \tag{10} \]

\[ G_N^{(m)} = \exp[-\Delta^2/2E_0^{(m)}], \]

\[ E_0^{(m)} \approx \frac{\sqrt{E_0^2m^2 - \Delta^2}}{S^2}, \]

\[ \xi^{(m)} = \frac{\xi m^2}{S}, \]

where \( \Delta_m \) is the tunneling matrix element of the \( m \)-th electron spin doublet, to be calculated by exact diagonalization of the giant spin Hamiltonian. The factor \( G_N^{(m)} \) expresses the fact that the spin-bath mediated tunneling rate vanishes when \( \Delta_m \gg E_0^{(m)} \), i.e. when the spread of nuclear energies is not sufficient to sweep the hyperfine bias through the tunneling resonance. The parameters \( E_0^{(m)}, \xi^{(m)} \) are generalizations to arbitrary electron spin doublets of the quantities \( E_0, \xi \) defined before for the ground doublet \( |m| = S \), while \( \xi_0 \) is assumed \( m \)-independent. To obtain the total tunneling rate through the \( m \)-th doublet we average Eq. (10) over the distribution of dipolar biases:

\[ P_m(\xi) = \frac{1}{\sqrt{2\pi E_D^{(m)}}} \exp(-\xi^2/2E_D^{(m)}), \tag{11} \]

In the real situation considered here, the spread of dipolar biases in the sample is much larger than the tunneling window allowed by hyperfine couplings, \( E_D \gg \xi_0 \). This means we can estimate \( \Gamma_m^N \) by calculating the fraction \( x_m^N \) of molecules with bias \(-\xi_0^{(m)} < \xi < \xi_0^{(m)}\), for which we may approximate \( \Gamma_m^N(\xi) \approx \Gamma_m^N(0) \), and by neglecting the contribution of the molecules whose bias is larger than \( \xi_0 \) and which tunnel at an exponentially small rate:

\[ \int_{-\infty}^{+\infty} P_m(\xi)\Gamma_m^N(\xi)\,d\xi \simeq x_m^N\Gamma_m^N(0), \tag{12} \]

\[ x_m^N = \int_{-\xi_0}^{+\xi_0} P_m(\xi)\,d\xi. \tag{13} \]

Finally, the global spin-bath driven tunneling rate, \( \Gamma^N \), is obtained by summing over the \( m \)-th doublet levels weighted with the appropriate Boltzmann occupation factor:

\[ \Gamma^N(T) \approx \frac{1}{Z} \sum_m \exp\left(-\frac{E_m}{k_BT}\right) x_m^N \frac{2\Delta^2m^2G_N^{(m)}}{\sqrt{\pi}hE_0^{(m)}}, \tag{14} \]

where \( \{E_m\} \) are the average energies of the \( m \)-th doublets and \( Z \) is the partition function. Notice that the spin-bath driven tunneling rates are individually \( T \)-independent: the temperature enters only in the Boltzmann factors for the occupation of the \( m \)-th doublets, and thereby in their contribution to the global tunneling rate \( \Gamma^N(T) \). Also, since \( P_m(\xi) \) is essentially constant in the interval \(-\xi_0 < \xi < \xi_0\), we have \( \Gamma_m^N \propto x_m^N \propto \xi_0 \). This immediately explains why the isotopic substitution of \( ^2\text{H} \) for \(^1\text{H} \) yields a decrease in tunneling rate [Fig. [9 a]], since these are the nuclei that mostly contribute to \( \xi_0 \).

B. Phonon-induced tunneling rate

For comparison, we also discuss the case where the electron spin tunneling is caused by spin-phonon couplings. The phonon-driven tunneling rate though the \( m \)-th doublet, \( \Gamma_m^\phi \), is related to the \((T\text{-dependent})\) broadening of the electron spin states, \( w_m(T) \), by

\[ \Gamma_m^\phi(\xi) \approx \frac{\Delta^2w_m(T)}{\xi_0^m + \Delta_m^2 + \hbar^2w_m^2(T)} \tag{15} \]

The phonon-induced broadenings are obtained as a function of the sample density, \( \rho \), the sound velocity, \( c_s \), and the uniaxial anisotropy parameter, \( D \), as

\[ w_m(T) = p_{m+1,m} + p_{m-1,m} + p_{m+2,m} + p_{m-2,m} \tag{16a} \]

\[ p_{m \pm 1,m} = \frac{D^2}{12\pi\rho c_s^2k_BT} \exp\left(E_{m \pm 1,m} - E_{m,m}\right)/k_BT - 1 \tag{16b} \]

\[ p_{m \pm 2,m} = \frac{17D^2}{192\pi^2\rho c_s^4k_BT} \exp\left(E_{m \pm 2,m} - E_{m,m}\right)/k_BT - 1 \tag{16c} \]

with \( s_{\pm 1} = (S \mp m)(S \pm m + 1)/4(2m + 1)^2 \) and \( s_{\pm 2} = (S \mp m)(S \pm m + 1)(S \mp m + 1)/4(S \pm m + 2) \).

Again, we calculate the fraction of molecules with highest tunneling rate, \( x_m^\phi \), as those whose bias is within the width of the Lorentzian function (17):

\[ x_m^\phi = \int_{-\Delta_m^\phi + \hbar^2w_m^2(T)}^{+\Delta_m^\phi + \hbar^2w_m^2(T)} P_m(\xi)\,d\xi, \tag{17} \]

and weigh the contribution of the \( m \)-th levels with their Boltzmann factor to obtain the total phonon-driven tunneling rate:

\[ \Gamma^\phi(T) \approx \frac{1}{Z} \sum_m \exp\left(-\frac{E_m}{k_BT}\right) x_m^\phi \frac{\Delta_m^2w_m(T)}{\Delta_m^2 + \hbar^2w_m^2(T)}. \tag{18} \]

Contrary to the nuclear-driven case, here each individual \( m \)-th doublet tunneling rate \( \Gamma_m^\phi \) is \( T \)-dependent by itself, besides being weighed by Boltzmann factors. This means that the phonon-driven tunneling rate never shows a \( T \)-independent plateau, even at very low-\( T \) when tunneling occurs only through the ground doublet.

C. Tunneling rate - longitudinal spin relaxation rate

To relate the electron spin tunneling rates, \( \Gamma^N,\phi(T) \), to the observed LSR rate, \( W \), we apply the remarks made above on the behavior of the nuclear spins upon a sudden change of the electron spin direction. In particular, we
shall compare theory and experiments for the Mn\(^{(1)}\) site, where (ideally) the hyperfine coupling would be strictly scalar.\(^{26}\) This implies that the \(^{55}\)Mn spin at Mn\(^{(1)}\) sites do not coflip by “precessional decoherence”, since \(\omega_k^\parallel \approx 0\), neither do they coflip by “topological decoherence” due to the very small values of \(\omega_k^\parallel /\Omega_0\). Thus, each electron spin tunneling event corresponds to the inversion of the populations of the local nuclear Zeeman levels. The LSR rate arising from this situation is easily obtained and can be found in the literature,\(^{20, 28, 61, 72}\) but we repeat here the derivation because it will allow us to point out exactly why no known theory can explain our data. The answer is most easily obtained for nuclear spins \(I = 1/2\), but remains valid for arbitrary spin values.

We start by writing a master equation for the populations of the nuclear Zeeman levels relative to the local hyperfine field direction, calling \(N_+\) the number of nuclei in the excited Zeeman state and \(N_-\) those in the ground state. For simplicity, since the internal equilibrium is reestablished within a time \(T_2 \ll \tau_{\text{r}}\) after each tunneling event, we assume that just before tunneling all clusters have the same values of \(N_+\) and \(N_-\), neglecting fluctuations around the mean values. If a fast-relaxing molecule tunnels at time \(t\), the polarization of its own nuclei is abruptly inverted. Each time a tunneling transition lowers the energy of the local nuclei, which occurs at a rate \(w_1\), then \(N_-\) nuclei have been added to the total number of nuclei in the Zeeman ground state. After a time \(T_2\) this decrease in local hyperfine bias has been redistributed over the sample: calling \(x_{\text{FRM}}\) the fraction of FRMs over the total, then the tunneling event has increased \(N_+\) to \(N_+ + x_{\text{FRM}} N_-\). The same reasoning holds for transitions that increase the hyperfine bias. The master equation is therefore:

\[
\frac{dN_+}{dt} = x_{\text{FRM}} N_- w_1 - x_{\text{FRM}} N_+ w_1. \tag{19}
\]

From here the LSR rate can be obtained by standard textbook calculations.\(^{24}\) Writing \(N_+ = (N + n)/2\) and \(N_- = (N - n)/2\), Eq. \((19)\) becomes:

\[
\frac{dn}{dt} = x_{\text{FRM}} (N(w_1 - w_\uparrow) - x_{\text{FRM}} n(w_1 + w_\uparrow), \tag{20}
\]

which can be rewritten as:

\[
\frac{dn}{dt} = 2W(n_0 - n), \tag{21}
\]

\[n_0 = N\frac{w_1 - w_\uparrow}{w_1 + w_\uparrow}, \tag{22}
\]

\[W = x_{\text{FRM}} \frac{w_1 + w_\uparrow}{2} = x_{\text{FRM}} \Gamma^{N,\phi}, \tag{23}
\]

where \(n_0\) is the equilibrium nuclear polarization and \(W\) is the desired LSR rate, since the solution of \((21)\) is precisely of the form \(n(t) = n(0) - [n(0) - n_0][1 - \exp(-2Wt)]\).

We now attempt to fit the measured LSR rate in zero field at the Mn\(^{(1)}\) site in ZFC sample, using Eqs. \((15)\) and \((23)\). To this end we calculate the energy levels scheme of the FRMs using the effective spin Hamiltonian:

\[
\mathcal{H}_{\text{FRM}} = -D S_z^2 + E(S_x^2 - S_y^2) - C(S_+^1 + S_-^1). \tag{24}
\]

Unfortunately, very little is known about the parameter values in \((24)\). To the best of our knowledge, it’s not even established whether FRMs in Mn\(_{122}\)-ac have lowest total spin state \(S = 10\) or, for instance, \(S = 9\). The analysis of a Mn\(_{12}\) variant containing only FRMs\(^{27}\) seemed to support an \(S = 10\) ground state, but it’s not clear to what extent the FRMs in Mn\(_{122}\)-ac have the same properties as those analyzed in Ref. \(^{27}\). For instance, Ref. \(^{27}\) finds the first level crossing transition, i.e. the value of longitudinal field at which \(E_S = E_{-S+1}\), at \(B^x_{25, S+1} \approx 0.27\) T, quite different from the value observed for the actual FRMs in Mn\(_{122}\)-ac, \(B^x_{25, S+1} \approx 0.39\) T.\(^{25}\) We shall try both \(S = 10\) and \(S = 9\) and discuss how the different behaviors compare to the experimental data. To avoid having too many fitting parameters, we choose to keep \(C\) fixed at the value commonly used for the majority species of Mn\(_{122}\)-ac, \(C = 4.4 \times 10^{-5}\) K.\(^{25}\) The uniaxial anisotropy, \(D\), is obtained by imposing the condition \(B^x_{S+1, S+1} \approx 0.39\) T\(^{25}\) yielding \(D = g\mu_B \times 0.39 = 0.524\) K. Although we tried adding also a fourth order term, \(-B^4_{S}\), it turned out that the best fits are obtained by leaving \(B = 0\), so we shall not discuss this further. The rhombic anisotropy term, \(E\), is used as the actual fitting parameter since it most directly influences the value of the tunneling splittings \(2\Delta_m\) and thereby the tunneling rates \(\Gamma^{N,\phi}\). Cerreta et al.\(^{28}\) showed that the effective \(\Delta\) is extremely sensitive to the gap between the lowest lying total spin manifolds (“S-mixing”), and could explain why the observed Landau-Zener tunneling probabilities in Fe\(_8\) are much larger than what would be expected on basis of the spin Hamiltonian parameters for the \(S = 10\) manifold.\(^{22}\) A small gap between lowest lying total spin manifolds is quite expectable for FRMs, so the values of \(E\) we need to justify the \(\Gamma^{N,\phi}\) extracted from experiment should not be taken literally as an estimate of the anisotropy parameter. In other words, the values of \(E\) used in our calculations account also for the possible S-mixing due to an energetically close manifold with different total spin \(S\), and do not necessarily correspond to the values that one would obtain from neutrons scattering or EPR experiments. We take as fixed parameters the sound velocity \(c_s = 1.5 \times 10^3\) m/s (Ref. \(^{80}\)), the density \(\rho = 1.83 \times 10^3\) g/m\(^3\) (Ref. \(^{31}\)), \(E_D = 0.32\) K (Ref. \(^{63}\)) and \(E_0 = 0.082\) K (Ref. \(^{74}\)), whereas \(E_0\) is allowed to vary. When comparing nuclear- and phonon- driven tunneling rates, we impose the same parameters for the spin Hamiltonian \((21)\). The results of the calculations are shown in Fig. \(^{18}\) for the set of parameters given in Table \(^{III}\).

By looking at the theoretical curves alone we find that, given a fixed set of parameters for the FRMs’ spin Hamiltonian \((24)\), the nuclear-driven tunneling process always dominates over the phonon-driven one, both in the low-\(T\) and in the high-\(T\) regime. The situation may be reversed in the high-\(T\) regime by assuming the sound velocity is
FIG. 18: (Color online) Calculated nuclear spin-lattice relaxation rates, $W$, as a function of temperature, for spin-bath [panels (a) and (c)] and phonon [panels (b) and (d)] mediated tunneling. In panels (a) and (b) a total spin $S = 10$ is assumed for the FRMs; in panels (c) and (d), $S = 9$. The complete parameter sets are given in table II. Black dots: experimental data; thick black lines: calculated $W$; thin lines: contributions of the $m$-th electron spin doublets to the total rate.

| Panel | $S$ | $D$ (K) | $E$ (K) | $\xi_0$ (mK) | $\Delta S$ (µK) |
|-------|-----|---------|---------|-------------|--------------|
| a     | 10  | 0.524   | 0.204   | 10          | 5.4          |
| b     | 10  | 0.524   | 0.204   | -           | 5.4          |
| c     | 9   | 0.524   | 0.178   | 10          | 5.6          |
| d     | 9   | 0.524   | 0.178   | -           | 5.6          |

TABLE II: Parameter values for the calculations shown in Fig. 18. In bold are given the free fitting parameters. The tunneling matrix element in the lowest doublet, $\Delta S$, is obtained from the Hamiltonian (24), i.e. it is not introduced by hand.

lower than the literature value used here, but $\Gamma^\phi > \Gamma^N$ would never hold at low-$T$ under realistic circumstances. A comparison with the experimental data shows that both nuclear- and phonon- driven mechanisms yield a correct slope of $W(T)$ in the thermally-assisted regime, $T > 0.8$ K, whereas the phonon process can never reproduce the low-$T$ plateau. An almost perfect fit of the data is obtained by assuming that the FRMs have a total spin $S = 9$, while the $S = 10$ case has a $T$-dependent region systematically starting at too high temperatures. In the nuclear-driven case, we used an optimal value of $\xi_0 \approx 10$ mK which seems very reasonable, since the main contribution to $\xi_0$ arises from the coupling to protons. Conversely, the values used for $E$ appear very high, since to fit the NMR data we need to assume $D/E \approx 2.5$. As mentioned before, however, such a high value of $E$ should not be interpreted as the spectroscopic rhombic term in the spin Hamiltonian, since it is used here as the parameter that tunes the tunneling splitting of the
ground doublet, and therefore incorporates the effect of S-mixing if a manifold with different total spin value is energetically close to the $S$ ground state.

An important remark is that our calculations, which only account for tunneling fluctuations as a source of nuclear LSR, can accurately reproduce the observed LSR rate also in the thermally activated regime, $T > 0.8$ K. All the previous NMR experiments in that regime have been interpreted in terms of the “intrawell” electron spin fluctuations, that arise from thermal excitation of the electron spin state on the same side of the anisotropy barrier [see Fig. 1(b)]. As pointed out by Goto et al.,

that reasoning is inappropriate when applied to the LSR of nuclei belonging to Mn$^{3+}$ ions, since the hyperfine coupling tensor is diagonal. In that case, a fluctuation in the $\hat{z}$ projection of the electron spin does not result in a fluctuating field perpendicular to the nuclear quantization axis (which is $\hat{z}$ itself), and cannot account for longitudinal nuclear spin relaxation. As we show in Fig. 1(b), including the effect of electron spin tunneling through $|m| < S$ doublets solves what appeared to be a paradox, since the tunneling fluctuations induce nuclear LSR also in the absence of non-diagonal hyperfine coupling terms. For the nuclei in Mn$^{3+}$ ions, the intrawell electron spin transitions do provide an additional channel for nuclear relaxation, which may explain why the LSR rate at $T > 1$ K in the Mn$^{3+}$ sites is larger than that in the Mn$^{4+}$ ones.

**D. Thermal equilibrium**

In the preceding discussion, it may seem that we have not explicitly used the condition that the nuclear spins are in thermal equilibrium, which is what we observe in the experiment. This condition, however, is automatically implied in the application of Eq. (2) to the LSR rate. For Eq. (2) to actually represent the rate at which the nuclear spins exchange energy with a thermal bath and thereby return to the equilibrium magnetization after a perturbing NMR pulse, one needs to include the detailed balance condition:

$$\frac{w_{\uparrow}}{w_{\downarrow}} = \exp \left( -\frac{\hbar \omega_N}{k_B T} \right).$$ (25)

In other words, if the nuclear spin temperature has to reach equilibrium with the thermal (phonon) bath via the process described by the rates $w_{\uparrow}$ and $w_{\downarrow}$, the latter must satisfy (25). The detailed balance condition is often taken for granted, but in this case one needs to be more careful. $w_{\uparrow}$ and $w_{\downarrow}$ represent the rates of electron spin transitions that increase or lower the nuclear energy, respectively. The crucial point is that both are rates for tunneling transitions, which occur when the total energy of the “electron plus nuclear spins” system is the same before and after the electron spin flip. Thus, the difference between $w_{\uparrow}$ and $w_{\downarrow}$ is simply that, e.g., $w_{\uparrow}$ is the rate for a tunneling transition that increases the nuclear spin energy while reducing the electronic one. That is, after the flip most of the nuclei are oriented against their local hyperfine field, while the electron spin is favorably aligned with respect to the local field (in particular the dipolar one, when $B_z = 0$). $w_{\downarrow}$ does the opposite and, interestingly, this means that the instantaneous local spin temperature (local referring to the nuclei belonging to a specific molecule that has just flipped) is negative. This situation is clearly very different from the standard NMR picture of nuclear relaxation by coupling to paramagnetic centers, where the latter make spin-phonon transitions between Zeeman-split levels having different thermal populations.

Now we can summarize the meaning of our experimental results for the description of electron spin tunneling in the presence of a nuclear spin bath:

(i) The Prokof’ev-Stamp theory of the spin bath, as developed so far and reviewed in §4, quantitatively and qualitatively reproduces the nuclear LSR rate in the whole temperature regime of our measurements, by assuming that the LSR is due to tunneling events in a minority of fast-tunneling molecules;

(ii) The additional observation that the nuclear spins are in thermal equilibrium with the phonon lattice at all temperatures implies that the rates $w_{\uparrow}$ and $w_{\downarrow}$ must be different. For this to happen, it is necessary to explicitly include the role of spin-phonon interactions in the nuclear-mediated tunneling process. Importantly, the results of the calculations shown in Fig. 1(b) indicate that it is not sufficient to attribute the thermal relaxation to a phonon-assisted tunneling process as described in §4 working “in parallel” to the nuclear-spin mediated tunneling process. At the lowest temperatures, even the longest thermalization times observed in our experiments (§4.4) are still much shorter than $(T^*)^{-1}$ as calculated from phonon-assisted tunneling alone (§4.5), thus reinforcing the need for a theory that includes nuclear-spin and phonon mediated tunneling at the same time;

(iii) Our statement that the nuclear relaxation has to be mediated by inelastic electron spin tunneling processes, is further supported by specific heat experiments that show that a system of dipolarly-coupled tunneling molecules can relax to the long-range ferromagnetically ordered state, provided that the tunneling rate is fast enough for the experimental detection of the ordering anomaly. This means that there is a mechanism for the ensemble of electron spins to find its thermodynamic ground state, even at temperatures so low that the relaxation can only proceed by quantum tunneling. We argue here that such inelastic tunneling mechanism is the same mechanism that is responsible for the thermalization of the nuclear spins. Indeed, by extending the specific heat measurements below the ordering temperature, one even observes the equilibrium specific heat contribution of the nuclear spins, meaning that both the electron spins and the nuclear spins can attain thermal equilibrium within the time-scale of the specific heat experiment (10 - 100
s) at all temperatures reached.

All the work presented here is dedicated to the small-\(\Delta_0\), incoherent tunneling regime for the central spin. Having shown that the description of the nuclear-spin mediated tunneling is incomplete without the inclusion of spin-phonon couplings, some concerns may be raised also on the current description of the spin bath effects on the electron spin in the large-\(\Delta_0\), coherent tunneling regime.\textsuperscript{42,43} This work cannot address that issue, and we think that the answer will have to come from low-\(T\) NMR experiments in large transverse field, and quantitative analysis of pulsed-ESR experiments.

VI. CONCLUDING REMARKS

The purpose of the research presented here is to illustrate and analyze a prototypical example of quantum tunneling of a macroscopic variable (the giant spin of single-molecule magnet) in the presence of a spin bath environment. Instead of looking at the macroscopic variable itself and deducing the effect of the environment on its dynamics, as is most often done, we have directly observed the behavior of the spin bath by means of low-T NMR experiments.

We have provided compelling evidence that the longitudinal nuclear spin relaxation in the 55Mn nuclei of Mn\(_{12}\)-ac is driven by electron-spin quantum tunneling fluctuations. The nuclear LSR rate, \(W\), indeed contains all the features that are expected to be associated with tunneling of the molecular spin: i) A \(T\)-independent plateau of the LSR rate for \(T < 0.8\) K; ii) A strong dependence of \(W\) on a longitudinal magnetic field, that destroys the resonance condition for electron spin tunneling; iii) The slowing down of the nuclear LSR upon isotropic substitution of \(^1\)H by \(^2\)H in the ligands, by an amount identical to the slowing down of the quantum relaxation of the magnetization observed in similar systems. Because of the short timescale of the observed LSR, we argued that the tunneling fluctuations must take place in a minority of fast-relaxing molecules, which are indeed known to be present in Mn\(_{12}\)-ac. For these fluctuations to relax the nuclear magnetization in the entire sample, an additional mechanism is required which equilibrates the nuclear spin polarization across neighboring molecules, i.e. intercluster nuclear spin diffusion. Our data on the transverse nuclear spin relaxation show that the intercluster spin diffusion is indeed present and effective. All the above observations confirm and support the picture of nuclear-driven quantum tunneling of magnetization as originally formulated by Prokof’ev and Stamp. However, a crucial outcome of our experiments is the demonstration that the nuclear spins are in thermal equilibrium with the lattice phonons down to the lowest temperatures, where only quantum tunneling fluctuations of the electron spins are still present. This observation cannot be explained within the present theory of the spin bath.

The implications of our results are potentially very profound, particularly because of the growing interest toward a coherent manipulation of spins for quantum information processing. The spin-bath environment, describing localized two-level systems, has been repeatedly identified as the most important source of decoherence in solid-state qubits. This includes superconducting systems,\textsuperscript{84} quantum dots,\textsuperscript{85,86} NV centers in diamond,\textsuperscript{87} and, of course, molecular magnets.\textsuperscript{22} We have investigated here the incoherent tunneling regime, but the theoretical formalism to describe the coupling between central spin and spin bath is identical in the case of coherent spin dynamics. Therefore, the main finding of our work - that the role of phonons in the nuclear-spin mediated tunneling is currently lacking a proper description - suggests that also the contribution of the nuclear spin bath to the decoherence rate of realistic spin qubits may need to be revisited.

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* Electronic address: a.morello@unsw.edu.au

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