Nuclear Spin Dynamics in the Quantum Regime of a Single-Molecule Magnet

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We show that the nuclear spin dynamics in the single-molecule magnet Mn_{12}-ac below 1 K is governed by quantum tunneling fluctuations of the cluster spins, combined with intercluster nuclear spin diffusion. We also obtain the first experimental proof that—surprisingly—even deep in the quantum regime the nuclear spins remain in good thermal contact with the lattice phonons. We propose a simple model for how T-independent tunneling fluctuations can relax the nuclear polarization to the lattice that may serve as a framework for more sophisticated theories.

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Single-molecule magnets (SMMs) are nanometer-sized high-spin molecular clusters organized in a crystalline array, which sets the direction for the anisotropy axis [1]. Reversal of the cluster spin can occur either classically, by thermal activation, or quantum mechanically, by tunneling through the barrier [1,2]. SMMs are attractive model systems to study the effects of coupling magnetic qubits to the environment (nuclear moments, phonons), with the associated problems of decoherence and the limits of quantum mechanics at the large scale [3,4]. For both aspects the hyperfine coupling between cluster spin and nearby nuclear spins is expected to play a crucial but subtle role: since this coupling is many orders larger than the quantum tunneling splitting, a *static* hyperfine interaction completely blocks tunneling. Contrariwise, by considering it as a *dynamic bias* that sweeps the electron spin levels through the tunneling resonance, Prokof'ev and Stamp (PS) have argued that this interaction in fact *promotes* incoherent tunneling events [5].

Experimentally, although time-dependent magnetization experiments [6] showed a $\sqrt{t}$ dependence and isotope effects agreeing with the PS predictions [7], fundamental aspects of the spin dynamics, like the essential role of nuclear spin diffusion, remain to be verified. Further, in the PS model the quantum relaxation of the cluster spin is to the nuclear spin bath and is expected to be many orders of magnitude faster than conventional spin-lattice relaxation to phonons. A crucial test is thus whether or not the experimental nuclear polarization relaxes to the lattice (phonon) temperature, even at such low T that only electron spin *tunneling* fluctuations are left ("quantum regime"). Interestingly, whereas in order to relax to the lattice the nuclear spins generally need electron spin fluctuations, in the quantum regime those same nuclei would provide the only source for such fluctuations via the PS nuclear-spin-mediated quantum tunneling model. It is by no means obvious how such a T-independent process could establish thermal equilibrium between spins and lattice. Here we report a NMR study of the dynamics of ^{55}Mn nuclei in $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ (Mn_{12}-ac), which experimentally answers the above points and poses a crucial test for a realistic description of the coupling between a magnetic qubit and its environment.

Mn_{12}-ac is the SMM with the highest anisotropy barrier (~ 65 K) discovered so far; its core is composed of four Mn^{4+} ions (electron spin $s = 3/2$), and eight Mn^{3+} ions ($s = 2$) in two inequivalent crystallographic sites. The intracluster superexchange interactions lead to a total spin $S = 10$ for the cluster. Below $T \approx 3$ K the electron spins are effectively frozen along the anisotropy axis, thereby enabling ^{55}Mn NMR even in zero applied field, by exploiting the local hyperfine field B_{hyp} felt by the nuclei. This allows the use of nuclear spins as local probes for the fluctuations of the cluster spin by studying the nuclear-spin-lattice relaxation (NSLR) and the transverse spin-spin relaxation (TSSR), *without disturbing the zero-field tunneling resonance*. We have chosen the resonance line of the ^{55}Mn nuclei in Mn^{4+} ions, having a central Larmor frequency $\omega_N/2\pi \approx 230$ MHz and a relatively small quadrupolar splitting [8]. The experiments were performed on Mn_{12}-ac crystallites, cast in Stycast 1266 epoxy and oriented in 9.4 T magnetic field at room temperature. The NMR coil with the sample was placed inside the elongated tail of the plastic mixing chamber of a specially designed dilution refrigerator. This allows a continuous flow of ^{3}He around the sample and assures excellent thermalization. The NMR signal was detected by spin-echo technique, with typical duration $t_{\pi/2} = 10\ \mu$s for the 90° pulse. Since the ^{55}Mn nuclei have spin $I = 5/2$, the recovery of the nuclear magnetization, $M_z(t)$, after an inversion pulse obeys [9]: $M_z(t)/M_z(\infty) = 1 - [(100/63)\exp(-30Wt) + (16/45)\exp(-12Wt) + (2/35)\exp(-2Wt)]$, where W is the NSLR rate [10] [Fig. 1(c), solid lines]. The TSSR rate T_2^{-1} is obtained by a single exponential fit of the decay of transverse magnetization, $M_{xy}(t) = M_{xy}(0)\exp(-t/T_2)$, except at the lowest T where also a Gaussian component T_{2G}^{-1} needs to be included, yielding $M_{xy}(t) = M_{xy}(0)\exp(-t/T_2) \times \exp[-0.5(t/T_{2G})^2]$ [Fig. 1(b), solid lines].

Between 1 and 2 K, both the NSLR and the TSSR show a roughly exponential T dependence [dashed curves in

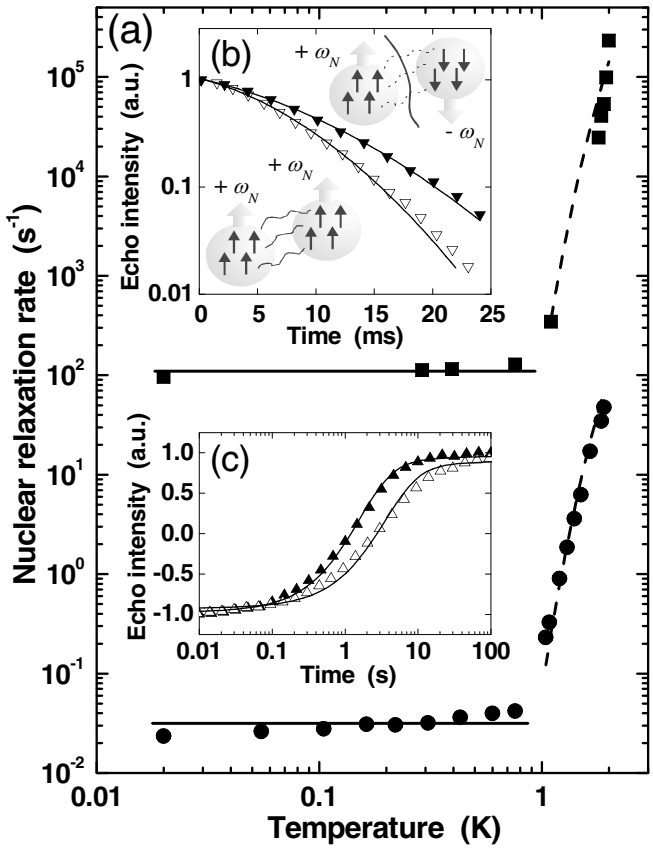

FIG. 1. (a) T-dependence of the NSLR (●) and TSSR (■) rates in zero field and ZFC sample. (b) Decay of echo intensity at $T = 20$ mK in ZFC (▼) and FC (▽) sample. Inset: in the ZFC sample half of the nuclear spins (black arrows) has Larmor frequency $-\omega_N$ instead of $+\omega_N$ because of the reversed orientation of the cluster spin (gray). (c) Recovery of nuclear magnetization after an inversion pulse, at $T = 20$ mK in ZFC (▲) and FC (△) sample.

Fig. 1(a)], which is well understood in terms of the fluctuations of $B_{\rm hyp}$ produced by thermal activation of the electron spin levels [11–13]. The NSLR rate can be obtained from the spectral density at $\omega = \omega_N$ of the transverse component of the fluctuating part of $B_{\rm hyp}$, with the implicit assumption that $B_{\rm hyp}$ fluctuates around its average direction (which coincides with the molecule's anisotropy axis) but does not flip over, as in a tunneling event. Extrapolating the observed high-T NSLR to the mK range would lead to astronomically long relaxation times. In a preliminary work [13] we observed that, upon cooling down to 20 mK, the NSLR saturates to a roughly T-independent plateau, indicating that only fluctuations due to quantum tunneling within the ground doublet are contributing to the relaxation. The crossover between the thermally activated regime and the quantum regime [Fig. 1(a), solid lines] is clearly visible at 0.8 K, in agreement with magnetization experiments [14].

The value $W_0 \approx 0.03\ {\rm s}^{-1}$ of the NSLR found below 0.8 K is surprisingly high, considering that the relaxation of the global magnetization in Mn_{12}-ac takes years at low T. On the other hand, it is well known that any real sample of Mn_{12}-ac contains a fraction of fast relaxing molecules (FRMs), which are characterized by one or two distorted local anisotropy axes for the Mn^{3+} ions [15]; for those molecules the barrier is reduced to 35 K or even 15 K [16], yielding much faster tunneling dynamics. At the same time, however, we have verified that the observed NMR signal comes from nuclei in standard, slow relaxing molecules, even though the electron spin of such molecules remains frozen during the experiment. The fluctuating dipolar field produced by a tunneling FRM on the nuclei of neighboring (frozen) molecules is far too small to account for the observed NSLR, so we have suggested [13] that the relaxation mechanism should involve *intercluster* nuclear spin diffusion (not included in Refs. [5,7]), linking nuclei in frozen molecules to those in FRMs. By studying the magnetization dependence of T_2^{-1} we can now provide strong evidence for the proposed mechanism. When comparing the TSSR in a demagnetized, zero-field-cooled (ZFC) sample (where the cluster spins are randomly oriented up or down) with a saturated, field-cooled (FC) sample (where all spins have the same direction), we find that the FC sample has a faster TSSR, with a ratio $T_{2G}^{-1}({\rm FC})/T_{2G}^{-1}({\rm ZFC}) \approx 1.35$, very close to $\sqrt{2}$ [Fig. 1(b)]. In terms of intercluster spin diffusion this has a simple explanation: in a FC sample the nuclei in equivalent crystallographic sites of different molecules have the same Larmor frequency, ω_N, thus flip-flop transitions are possible with all neighbors. In a ZFC sample the nuclei are divided in two groups having Larmor frequencies $+\omega_N$ or $-\omega_N$, depending on the local spin orientation; for the nuclear dipole-dipole interaction this is equivalent to having diluted the FC system by a factor 2, yielding a $\sqrt{2}$ times smaller TSSR [17] [see inset of Fig. 1(b)]. The presence of a predominantly Gaussian component as found in the TSSR at low T confirms the importance of nuclear dipolar couplings.

Further insight in the relationship between the dynamics of the central quantum spin and the nuclei is provided by the field dependence of the NSLR. Applying an external field B_z parallel to the anisotropy axis destroys the resonance condition for tunneling, thereby hindering the fluctuations needed for the NSLR; this explains the pronounced peak in $W(B_z)$ found around zero field as shown in Fig. 2(a). In comparing ZFC and FC samples, it is seen that both the width of the resonance and the zero-field value are quite different. In particular, one may conclude that there are more tunneling events at zero field in the ZFC sample, as could be seen already from the difference in nuclear inversion recovery [Fig. 1(c)]. Such an observation, which is obviously impossible to obtain by means of "macroscopic" magnetization measurements, should provide a critical test for more detailed models of the NSLR. The signature of tunneling fluctuations at the first

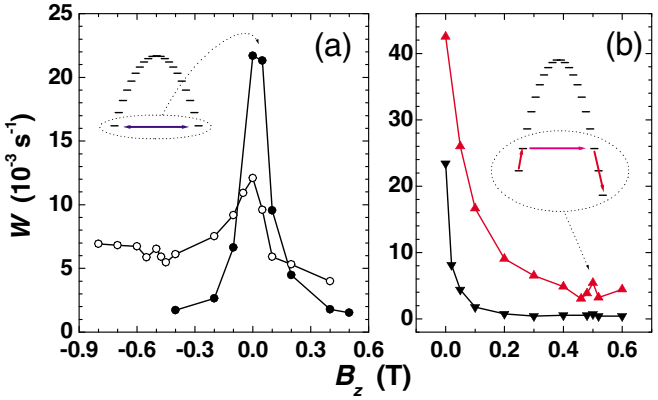

FIG. 2 (color online). (a) Longitudinal field dependence of the NSLR rate $W(B_z)$ at $T = 20$ mK in the ZFC (●) and FC (○) sample. The measuring frequency was set to $\omega_N(B_z)/2\pi = 230 + 10.57B_z$ MHz. (b) $W(B_z)$ in ZFC sample at $T = 20$ mK (▼) and $T = 720$ mK (▲): a small peak is visible at the first level crossing $B_z \approx 0.5$ T only at the highest temperature. In this dataset we used $\omega_N(B_z)/2\pi = 231 + 10.57B_z$ MHz, which better matches the center of the NMR line at high T. The insets show a sketch of the electronic level scheme with the observed transitions.

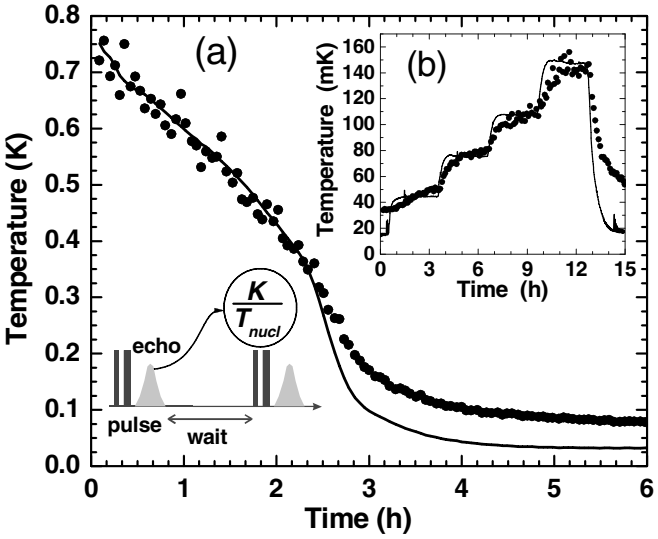

FIG. 3. Comparison of bath temperature $T_{\rm bath}$ (solid lines) and nuclear spin temperature $T_{\rm nucl}$ (circles), while cooling down (a) and while applying steplike heat loads (b). The waiting time between NMR pulses (see inset) was 60 s in (a) and 180 s in (b). Both datasets are at zero field in ZFC sample.

level crossing around $B_z \approx 0.5$ T, i.e., when the spin states with $S_z = +10, +9, \ldots$ come in resonance with $S_z = -9, -8, \ldots$, becomes visible as a small peak in $W(B_z)$ only upon warming up to $T = 0.72$ K, i.e., close to the border with the thermally activated regime [Fig. 2(b)] [18].

Finally, we address another essential aspect of the dynamics of the coupled system of nuclear and cluster spins, so far not studied theoretically or experimentally, namely: "What is the nuclear spin temperature?" In other words, is the nuclear spin polarization indeed relaxing to an equilibrium value dictated by the lattice phonons, which are in thermal contact with the ^{3}He bath at temperature $T_{\rm bath}$? In that case the intensity of the NMR signal as a function of temperature should obey the Curie law $M_z(T) = K/T$. The calibration factor K can be defined at the highest T by assuming that there the nuclear spin temperature $T_{\rm nucl}$ equals $T_{\rm bath}$, and then be used to convert the NMR signal intensity into an equivalent $T_{\rm nucl}$ while cooling down the system. As shown in Fig. 3(a), we find that $T_{\rm nucl}$ indeed follows the time evolution of $T_{\rm bath}$, the small discrepancy below 0.2 K being most probably due to heating effects of the NMR pulses. Data taken with a lower pulse rate [Fig. 3(b)] demonstrate that, even below 0.1 K, the nuclei always closely follow the evolution of $T_{\rm bath}$. This direct experimental proof of an energetic contact between nuclear spins and phonons confirms earlier results from the (field-dependent) low-T specific heat [19], in which sizable amounts of nuclear and electron magnetic entropy were observed to be removed below 0.5 K. Since there is no relevant direct energetic coupling between phonons and nuclei, the thermalization of the nuclear spin system must involve the interplay with the electron spins and their coupling to the lattice, even in the T-independent quantum tunneling regime.

A basic question to answer is what happens to those nuclei that belong to a molecule where a tunneling event takes place (in our case a FRM), assuming that the neighboring molecules are frozen. For the ease of discussion, we shall consider N nuclear spins $I = 1/2$ per cluster, subject to a hyperfine field $B_{\rm hyp}$ parallel to the anisotropy axis of the molecule: the latter assumption simulates the real situation for ^{55}Mn in Mn_{12}-ac. The standard way of calculating the rate of transition between nuclear Zeeman levels as a consequence of a perturbing fluctuating field is useless here, since the Zeeman levels themselves completely change after each electron spin flip, so perturbation theory is not applicable. A more realistic approach is to recall that each electron spin level is split by hyperfine interactions into a quasicontinuum manifold of levels [8,20] that can be labeled by the local nuclear polarization $\Delta N = N^{\uparrow} - N^{\downarrow}$, which yields a hyperfine bias ξ_N (typically ~0.1 K). Since the hyperfine fields before and after the flip of the cluster spin are just antiparallel, the manifolds of Zeeman levels on either side of the anisotropy barrier are simply the mirror of each other. Moreover, since the tunneling traversal time is much shorter than $1/\omega_N$, the probability that a nuclear spin would coflip with the electron spin is negligible. This implies that the only relevant tunneling transitions are those that do not require any nuclear coflip, thus $\Delta N =$ const [5]. Considering the small additional bias ξ_D due to dipolar fields from neighboring cluster spins, the tunnel-

ing transition with $\Delta N = \text{const}$ requires an initial hyperfine bias such that $\xi_N = \xi_D$. Once the molecule has tunneled, the hyperfine bias becomes $\xi_N = -\xi_D$ since the nuclear polarization is unchanged but B_{hyp} is reversed; the new local hyperfine energy can then be redistributed to other nuclei via intercluster spin diffusion until the equilibrium within the nuclear spin bath is achieved. In this way the effect of tunneling is the "conversion" of dipolar into hyperfine energy and vice versa.

Our data show that this description is still insufficient: to obtain a nuclear magnetization in thermal equilibrium with the lattice, tunneling events must be accompanied by creation or annihilation of phonons. In our opinion a crucial role may be played by the Waller mechanism [21], i.e., the change in the dipolar field when the distance between neighboring molecules is modulated by lattice vibrations. Even at very low T we can expect the existence of low-energy phonon modes that correspond to displacements of the clusters with respect to each other. Here we consider the cluster cores as rigid objects within the soft matrix (with Debye temperature $\theta_D \approx 20$ K) of the ligand molecules, an approach successfully used to account for the Mössbauer recoil-free fractions of metal cluster molecules [22]. The modulation of the dipolar field, whereby the total bias may sweep back and forth through the tunneling resonance, can thus provide a probability of incoherent tunneling with emission or absorption of phonons, whose energy would be released or extracted from the nuclear spins in the way described above, i.e., using the tunneling of electron spins as intermediary. The detailed balance between emission and absorption may then provide the equilibration of nuclear spin and lattice temperatures.

In conclusion, we have shown that the nuclear spin dynamics in Mn_{12}-ac below 0.8 K is driven by tunneling fluctuations of the cluster electron spin, in combination with intercluster nuclear spin diffusion and thermal equilibrium between nuclear spins and phonon bath; the latter aspect calls for the extension of existing theories of incoherent quantum tunneling within the ground doublet to include inelastic processes.

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[1] D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, Science **265**, 1054 (1994); D. Gatteschi and R. Sessoli, Angew. Chem., Int. Ed. Engl. **42**, 268 (2003).
[2] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996); J. M. Hernández, X. X. Zhang, F. Luis, J. Bartolomé, J. Tejada, and R. Ziolo, Europhys. Lett. **35**, 301 (1996); L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).
[3] P. C. E. Stamp and I. S. Tupitsyn, Phys. Rev. B **69**, 014401 (2004).
[4] A. J. Leggett, J. Phys. Condens. Matter **14**, R415 (2002).
[5] N. V. Prokof'ev and P. C. E. Stamp, J. Low Temp. Phys. **104**, 143 (1996).
[6] W. Wernsdorfer, A. Caneschi, R. Sessoli, D. Gatteschi, A. Cornia, V. Villar, and C. Paulsen, Phys. Rev. Lett. **84**, 2965 (2000).
[7] N. V. Prokof'ev and P. C. E. Stamp, Phys. Rev. Lett. **80**, 5794 (1998).
[8] T. Kubo, T. Goto, T. Koshiba, K. Takeda, and K. Awaga, Phys. Rev. B **65**, 224425 (2002).
[9] A. Suter, M. Mali, J. Roos, and D. Brinkmann, J. Phys. Condens. Matter **10**, 5977 (1998).
[10] In the simple case of a spin 1/2, where the NSLR is described by a single exponential, W is related to the relaxation time T_1 by $2W = T_1^{-1}$.
[11] Y. Furukawa, K. Watanabe, K. Kumagai, F. Borsa, and D. Gatteschi, Phys. Rev. B **64**, 104401 (2001).
[12] T. Goto, T. Koshiba, T. Kubo, and K. Awaga, Phys. Rev. B **67**, 104408 (2003).
[13] A. Morello, O. N. Bakharev, H. B. Brom, and L. J. de Jongh, Polyhedron **22**, 1745 (2003).
[14] L. Bokacheva, A. D. Kent, and M. A. Walters, Phys. Rev. Lett. **85**, 4803 (2000); I. Chiorescu, R. Giraud, A. G. M. Jansen, A. Caneschi, and B. Barbara, *ibid.* **85**, 4807 (2000).
[15] Z. Sun, D. Ruiz, N. R. Dilley, M. Soler, J. Ribas, K. Folting, M. B. Maple, G. Christou, and D. N. Hendrickson, Chem. Commun. 019 (1999) 1973.
[16] W. Wernsdordfer (unpublished).
[17] In reality also in a ZFC sample some agglomerates of clusters may locally have the same orientation, whereby this ratio becomes less than $\sqrt{2}$, as observed.
[18] Notice that $B_z \approx 0.5$ T is the level crossing field only for the majority of molecules with 65 K barrier, whereas the crossing fields for FRMs are distributed between 0.2 and 0.4 T and do not give sharply visible features.
[19] F. Luis, F. L. Mettes, J. Tejada, D. Gatteschi, and L. J. de Jongh, Phys. Rev. Lett. **85**, 4377 (2000); F. L. Mettes, F. Luis, and L. J. de Jongh, Phys. Rev. B **64**, 174411 (2001); M. Evangelisti, F. Luis, F. L. Mettes, N. Aliaga, G. Aromí, J. J. Alonso, G. Christou, and L. J. de Jongh, Phys. Rev. Lett. **93**, 117202 (2004).
[20] F. Hartmann-Boutron, P. Politi, and J. Villain, Int. J. Mod. Phys. B **10**, 2577 (1996).
[21] I. Waller, Z. Phys. **79**, 370 (1932).
[22] P. M. Paulus, A. Goossens, R. C. Thiel, A. M. van der Kraan, G. Schmid, and L. J. de Jongh, Phys. Rev. B **64**, 205418 (2001).