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Through quantum tunneling to dipolar order: the effect of varying magnetic anisotropy in three structurally related Mn_4 molecular clusters

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Abstract

By means of time-dependent specific heat experiments, we have studied the long-time electron spin-lattice relaxation mechanisms of three tetranuclear mixed-valence clusters of manganese ions (Mn_4Cl, Mn_4Ac and Mn_4Me), which have the same magnetic core but different ligand molecules, and thus varying anisotropy. The relaxation of the spins towards equilibrium takes place, below 1 K, via an incoherent tunneling mechanism in the magnetic ground doublet, in which process energy is exchanged with the phonon bath. It is shown that the spin-lattice relaxation rate increases when the tunneling probabilities increase, thus indicating that quantum tunneling brings the spins towards equilibrium. For Mn_4Me, this fast relaxation enables the magnetic system to undergo a transition to a long-range ordered state below $T_C = 0.21$ K.

Keywords: Single-molecule magnets; Mn_4; Spin-lattice relaxation; Quantum tunneling of the magnetic moment; Magnetic order; Very-low-temperature time-dependent specific heat

1. Introduction

Single-molecule magnets are the subject of an ongoing research because they could serve as small magnetic memory units [1,2]. The magnetic core of these molecules may be described with a single high spin at low temperatures, resulting from very strong exchange interactions between the magnetic ions constituting the core itself. By lowering the temperature, the crystal field anisotropy tends to block the cluster magnetic moments along the preferred direction. Consequently, for zero-applied-field, the relaxation of the spin towards thermal equilibrium with the lattice becomes extremely slow at low temperatures ($T < 1$ K). It is well established by now that, when the temperature of the system is in the liquid helium range, the relaxation of the electronic spins may proceed via phonon-assisted quantum tunneling through the anisotropy energy barrier via the excited magnetic states [3–5]. By further decreasing the temperature below 1 K, the thermal population of the excited states becomes very small and this relaxation process cannot take place anymore. Without the possibility of being excited to higher magnetic states, the spins can, thus, only relax directly between the states which are lowest in energy, i.e., the magnetic ground doublet [6,7]. In such a tunneling regime, the tunneling process is dictated not only by the crystal field anisotropy but also by the influence of the coupling of the individual spins to the environment, i.e., nuclear spins and intermolecular interactions [8,9]. Theories have so far not given a

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complete detailed explanation of this sophisticated process of incoherent tunneling involving only the ground state. An important question which remains to be answered is whether this tunneling process may provide a relaxation mechanism for the electronic spins sufficient to reach thermal equilibrium with the lattice and to reach a magnetically ordered state arising from the intercluster interaction. In this paper, we want to address this problem from the experimental point of view. We present specific heat measurements on three tetranuclear mixed-valence clusters of manganese ions (Mn_4Cl, Mn_4Ac and Mn_4Me). These molecules have the same magnetic core but different ligand molecules, resulting in slightly different anisotropies. Magnetic measurements above 1 K have already proven that these molecular clusters behave as single-molecule magnets with a net spin $S = 9/2$ at low enough temperatures [10–12]. From field-dependent specific heat studies, we have also shown that, in spite of the predicted quenching at zero-applied-field of the ground state tunneling splitting for clusters of half-integer spin, the tunneling between the $S = +9/2$ and $S = -9/2$ is still possible due to the action of effective fields arising from the environment [13]. The same conclusion was also recently reported for another Mn_4 molecular cluster with net spin $S = 9/2$ [14]. To study the spin-lattice relaxation, a suitable probing tool is the time-dependent specific heat. Indeed, time-dependent specific heat experiments give direct information on the electron spin-lattice relaxation mechanism [15], as soon as the associated relaxation time of the electron spin becomes of the order of the experimental time constant τ_e involved ($1–10^3$ s).

2. Molecular structure and experimental details

Analytically pure samples of the compounds $Mn_4O_3X(OAc)_3(dbm)_3$, with X = Cl, OAc, and $Mn_4O_3(O2CR)_4(dbm)_3$, with $R = C_6H_4$-p-Me, that we hereafter abbreviate as Mn_4Cl, Mn_4Ac and Mn_4Me, respectively, were prepared as described in Refs. [10–12]. All compounds were characterized by elemental analysis. The series of molecules possess a distorted cubane core of one Mn^{4+} ion (spin $S = 3/2$) and three Mn^{3+} ions ($S = 2$), super-exchange coupled by three oxygen ions, see Fig. 1. The first two molecular cores have a local virtual C_{3V} symmetry, whereas the more bulky carboxylate ligand distorts and lowers the symmetry (C_S) of the third in the solid state. The exchange couplings between the four Mn ions have been studied by magnetic susceptibility measurements [10–12]. The coupling between the Mn^{3+} ions was found to be ferromagnetic, whereas the Mn^{4+} ion couples antiferromagnetically to the Mn^{3+} ions. At low temperatures, the four Mn spins become ordered with a net total spin $S = 9/2$, which is subject to an uniaxial crystal field [16], with symmetry axis running through the Mn^{4+} ion and the X or R ligand. The X- or R-ligand acts as a bridge between the three Mn^{3+} ions and by changing it the magnitude of the uniaxial anisotropy along the Mn^{4+}-ligand symmetry axis is affected [12,16].

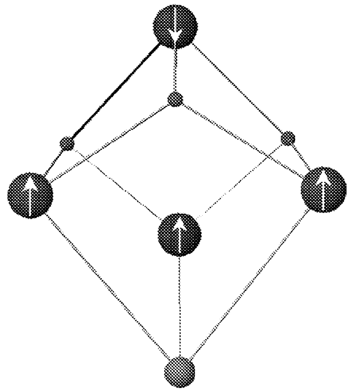

Fig. 1. Representation of the cluster core.

All very-low-temperature time-dependent specific heat measurements were performed as described in Refs. [17,18]. The samples measured consisted of 1–3 mg of polycrystalline sample, which was mixed with 2–5 mg of Apiezon-N grease to ensure good thermal contact.

3. Results and discussion

The magnetic specific heat C_m/R of Mn_4Cl is shown in Fig. 2. In order to obtain C_m we have subtracted from the original data the contribution of the lattice to the total specific heat. This contribution dominates at $T > 4$ K and follows the low-T Debye approximation

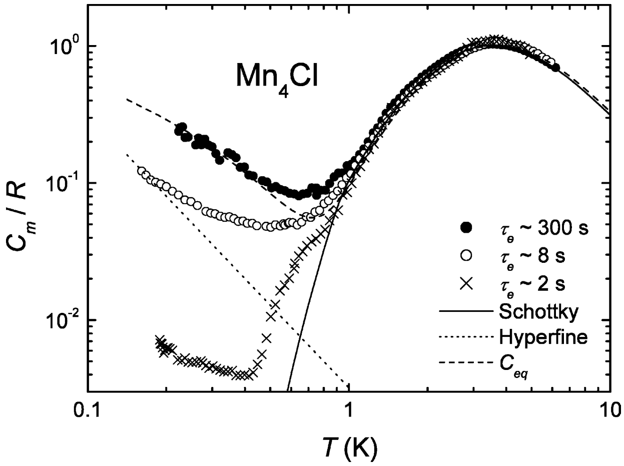

Fig. 2. Temperature dependence of the zero-field specific heat of Mn_4Cl measured for $\tau_e \approx 300$ s (●), $\tau_e \approx 8$ s (○) and $\tau_e \approx 2$ s (×). The solid line represents the contribution due to the splitting of the $S = 9/2$ multiplet, whereas the dotted line is the calculated hyperfine contribution, and the dashed line is the calculated equilibrium specific heat C_{eq}.

$C_{\mathrm{lattice}} \propto T^3$, with Debye temperatures $\Theta_{\mathrm{D}} = 41$, 41 and 39 K, for Mn_4Cl, Mn_4Ac and Mn_4Me, respectively. For $T > 1$ K, C_{m} is the same for the three sets of data, which correspond to three different experimental times ($\tau_{\mathrm{e}} \approx 2$, 8 and 300 s, as estimated at $T = 0.4$ K) for each temperature. In this temperature region, the specific heat is dominated by transitions between energy levels split by the crystal field. When we neglect in first approximation the (Zeeman) splittings due to effective fields representing the hyperfine interaction and the intercluster magnetic coupling, the spectrum of energy levels is doubly degenerate at zero-applied-field, so that the specific heat only depends on the population of levels inside each of the potential wells that are separated by the anisotropy energy barrier DS^2. We shall call this the intra-well contribution to C_{m}. The associated multilevel Schottky anomaly, calculated with the eigenvalues of the spin Hamiltonian:

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

accounts well for the experimental data with parameters D, E and A_4 obtained independently from inelastic neutron scattering measurements [19]. The intra-well specific heat decreases exponentially as T decreases and, the first excited level being about $(2S-1)D = 5.5$ K, it becomes almost negligible when $T \leq 0.8$ K.

Below 1 K, we expect the equilibrium C_{m} to be dominated by two contributions. The first arises from energy excitations inside the ground state doublet that is split by the action of the above mentioned effective fields. The second is the specific heat C_{hf} of the nuclear spins of Mn, whose energy levels are split by the hyperfine interaction with the atomic electronic spins. The dotted line in Fig. 2 represents C_{hf} calculated with the hyperfine constants obtained from ESR [20]. The specific heat curve measured with the longest experimental time ($\tau_{\mathrm{e}} \approx 300$ s) shows indeed a large contribution, whereas it decreases for more than one order of magnitude when $\tau_{\mathrm{e}} \approx 2$ s (Fig. 2), evidencing that τ_{e} has a large effect on C_{m} in this temperature range. This shows that the equilibrium between the relative populations of the $+S$ and $-S$ states cannot be established within the time of the experiment when τ_{e} is too short. Moreover, we note that the low-T specific heat becomes, for the shortest τ_{e}, smaller than C_{hf}, indicating that the nuclear spins are also out of equilibrium as soon as the electronic spins are out of equilibrium. We can describe this dependence as [15]:

$$C_{\mathrm{m}} = C_0 + (C_{\mathrm{eq}} - C_0)[1 - \exp(-\Gamma\tau_{\mathrm{e}})] \tag{2}$$

where Γ is the spin-lattice relaxation rate and C_0 and C_{eq} are the adiabatic and equilibrium limits of the specific heat, respectively. For the electronic spins C_0 is approximately given by the intra-well specific heat, whereas the 'slow' specific heat corresponds to transitions between the two wells.

The specific heat of Mn_4Cl measured with the longest experimental time ($\tau_{\mathrm{e}} \approx 300$ s) corresponds to the equilibrium. We have calculated the equilibrium specific heat C_{eq} using the model proposed in Ref. [15]. The experimental curve can, indeed, be well fitted by introducing a Gaussian distribution of dipolar fields with a width of $\sigma = 250$ Oe and adding to it the calculated C_{hf} (Fig. 2).

The experimental specific heat of Mn_4Ac, taken with an experimental time of $\tau_{\mathrm{e}} \approx 30$ s, is depicted in Fig. 3 together with the calculated contribution due to the splitting of the $S = 9/2$ multiplet, the hyperfine contribution C_{hf} and the equilibrium specific heat C_{eq} calculated taking into account a width of $\sigma = 200$ Oe for the Gaussian distribution of dipolar fields and adding to it the calculated C_{hf}. It is seen that the experimental C_{m} is well reproduced by the calculated C_{eq} (Fig. 3), indicating that, for the experimental time used in the measurement, the spins of Mn_4Ac are in thermal equilibrium with the lattice down to the minimum temperature reached ($T \cong 0.1$ K). The effect of the crystal field on determining the rate of the spin-lattice relaxation at the lowest temperature can be qualitatively understood by comparison of the C_{m} of Mn_4Ac (Fig. 3) with the results shown in Fig. 2 for Mn_4Cl. The former has a classical energy barrier $U = DS^2 - A_4 S^4 \cong 13.5$ K, that is lower than $U \cong 15.5$ K of Mn_4Cl, and a somewhat larger value of the second-order off-diagonal term (A_4) in the Hamiltonian of Eq. (1) [19]. Consequently, also the tunnel splitting should be larger in Mn_4Ac than in Mn_4Cl.

The same conclusion may be drawn by comparison of the experimental specific heat of Mn_4Me, taken with an

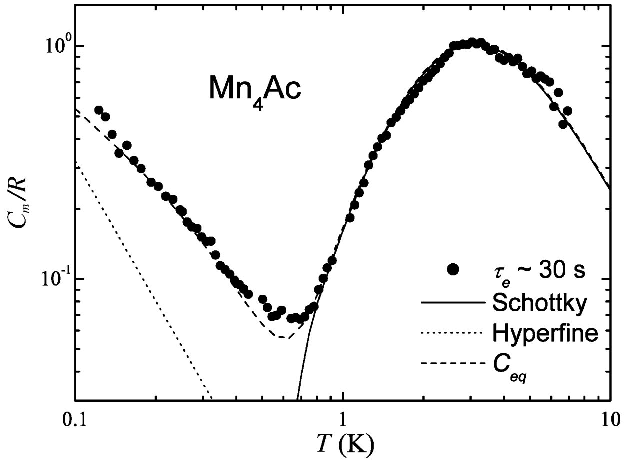

Fig. 3. Temperature dependence of the zero-field specific heat of Mn_4Ac measured for $\tau_{\mathrm{e}} \approx 30$ s. The solid line represents the contribution due to the splitting of the $S = 9/2$ multiplet, whereas the dotted line is the calculated hyperfine contribution, and the dashed line is the calculated equilibrium specific heat C_{eq}.

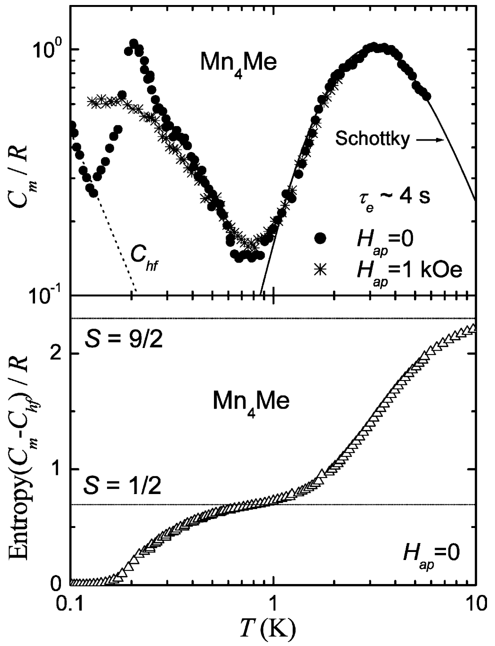

Fig. 4. *Upper:* temperature dependence of the specific heat measured for $\tau_e \approx 4$ s of Mn$_4$Me with $H = 0$ (●) and $H = 1$ kOe (*). The long-range magnetic order ($T_C = 0.21$ K) is suppressed by the applied-field. The solid line represents the contribution due to the splitting of the $S = 9/2$ multiplet, whereas the dotted line is the calculated hyperfine contribution C_{hf}. *Lower:* temperature dependence of the entropy variation after subtraction of the hyperfine contribution. The lines indicate the entropy values corresponding to $S = 1/2$ and $S = 9/2$.

experimental time of $\tau_e \approx 4$ s (Fig. 4), with the C_m of Mn$_4$Cl (Fig. 2), taken with a similar value of the experimental time ($\tau_e \approx 2$ s). The classical energy barrier in Mn$_4$Me is $U \cong 16.5$ K, somewhat larger than in Mn$_4$Cl, but also Mn$_4$Me presents a lower intrinsic symmetry. Ac-susceptibility data measured above 1.8 K show that, at zero field, the spin-lattice relaxation time of Mn$_4$Me is about a factor of 10 shorter than for Mn$_4$Cl, indicating that the tunneling probability is much higher. These results suggest that, as a result of the lower symmetry of Mn$_4$Me, the second-order off-diagonal term (E) in the Hamiltonian of Eq. (1), and therefore also the tunnel splitting, are larger for this compound. Our specific heat data show that, for a similar value of τ_e, the electron spins of the Mn$_4$Cl molecule become out of equilibrium below $T = 0.8$ K (Fig. 2), whereas C_m of Mn$_4$Me does not, apparently, show any deviation from equilibrium. We attribute the narrow peak observed in the specific heat of Mn$_4$Me at about $T_C = 0.21$ K (Fig. 4) to the onset of long-range magnetic order. For this compound, nearest neighbor molecules are well separated from each other by the shell of ligand molecules [21], with apparently only van der Waals bonding between cluster molecules. Therefore, this transition is likely induced by the dipole–dipole interactions between the molecules. This is supported by the fact that the peak is suppressed as soon as a small magnetic field $H_{ap} > 300$ Oe is applied to the sample. Since the materials are molecular crystals, with only van der Waals bonding between the magnetic molecules, magnetic exchange interactions can be safely neglected, leaving only the intercluster dipolar couplings. The situation is reminiscent of the ferromagnetic dipolar order recently observed in the isotropic molecular magnet Mn$_6$ at similarly low temperatures, $T_C = 0.16$ K [22]. Below 0.15 K, the experimental specific heat of Mn$_4$Me shows a clear upturn that agrees again very well with the calculated C_{hf} (Fig. 4), which indicates that the nuclear spins are also in thermal equilibrium down to very low temperatures. For the values of the parameters involved, i.e., dipolar energies and crystal anisotropy, the magnetic ordering peak and the contribution due to the splitting of the $S = 9/2$ multiplet are well separated in temperature (Fig. 4). It may be, therefore, interesting to analyse the temperature dependence of the entropy variation of the electronic spins in Mn$_4$Me. The entropy content can be evaluated by the relation

$$S/R = \int_0^\infty \frac{C_m(T) - C_{hf}(T)}{RT} \, dT \tag{3}$$

In order to calculate the entropy of the electronic spins of Mn$_4$Me, we carry out the integration in Eq. (3) using the experimental values of the specific heat after subtraction of the contribution due to the nuclear spins. The result, as a function of the temperature, is shown in Fig. 4. It can be seen that, as expected, the total entropy of the electronic spins tends to the limiting value of $\ln(2S+1)$ with $S = 9/2$. For the temperature region where the magnetic ordering process takes place ($T <$ 0.8 K), the entropy content indicates that Mn$_4$Me has an effective spin $S = 1/2$, as appropriate for a two-levels system. This result shows, therefore, that, in this temperature region, only the two-levels which are lowest in energy ($S = +9/2$ and $S = -9/2$) contribute effectively to the specific heat.

Our data clearly show that the spin-lattice relaxation rate increases when the tunneling probabilities increase, thus indicating that incoherent quantum tunneling brings the spins of these molecules towards the equilibrium state. The advantage of the series of tetranuclear clusters of manganese ions studied here is that the rates are fast enough so that the equilibrium and adiabatic limits are accessible to the experiment by varying either the anisotropy or the measurement time scales.

4. Concluding remarks

By very-low-temperature time-dependent specific heat experiments in three structurally related Mn$_4$ molecular clusters with net spin $S = 9/2$, we have studied the tunneling process which takes place through the anisotropy energy barrier directly between the magnetic states which are the lowest in energies. In half-integer spin molecular clusters, the ground state tunneling is made possible at zero-applied-field by the assistance of the environment, such as hyperfine and dipolar couplings or small intermolecular superexchange interaction [13,14]. Even so, the tunneling probability is still very small. Nevertheless, our experimental results show that incoherent tunneling can bring the electronic spins towards equilibrium with the lattice at very low temperatures ($T < 1$ K). In view of the prediction of Ref. [9], we can assert that probably the tunneling rate is enhanced through dynamic hyperfine interactions. The approach to thermal equilibrium with the lattice therefore proceeds via a complicated tunneling process in which both phonons and nuclear spins play a role. A model which takes into account both degrees of freedom acting simultaneously will be required to explain quantitatively our experimental results, and will be discussed in a forthcoming publication.

In one of the systems studied here, Mn_4Me, we have found evidence of long-range magnetic order at $T_C = 0.21$ K induced by dipolar interactions between clusters. Our result is supported by a model recently reported based on molecular magnets coupled only by dipolar interaction, where, for a suitable ratio of the involved parameters, i.e., crystal field anisotropy and intercluster dipolar energy, long-range magnetic order may be observed [23].

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