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Magnetic Long-Range Order Induced by Quantum Relaxation in Single-Molecule Magnets

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Can magnetic interactions between single-molecule magnets (SMMs) in a crystal establish long-range magnetic order at low temperatures deep in the quantum regime, where the only electron spin fluctuations are due to incoherent magnetic quantum tunneling (MQT)? Put inversely: can MQT provide the temperature dependent fluctuations needed to destroy the ordered state above some finite T_c, although it should basically itself be a T-independent process? Our experiments on two novel Mn_4 SMMs provide a positive answer to the above, showing at the same time that MQT in the SMMs has to involve spin-lattice coupling at a relaxation rate equaling that predicted and observed recently for nuclear-spin-mediated quantum relaxation.

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Despite the large number of studies on magnetic quantum tunneling (MQT) in molecular crystals of single-molecule magnets (SMMs) [1], the question whether it is able to bring the spin system into thermal equilibrium with the lattice, remains unsolved. Prokof'ev and Stamp [2,3] suggested that interaction with rapidly fluctuating hyperfine fields can bring a significant number of electron spins into resonance. Coupling to a nuclear-spin bath indeed allows ground-state tunneling over a range of local bias fields ξ much larger than the tunnel splitting Δ, whereas, in its absence, tunneling would happen only if ξ is $\sim\Delta$ or less. Within this theory, magnetic relaxation could thus in principle occur with no exchange of energy with the phonons of the molecular crystal [4]. Support for the Prokof'ev/Stamp model came from magnetic relaxation studies on the Fe_8 SMM [5]. However, these experiments covered only initial stages of the relaxation process, leaving open the question of whether the final state corresponds to a thermal equilibrium. When MQT is combined with coupling to a heat bath, dipolar couplings between cluster spins can induce long-range magnetic ordering (LRMO) [6]. This phenomenon has not been observed yet for any of the known SMMs relaxing by MQT in the ground state.

In this Letter, we present time-dependent specific heat measurements performed on two novel tetranuclear molecular clusters, both with net cluster-spin $S = 9/2$, denoted by Mn_4Cl and Mn_4Me, which have similar cluster cores but different ligand molecules. For both SMMs frequency-dependent susceptibility data [7,8] show superparamagnetic blocking for frequencies above 100 Hz in the T region near 2 K, and relaxation below $\sim$0.8 K can thus only proceed by incoherent MQT between the two lowest lying states $m = \pm S$. For both compounds we prove below that the MQT has to be inelastic. For Mn_4Me, the tunneling rates are even found sufficiently high to establish thermal equilibrium down to the lowest temperatures ($\sim$0.1 K), so that the MQT channel enables the occurrence of LRMO between the cluster spins at $T_c = 0.21$ K. Comparing the magnitude of T_c with Monte Carlo simulations suggests the coexistence of dipolar and weak superexchange interactions between clusters. In view of the essential role of the dynamic nuclear bias in the MQT mechanism, our results call for an extension of the nuclear-spin-mediated quantum relaxation model [2,3] to include inelastic processes, where MQT is accompanied by phonon creation or annihilation.

Analytically pure samples of $Mn_4O_3L(dbm)_3$, with $L = Cl(OAc)_3$ or $[O_2C(C_6H_4\text{-}p\text{-}Me)]_4$, hereafter abbreviated as Mn_4Cl and Mn_4Me, were prepared as described in Ref. [7]. Both molecules possess a distorted cubane core with one Mn^{4+} ion (spin $s = 3/2$) and three Mn^{3+} ions ($s = 2$), superexchange coupled via oxygen ions. The *intracluster* exchange couplings were studied by magnetic measurements [7]. Below $T \lesssim 10$ K, the Mn spins become ordered inside the cluster with a net spin $S = 9/2$ subject to a uniaxial crystal field [9], with symmetry axis running approximately through the Mn^{4+} ion and the L ligand. Whereas Mn_4Cl has a local virtual C_{3V} symmetry, the more bulky carboxylate ligand of Mn_4Me distorts and lowers the symmetry (C_S) in the crystal, thereby increasing the magnitude of the transverse anisotropy component [7,9].

Low-temperature specific heat measurements were performed in a homemade calorimeter using a thermal relaxation method, see Ref. [10]. By varying the thermal resistance of the thermal link between calorimeter and cold-sink, the characteristic time scale τ_e of the experiment can be varied. Thus time-dependent specific heat measurements can be exploited to investigate spin-lattice relaxation when the relaxation time becomes of the order of τ_e ($\sim$0.1–1000 s) that varies slowly with temperature

[10,11]. The samples consisted of 1–3 mg of polycrystalline material, mixed with 2–5 mg of Apiezon-*N* grease to ensure good thermal contact. The high-T ($2\ \mathrm{K} < T < 300\ \mathrm{K}$) specific heat was measured for a Mn_4Cl pellet sample of about 40 mg using a commercial calorimeter.

The specific heat C/R of Mn_4Cl is shown in Fig. 1, which displays data obtained for different time-scales, i.e., $\tau_e \approx 2$, 8, and 300 s as estimated at $T = 0.4$ K, together with those obtained with the high-T calorimeter. Let us first consider data measured for $T > 1$ K, where C is independent of τ_e. A λ-type anomaly is observed at $T \simeq 7$ K, having a relative height of 2.5 R. Susceptibility measurements, as well as specific heat in magnetic fields (not presented) show that this anomaly is of nonmagnetic origin, probably associated with a structural transition. Between 1 and 7 K, C is dominated by contributions from the lattice phonons and from transitions between energy levels of the $S = 9/2$ multiplet split by the crystal field. Neglecting, in first approximation, the hyperfine and the *intercluster* magnetic couplings, the spectrum of energy levels is doubly degenerate at zero field, so that C only depends on transitions between levels inside each of the potential wells that are separated by the anisotropy energy barrier U. We shall call this the *intrawell* contribution. The associated multilevel Schottky anomaly is calculated with the eigenvalues of the spin Hamiltonian

$$\mathcal{H} = -DS_z^2 - E(S_x^2 - S_y^2) + A_4 S_z^4 \qquad (1)$$

with D, E, and A_4 obtained independently from inelastic neutron scattering and high-frequency EPR measurements [12,13]. The intrawell C decreases exponentially as T decreases and, since the first excited $m = \pm 7/2$ level is about $(2S-1)D = 5.5$ K above the $m = \pm 9/2$ ground-state doublet, it becomes almost negligible when $T \leq 0.8$ K (Fig. 1). Adding the lattice contribution, calculated with a Debye temperature $\theta_D \simeq 15$ K, to the Schottky accounts well for the experiment (solid line in Fig. 1).

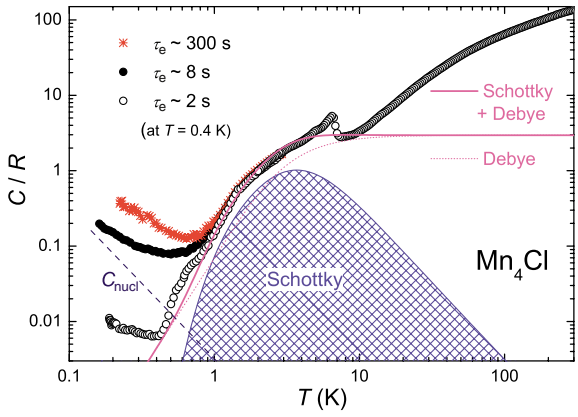

FIG. 1 (color online). T-dependent specific heat of Mn_4Cl measured for $\tau_e \approx 2$, 8, and 300 s. Solid line, sum of the Debye term (dotted line) plus the Schottky contributions; dashed line, calculated nuclear contribution C_{nucl}.

The lattice C above 10 K appears to be composed of a number of Einstein-type contributions (not shown).

Below 1 K, we expect the equilibrium magnetic specific heat (C_m) to be dominated by two contributions. The first arises from incoherent MQT events inside the ground-state doublet that is split by the action of the effective fields arising from hyperfine interactions and intercluster dipolar coupling. The second is the specific heat C_{nucl} of the nuclear spins of Mn, whose energy levels are split by the hyperfine interaction with the atomic electron spins. The dashed line in Fig. 1 represents C_{nucl} calculated with the hyperfine constants $A_{hf} = 7.6$ mK and $A_{hf} = 11.4$ mK for, respectively, Mn^{3+} and Mn^{4+} ions, obtained from ESR on a similar (natural) Mn_4 cluster [14]. Experiments performed for the longest $\tau_e \approx 300$ s show indeed a large low-T contribution. By contrast, the specific heat decreases by almost 2 orders of magnitude when $\tau_e \approx 2$ s, evidencing that τ_e has a large effect in this temperature range. This shows that the equilibrium between the relative populations of the $+9/2$ and $-9/2$ states cannot be established within τ_e if this is too short. We note that, for the shortest τ_e, the low-T specific heat becomes even smaller than C_{nucl}, indicating that both nuclear and electron spins are out of equilibrium. This is understandable, since the only channel for the nuclear spins to exchange energy with the lattice is via the electron spins. The strong connection between nuclear and electron spin-lattice relaxation has also been observed for Mn_{12}, Mn_6 and Fe_8 [10,15].

The experimental C/R of Mn_4Me, measured for $\tau_e \approx 4$ s (as estimated at $T = 0.4$ K), is shown in Fig. 2 together with the calculated contributions of the lattice and the nuclear spins, and the intrawell Schottky contribution.

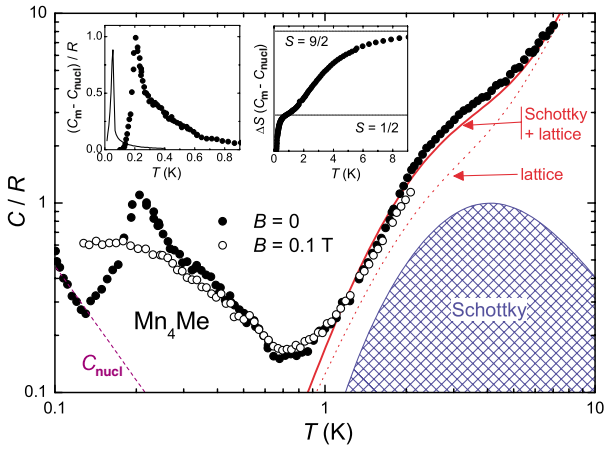

FIG. 2 (color online). T-dependent specific heat of Mn_4Me measured for $\tau_e \approx 4$ s, with zero field (●) and $B = 0.1$ T (○). Dashed line: calculated nuclear contribution C_{nucl}; solid line: sum of lattice (dotted line) plus Schottky contributions. Insets: electronic C_m and entropy variation ΔS, after subtraction of C_{nucl}. Solid line: calculated dipolar ordering for the easy axis along the (110) direction (see text); dashed lines: high-T entropy limits for $S = 1/2$ and $S = 9/2$.

The experimental data display a λ anomaly at $T_c = 0.21$ K that we attribute to the onset of LRMO. In a field of 0.1 T the peak is already suppressed, proving its magnetic origin. The Schottky anomaly is calculated as for Mn_4Cl with parameters obtained from high-frequency EPR [12,13]. For $T > 1$ K, the remaining contribution is given by the lattice and is well described by the sum of a Debye term (with $\theta_D \simeq 12.3$ K) for the acoustic low-energy modes plus an Einstein term ($\theta_E \simeq 22$ K) for a higher energy mode. Below 0.15 K, the specific heat of Mn_4Me shows a clear upturn that can be described by $C_{nucl}/R \simeq 4.27 \times 10^{-3}/T^2$. This contribution is well fitted using hyperfine constants $A_{hf} = 8.7$ and $A_{hf} = 13.8$ mK for, respectively, Mn^{3+} and Mn^{4+} ions. These values are close to those reported by Zheng and Dismukes cited above [14].

As seen in Fig. 2, the magnetic ordering peak and the calculated Schottky due to the splitting of the $S = 9/2$ multiplet are well separated in temperature. This is confirmed by the analysis of the temperature dependence of the electronic entropy $\Delta S(T) = \int_0^\infty [C_m(T) - C_{nucl}(T)]/T dT$ (right inset of Fig. 2). As expected, the total entropy of the electron spins tends to $R \ln(2S + 1)$, with $S = 9/2$, at high temperatures. However, for the magnetic ordering region ($T < 0.8$ K), ΔS corresponds to an effective spin $S = 1/2$, as appropriate for a two-level system. This proves that there only the two lowest levels ($m = \pm 9/2$) are populated and contribute to C_m solely by MQT fluctuations. This contrasts with previously observed ordering phenomena in other SMMs with either (much) lower anisotropy [15] or stronger intercluster coupling [16]. The "high-T tail" of the peak can be ascribed to short-range order effects and/or a splitting of the doublet by the hyperfine coupling.

We note that, although the anisotropy barrier $U \simeq DS^2 - A_4 S^4 - |E|S^2$ is ≈ 14 K for both Mn_4Me and Mn_4Cl, due to the lower symmetry of Mn_4Me, the 2nd-order off-diagonal E term, and thus also Δ of the ground state, are much larger for this compound. High-frequency EPR experiments give $E/D \simeq 0.21$, i.e., nearly 5 times larger than for Mn_4Cl [12,13]. Accordingly, we estimate $\Delta \sim 10^{-7}$ and 10^{-5} K for Mn_4Cl and Mn_4Me, respectively. Clearly, this difference has a very large influence on the spin-lattice relaxation. For similar τ_e values, the electron spins of Mn_4Cl go off equilibrium below $T = 0.8$ K (Fig. 1), whereas for Mn_4Me we observe thermal equilibrium for electron and nuclear spins down to the lowest temperature. We conclude this from the fact that (i) the total electronic entropy contribution equals the expected limit for $S = 9/2$; (ii) the remaining specific heat below 0.15 K agrees well with the expected C_{nucl}.

As commonly found in molecular clusters, the magnetic core of Mn_4Me is surrounded by a shell of nonmagnetic ligand molecules. It follows that intercluster superexchange interactions are very weak so that intercluster dipolar coupling may become the main source for magnetic ordering [15]. To check this for Mn_4Me, we performed Monte Carlo simulations, as described in Ref. [6], for a $S = 9/2$ Ising model of magnetic dipoles regularly arranged on the Mn_4Me lattice. We repeated our calculations for several orientations of the molecular easy axis [an example is given in the left inset of Fig. 2 for the easy axis along the (110) direction]. The calculated T_c's are always smaller than the experimental value. Consequently, the Mn_4Me molecules are also coupled by weak superexchange interactions. Indeed, by adding an intercluster nearest-neighbor exchange interaction $|J|/k_B \simeq 0.14$ K to our dipolar calculations, we reproduce the experimental T_c value [17].

To estimate the spin-lattice relaxation rate Γ for Mn_4Cl at low T, we used the relation for the time-dependent specific heat $C_m(t) = C_0 + (C_{eq} - C_0)[1 - e^{-\Gamma \tau_e}]$, where C_0 and C_{eq} are, respectively, the adiabatic and equilibrium limits of the specific heat [11]. For the electron spins, C_0 is to good approximation given by the intrawell Schottky specific heat, whereas the "slow" specific heat at equilibrium corresponds to excitations involving transitions between the two wells. We fitted, thus, the $C_m(\tau_e)$ data of Mn_4Cl taking for τ_e the values measured at each temperature and for C_{eq} the corresponding $C_m(T)$ of Mn_4Me (in the range $T > T_c$). We show $\Gamma(T)$ in Fig. 3, together with data from ac susceptibility and (short-time) magnetic relaxation experiments [8]. For $T > 1.7$ K, Γ follows the Arrhenius law, with $U \simeq 13.5$ K and $\tau_0 \approx 1.4 \times 10^{-7}$ s. For $T \lesssim 0.8$ K, Γ deviates from this thermal-activation law, in remarkable agreement with the magnetic relaxation data. Its weak temperature dependence confirms that relaxation to thermal equilibrium is dominated by direct MQT transitions within the ground-state doublet.

Summing up, even far below the superparamagnetic blocking, thermal contact between spins and lattice is still

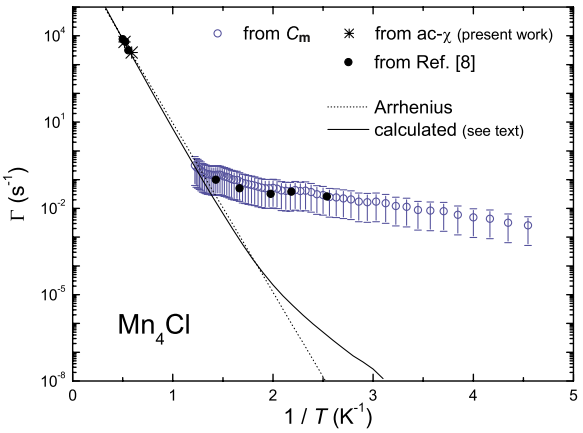

FIG. 3 (color online). Spin-lattice relaxation rate of Mn_4Cl: (*) and (●) [8] obtained from ac susceptibility and magnetic relaxation data; (○) obtained by fitting the $C_m(\tau_e)$ data of Fig. 1 (see text). Dashed line: fit of high-T data to Arrhenius law; solid line is calculated for magnetic fields $B_x = 150$ and $B_z = 350$ G (see text).

established for both compounds by MQT fluctuations. For Mn_4Me, the associated rate is even fast enough to produce thermal equilibrium down to the lowest T and thus enable LRMO. This implies $\Gamma \gtrsim 1/\tau_e \simeq 1\ s^{-1}$. For Mn_4Cl, we find a lower rate (10^{-1}–$10^{-3}\ s^{-1}$) for $T \lesssim 0.8$ K. It is of interest to compare the experimental Γ for Mn_4Cl with predictions from conventional models for spin-lattice relaxation, assuming that the $m = \pm 9/2$ energy levels of the cluster spins are time independent. We simulated the effect of intercluster dipolar coupling and hyperfine interactions by introducing static magnetic fields $B_x = 150$ and $B_z = 350$ G [18]. The presence of these Zeeman terms is essential, otherwise tunneling would be forbidden for half-integer spin [19]. We calculated Γ by solving a master equation, including intra- as well as interwell transitions, induced by phonons only, between exact eigenstates of the spin Hamiltonian of Eq. (1), as discussed in Ref. [11] and recently applied to the analysis of C_m of Fe_8 and Mn_{12} clusters [10]. The result (solid line in Fig. 3) agrees well with the activated behavior observed at high-T, but fails to account for Γ measured below 0.5 K by 6 orders of magnitude. This large discrepancy cannot be ascribed to errors in the estimated elastic properties of the lattice. Both the prefactor of the Arrhenius law and the measured value of θ_D give a value of $c_s \simeq 5(1) \times 10^2$ m/s for the speed of sound. By contrast, Γ observed at low T would require c_s and θ_D to be 15 times smaller. This would give rise to a large lattice specific heat well below 1 K, which is not observed.

It appears therefore that extension to *dynamic* hyperfine fields acting on the cluster-spin levels [2,3], is indeed a necessary prerequisite for any model for the MQT of SMMs. Such dynamic bias fields will sweep the tunneling levels with respect to one another, thereby enabling incoherent Landau-Zener type tunneling events. The model predicts quantum relaxation rates agreeing with experiments [5], but so far the relaxation of the cluster spins was thought to occur solely/primarily to the nuclear-spin bath, relaxation to phonons was expected only at much longer time scales [2]. Recently [20], Chiorescu *et al.* found a crossover between different time scales in the magnetization relaxation of Mn_{12}-ac that they ascribed to coupling to environment (spins, phonons,...). Our specific heat experiments, in which obviously the heat is transferred to the spins via the lattice, clearly demonstrate that in fact spin-lattice relaxation *has to be* involved and at much the same fast rates. Since application of "conventional" models for spin-lattice relaxation leads to rates orders of magnitude too low, our data call for an extension of the Prokof'ev/Stamp model in which nuclear-spin-mediated MQT events are combined with creation or annihilation of phonons.

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[17] We consider $\mathcal{H}_{ex} = 2J\sum_{i\neq j} S_z^{(i)} S_z^{(j)}$. Taking $S = 1/2$ and $J \neq 0$ only for nearest dipoles ($z = 5$ in Mn_4Me), we calculate $T_c \simeq 0.2$ K for $|J|/k_B \simeq 0.14$ K, irrespective of the sign of J.
[18] Interaction with nuclear spins induces a distribution of bias ξ of width $E_0 \simeq N^{1/2}\hbar\omega_0/2$, where N is the number of nuclear spins and $\hbar\omega_0$ is the average hyperfine splitting [2]. Off-diagonal terms of the hyperfine interaction are of the same order of magnitude [14]. In addition, intercluster dipolar energies E_{int} further broaden the distribution of bias. We roughly estimate $E_0 \approx 9 \times 10^{-2}$ K and $E_{int} \approx k_B T_c = 0.2$ K, from which, we obtain typical fields $B_x = E_0/g\mu_B S \simeq 150$ G and $B_z = E_{int}/g\mu_B S \simeq 350$ G, respectively.
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