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Quantum tunnelling of magnetization in Mn_{12}-*ac* studied by ^{55}Mn NMR

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Abstract

We present an ultra-low temperature study (down to $T = 20$ mK) of the nuclear spin-lattice relaxation (SLR) in the ^{55}Mn nuclei of the molecular magnet Mn_{12}-*ac*. The nuclear spins act as local probes for the electronic spin fluctuations, due to thermal excitations and to tunnelling events. In the quantum regime (below $T \approx 0.75$ K), the nuclear SLR becomes temperature independent and is driven by fluctuations of the cluster's electronic spin due to the quantum tunnelling of magnetization in the ground doublet. The quantitative analysis of the nuclear SLR shows that the presence of fast-tunnelling molecules, combined with nuclear intercluster spin diffusion, plays an important role in the relaxation process.

Keywords: Molecular magnet; Nuclear relaxation; Quantum tunnelling

1. Introduction

The molecular cluster compound Mn_{12}-*ac* $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ was the first single-molecule magnet to show macroscopic quantum tunnelling of magnetization (QTM) [1]. Since then, its magnetic properties have been studied by means of a wide variety of techniques. Nevertheless, there are still difficulties in providing an accurate quantitative description of the tunnelling mechanism for the giant electronic spin $S = 10$. One reason is that the real Mn_{12}-*ac* samples contain (one or more) minority species [2,3], which differ from the majority molecules in the arrangement of the bound H_2O and carboxylate ligands, resulting in different anisotropy barriers, easy-axes of magnetization, and tunnelling splittings. A recent proposal also argues that a distribution of tunnelling splittings may take place in Mn_{12} crystals due to the effect of dislocations [4].

Furthermore, the study of QTM at very low temperatures (in what we shall call the 'quantum regime', i.e. where the electronic spin relaxation rates become temperature independent) is now widely recognized to be very sensitive to the dynamics of the nuclear spin system. So far, high-temperature NMR experiments on ^1H [5] and ^{55}Mn [6,7] nuclei in Mn_{12}-*ac* have demonstrated that the nuclear dynamics is strongly correlated with the thermal fluctuations of the cluster's electronic spin, whereas a study of the low-T nuclear dynamics (possibly driven by QTM) is still lacking.

It is the purpose of our study to fill this experimental gap; furthermore, the use of ^{55}Mn nuclei as local probes for the dynamics of the electronic spins in Mn_{12}, opens new possibilities for the study of QTM, since it doesn't require any macroscopic change in the electronic magnetization of the sample.

2. Magnetic structure and nuclear spectra

The structure of the Mn_{12}-*ac* molecule contains a core of four Mn^{4+} ions (Mn(1)) with electronic spin $s = 3/2$, and eight Mn^{3+} ions ($s = 2$) located on an outer ring with two crystallographically inequivalent sites (Mn(2) and Mn(3)). The superexchange interactions between ions lead to a ground-state total spin $S = 10$ for the whole cluster.

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A simple spin Hamiltonian for the cluster is:

$$H = -DS_z^2 - BS_z^4 - g\mu_B \mathbf{S}\cdot\mathbf{B} + H_{dip} + H_{hyp} + H' \qquad (1)$$

where $D = 0.55$ K is the uniaxial anisotropy parameter, $g = 1.94$ is the gyromagnetic ratio, S_z is the component of the total spin **S** along the anisotropy axis and **B** is the applied magnetic field.

$H' = E({S_x}^2 - {S_y}^2) + C(S_+^4 + S_-^4)$ is the part of the Hamiltonian which does not commute with S_z and is therefore responsible for the tunnelling of electronic spin in zero external field. Although the fourfold symmetry of the Mn_{12} molecule should imply $E = 0$, it is now well documented that, in a real Mn_{12} sample, there are many clusters where the tetragonal symmetry is broken by the disorder in the acetic acid molecules of crystallization [8]. This, and the disorder in the H_2O molecules of crystallization, is responsible for the presence of a sizable concentration (5–10%) of clusters where the tunnelling rate can be much faster than in the 'majority species'.

H_{dip} describes the dipolar interaction between electronic spins, and plays an important role in determining the tunnelling probability for each molecule, since the dipolar field acts at low temperature as a quasi-static bias that brings the electronic energy levels out of resonance, inhibiting the tunnelling events [9].

The hyperfine Hamiltonian H_{hyp} can be expressed as follows:

$$H_{hyp} = A_1 \sum_{Mn(1)} \mathbf{I}_{i1}\cdot\mathbf{s}_{i1} + A_2 \sum_{Mn(2)} \mathbf{I}_{i2}\cdot\mathbf{s}_{i2} + A_3 \sum_{Mn(3)} \mathbf{I}_{i3}\cdot\mathbf{s}_{i3} + H_{protons} \qquad (2)$$

where A_1, A_2, A_3 are the hyperfine coupling constants for the three inequivalent Mn(1), Mn(2) and Mn(3) sites, and the sums run over the four electronic (**s**) and nuclear (**I**) spins at each site. Similar but more intricate expressions would describe the coupling $H_{protons}$ to the ^1H nuclei in the Mn_{12}-*ac* molecule. In principle the hyperfine field adds to the above mentioned bias field acting on the electronic spins due to the intercluster dipolar interaction. If both fields would be static, tunnelling would be completely suppressed since these effective bias fields are many orders of magnitude larger than the tunnelling splitting Δ_0. However, as pointed out by Prokof'ev and Stamp [9], by considering the dynamics of the hyperfine field one may argue that this provides a rapidly fluctuating component that sweeps the bias field over a range much larger than Δ_0, thus bringing molecules in resonance for certain instants of time so that incoherent tunnelling may occur.

The structure of the cluster's Hamiltonian described above is reflected in the resonance spectra of the ^{55}Mn nuclei. Below the blocking temperature, $T_B \cong 3$ K, i.e. when the cluster's electronic spins are aligned along the anisotropy z axis and thermal excitations to states with $|S_z| < 10$ become much slower than the experimental timescale, the hyperfine fields at the nuclear sites act effectively as strong static magnetic fields (of order 20–30 T), allowing the detection of three NMR lines in zero external field. The first line (P1) is the resonance of the nuclei belonging to the Mn^{4+} ions, whereas the other two (P2 and P3) correspond to the nuclei in the two crystallographically inequivalent Mn^{3+} sites. The maxima of the ^{55}Mn resonance lines are found at frequencies $f_1 = 231$ MHz, $f_2 = 277$ MHz and $f_3 = 365$ MHz for P1, P2 and P3, respectively.

Since the ^{55}Mn nuclei possess spin $I = 5/2$ and are placed in environments with symmetry lower than cubic, each of the three NMR lines actually consists of a group of five quadrupolar-split lines. The quadrupolar splitting $\Delta f_Q^{(1)} \cong 0.72$ MHz of the P1 line is much smaller than those of lines P2 and P3 ($\Delta f_Q^{(2)} \cong 4.3$ MHz and $\Delta f_Q^{(3)} \cong 2.9$ MHz). Furthermore, the hyperfine field in the Mn^{4+} ions is isotropic and directed along the anisotropy axis for the $S = 10$ electronic spin of the cluster, whereas the hyperfine coupling in Mn^{3+} ions is anisotropic [6]. For these reasons, our study of the nuclear relaxation in Mn_{12} was focused on the NMR signal of the line P1.

3. Experimental

The Mn_{12} crystallites were mixed with Stycast 1266 epoxy and allowed to orient at room temperature in 9.4 T magnetic field for one day. The oriented sample obtained in this way was mounted inside the plastic mixing chamber of a dilution refrigerator. In the design of the refrigerator, special care was taken to ensure good thermalisation of the sample, thanks to the continuous circulation of ^3He around it [10].

The nuclear spin-lattice relaxation (SLR) was investigated by means of the pulse NMR technique, monitoring the recovery of the nuclear magnetization $M(t)$ after an inversion pulse. Typically, the duration of a $\pi/2$ pulse was 10 μs. Since the ^{55}Mn nuclei have spin $I = 5/2$, the magnetization recovery is not described by a single exponential. The prediction for the recovery after inversion of the central of the five quadrupolar split lines, in the limit where the quadrupolar splitting is much smaller than the Zeeman splitting, has been obtained as [11]:

$$M(t)/M(\infty) = 1 - [100/63\ \exp(-30Wt) + 16/45\ \exp(-12Wt) + 2/35\ \exp(-2Wt)] \qquad (3)$$

where W is the nuclear SLR rate. Eq. (3) is found to fit very well the whole recovery curve, leaving only W as (time-related) fitting parameter.

4. Results and discussion

The nuclear SLR rate for the ^{55}Mn nuclei of Mn_{12} in the temperature range 1–3 K, has been previously studied by Furukawa et al. [7]. In that work, T_1^{-1} ($=2W$) was obtained from the magnetization recovery after saturation of the central line, fitting only the initial part of $M(t)$. Our results in the range 1–2 K, shown in Fig. 1, are in good agreement with those of Ref. [7], despite the use of different pulse sequences and fitting functions for the recovery curves.

As mentioned in Section 1, the ^{55}Mn nuclei are used as local probes for the fluctuations of the cluster's electronic spin. From the temperature dependence of the nuclear relaxation rate $W(T)$ above 1 K, it was deduced [7] that the electronic fluctuations arise from thermal excitations from the ground levels $|S_z| = 10$ to the nearest excited levels $|S_z| = 9$ inside each energy potential well, i.e. without crossing the anisotropy barrier. Such excitations produce a fluctuating transverse magnetic field $h_\perp$ at the nuclear site. Its time-correlation function can be written as $\langle h_\perp(0)h_\perp(t)\rangle = \langle h_\perp^2\rangle \exp(-t/\tau)$ where τ is the typical timescale for the fluctuations. Above 1 K, τ is determined by the timescale $\tau_{s\text{-}ph}$ of the spin-phonon excitations. Since in the investigated temperature range (up to 2 K) only the thermal excitations to the nearest excited level need to be considered, then $\tau_{s\text{-}ph} \sim \tau_0 \exp[(E_9 - E_{10})/k_B T]$, where $E_9 - E_{10}$ is the energy difference between the ground and the first excited state [7,12]. In this limit, the nuclear relaxation rate can be expressed as:

$$W \approx \frac{\gamma_N^2}{4}\langle h_\perp^2\rangle \frac{\tau_{s\text{-}ph}}{1 + \omega_N^2 \tau_{s\text{-}ph}^2} \quad (4)$$

where $\gamma_N = 10.57$ MHz T^{-1} is the nuclear gyromagnetic ratio, and $\omega_N/2\pi = 231$ MHz is the Larmor frequency. The solid line in Fig. 1 was obtained fixing $E_9 - E_{10} = 14.58$ K, as calculated from the spin Hamiltonian Eq. (1) using the experimental values $D = 0.55$ K and $B = 1.2 \times 10^{-3}$ K (see [7] and references therein), and obtaining $\langle h_\perp^2\rangle/\tau_0 \approx 2.8 \times 10^8$ T^2 s^{-1}. The fit could be slightly improved by leaving $E_9 - E_{10}$ as free parameter, yielding $E_9 - E_{10} \approx 12.1$ K and $\langle h_\perp^2\rangle/\tau_0 \approx 4.5 \times 10^7$ T^2 s^{-1}. This demonstrates that Eq. (4) indeed correctly describes the experimental data in the thermally activated regime for the electronic spin fluctuations.

Given the temperature dependence of $\tau_{s\text{-}ph}$, the above mechanism would lead to astronomically long nuclear relaxation at millikelvin temperatures. The main goal of our research was to find out whether the nuclear spins would still be able to relax at very low temperature, thanks to fluctuations due to incoherent quantum tunnelling of the cluster's electronic spin within the magnetic ground ($S_z = \pm 10$) doublet. The possibility for such tunnelling to occur even for extremely small values of the tunnelling splitting, was argued by Prokof'ev and Stamp [9], on basis of a formalism invoking the dynamics of the hyperfine interactions due to nuclear spin diffusion.

Fig. 2 shows the nuclear relaxation rate as measured down to $T = 20$ mK. Obviously, another relaxation mechanism is present, since $W(T)$ becomes temperature independent below $T \cong 0.75$ K. It is very tempting to ascribe such a behaviour to QTM, also because at a similar temperature the hysteresis loops for the cluster's magnetization were found to become temperature independent [13]. In fact, an equivalent phenomenon has very recently been observed for the proton NMR relaxation in Fe_8 [14], and also in that case the plateau in $W(T)$ appears at the same temperature where the magnetization loops become temperature independent. Additional evidence supporting the idea of tunnelling-driven nuclear relaxation is provided by the dependence of W on external magnetic field B_z applied along the anisotropy axis of the clusters. A comprehensive study

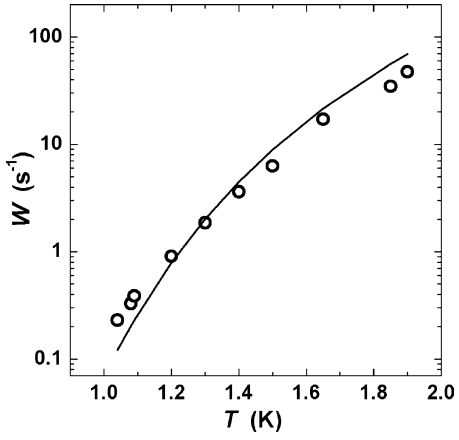

Fig. 1. Nuclear SLR rate above 1 K. Solid line: fit to Eq. (4), showing that the nuclear relaxation is produced by thermal fluctuations of the electronic spin.

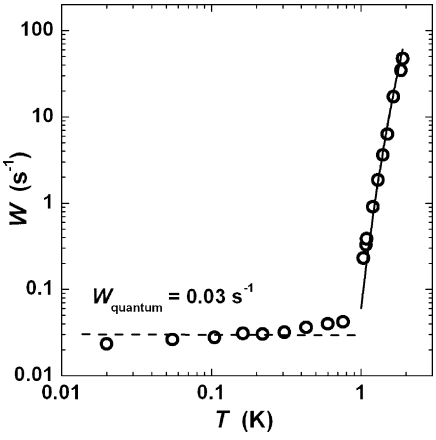

Fig. 2. Below $T \approx 0.75$ K the nuclear SLR becomes temperature independent and saturates at a value $W_{quantum} \approx 0.03$ s^{-1}. This reveals the presence of (temperature independent) tunnelling fluctuations.

of $W(B_z)$ at various temperatures is in preparation and will be published elsewhere.

The very fast nuclear relaxation rate $W \cong 0.03\ s^{-1}$ in the quantum regime is, at a first glance, quite astonishing. One could think of explaining it in terms of magnetic fluctuations directly felt by the nuclear spins as a consequence of a tunnelling event, thus using Eq. (4) and replacing $\langle h_\perp^2 \rangle$ and $\tau_{s\text{-}ph}$ by the amplitude and timescale for the fluctuations arising from the tunnelling of the cluster's electronic spin, but the result would be several orders of magnitude lower than the observed value. One possibility is to invoke the role of fast-relaxing molecules, which have a much higher tunnelling rate. However we can demonstrate that the signal we measure comes from the nuclei in the Mn^{4+} ions of all Mn_{12} clusters in the sample, i.e. not only those belonging to fast-relaxing molecules. When applying an external magnetic field B_z along the anisotropy axis of the clusters, this can add or subtract to the hyperfine field at the nuclear site, depending on whether the electronic spin is parallel or antiparallel to the applied field. Therefore, some nuclei will have their Larmor frequencies shifted up (when B_z is parallel to the electronic spin $\boldsymbol{S}$), the others down (B_z antiparallel to $\boldsymbol{S}$). By measuring the nuclear spin-echo signal intensity at the two possible Larmor frequencies, we can check the magnetization state of the sample (see also Ref. [6]), and we observe that, starting from a fully magnetized sample, its electronic magnetization (as seen from the nuclei) does not substantially relax even after 1 week of measurements. This implies that the nuclei we observe belong to all clusters, i.e. also those for which the tunnelling rates are extremely slow.

In view of the important role of nuclear spin diffusion in the model of Prokof'ev and Stamp, where it provides the dynamics of the hyperfine field acting on the electron spin, it seems likely that a correct quantitative interpretation of the nuclear relaxation rate should involve the role of nuclear spin diffusion as well. We have therefore measured the transverse nuclear spin–spin relaxation rate T_2^{-1}, shown in Fig. 3. Its low-temperature value $T_2^{-1} \cong 100\ s^{-1}$, agrees with the nuclear spin diffusion rate that we can calculate by taking into account the flip-flop term in the dipolar interaction between nuclei of Mn^{4+} ions belonging to all neighbouring clusters. This means that the intercluster spin diffusion is an effective mechanism to transport nuclear polarization across the sample, on a timescale much shorter than the observed SLR. The value of $1/(2WT_2) \sim 10^3$ means that about 10^3 nuclear flip-flop events can take place during the nuclear SLR time. Accordingly, the energy of the whole system of ^{55}Mn nuclei can be effectively transported by nuclear spin diffusion to the location of the fast-tunnelling electronic spins, which provide the necessary relaxation channel by incoherent tunnelling events.

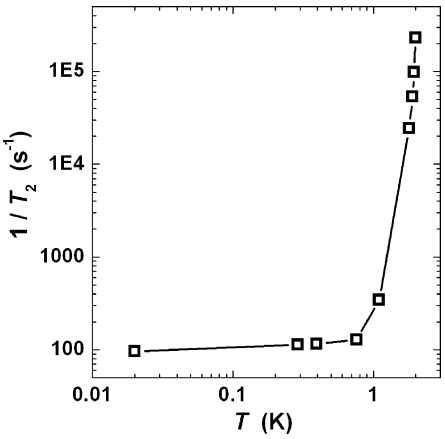

Fig. 3. Transversal nuclear spin–spin relaxation rate: the low-T value agrees with the calculated intercluster spin diffusion rate.

5. Conclusions

We have shown that the nuclear spins can be used as effective local probes for the detection of tunnelling fluctuations in the electronic spin of Mn_{12}-*ac*. In particular, the nuclear relaxation rate W becomes temperature independent below $T \cong 0.75$ K. The quantitative analysis of W suggests that the presence of a small concentration of fast-tunnelling electronic spins, combined with nuclear intercluster spin diffusion, provides the mechanism responsible for the observed nuclear SLR rate.

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