Thermal Fluctuations in the Magnetic Ground State of the Molecular Cluster $Mn_{12}O_{12}$ Acetate from μSR and Proton NMR Relaxation

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Measurements of the spin-lattice relaxation rate are reported for muons and protons as a function of temperature for different values of the applied magnetic field in the $Mn_{12}O_{12}$ molecular cluster. Strongly field dependent maxima in the relaxation rate versus temperature are observed below 50 K. The results are explained in terms of thermal fluctuations of the total magnetization of the cluster among the different orientations with respect to the anisotropy axis. The lifetimes of the different m components of the total spin, $S_T = 10$, of the molecule are obtained from the experiment and shown to be consistent with the ones expected from a spin-phonon coupling mechanism. No clear evidence for macroscopic quantum tunneling was observed in the field dependence of the proton relaxation rate at low T. [S0031-9007(98)07391-8]

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Large magnetic molecules which are the building blocks of solid crystal lattices are of interest for the study of magnetism at mesoscopic level [1,2]. A system that has recently attracted much attention is the molecule $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ (in short Mn12) whose magnetic core is made up of a tetrahedron of Mn^{4+} ions, each with $S = \frac{3}{2}$, at the center and eight Mn^{3+} ions with $S = 2$ on the outside [3,4]. The clusters crystallize into a tetragonal lattice in which the orbital angular momentum is quenched by the crystal field and the intermolecular magnetic interactions are negligible. Thus, the magnetic properties are largely determined by the intramolecular superexchange interactions J and by the strong single ion axial anisotropy (along tetragonal z axis) due to residual spin-orbit interactions [5]. The ground-state configuration determined by the relative strength of the antiferromagnetic J coupling constants has total spin $S_T = 10$ resulting from the four inner Mn^{4+} spins being parallel to each other ($S_T = 6$) and the other eight Mn^{3+} also parallel ($S_T = 16$) with the two groups antiparallel to each other. At low temperature ($T < 30$ K) the magnetic clusters are mostly in the $S_T = 10$ ground state [4], and the reorientation of the magnetization of the molecule determined by spin transition among the different m sublevels split by the axial anisotropy gives rise to spectacular superparamagnetic behavior [6,7]. At even lower temperature ($T < 3$ K) where the classical thermal fluctuations freeze out one still observes finite, although small, relaxation rates which have been attributed to macroscopic quantum tunneling phenomena [8–10]. There are several theoretical models to evaluate the reorientation rate of the total magnetization of the molecule at low T including the quantum tunneling [11–13]. One important issue is the interplay of thermal fluctuations and resonant tunneling in determining the average time τ for the magnetization of the molecule to change orientation (m) against the anisotropy barrier [14]. The field and temperature dependences of the thermal lifetimes of the m levels are necessary for a quantitative estimate of τ.

Nuclear magnetic resonance (NMR) and muon spin rotation (μSR) are suitable microscopic probes to investigate the spin dynamics of the Mn ions in the cluster [15]. In particular, the fluctuations of orientation of the magnetization of the cluster generate fluctuations in the local hyperfine interaction at the nuclear (or muon) site which in turn become responsible for the nuclear (muon) spin-lattice relaxation. In this Letter, we report a detailed investigation of the spin-lattice relaxation (SLR) of both muons and protons in Mn12 as a function of temperature and for different values of the applied external magnetic field H. The central result of this paper consists in the observation of maxima in the μSR SLR vs T, maxima which decrease in amplitude and are displaced towards lower temperature upon increasing H. The observed behavior for μSR is explained with a simple model which takes into account the random fluctuations of the total magnetization of the cluster in its $S_T = 10$ ground states among the different m sublevels. The same model explains the proton NMR SLR data versus field at $T = 4.2$ and 3 K. It is noted that the lifetimes of the different m levels obtained here are not easily determined from electron paramagnetic resonance (EPR) and/or neutron scattering.

Polycrystalline samples of $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4 2CH_3$-$COOH 4H_2O$ were prepared as described in Ref. [4]. In NMR measurements the powders were cooled down to the lowest temperature in the highest magnetic field; in this way most of the particles end up oriented with the z axis along the magnetic field. On the contrary, the low field μSR experiments were performed on randomly oriented powders. In this case a majority of the crystallites are oriented approximately with the z axis perpendicular to the magnetic field. The NMR spectrum broadens at low T as shown in Fig. 1. The low-T spectrum can be resolved into two components (see inset of Fig. 1). The main line A is unshifted while the second line has a shift which increases on lowering the temperature (see Fig. 1). The shifted B line can be ascribed to the protons in the H_2O molecules coupled by an isotropic hyperfine interaction to the Mn core. The main unshifted line originates from protons which are coupled to Mn moments via dipolar interactions only, which yield a broadening of the line but no net shift. The shift and the linewidth of both components have a temperature dependence which tracks the T dependence of the magnetic susceptibility [15]. The shift on line B in Fig. 1 saturates at low T at about 3 MHz independently of the applied field H, indicating that the local hyperfine field has a fixed value corresponding to the spontaneous magnetization of the molecule in its $S_T = 10$ ground state. The recovery of the nuclear magnetization is not exponential due to the distribution of relaxation rates of the different protons in the Mn12 cluster. The SLR, T_1^{-1}, was obtained from the initial part of the recovery, thus yielding an average value [15]. Measurements performed by irradiating the two lines yield essentially the same result indicating that the different groups of protons are strongly coupled via the nuclear dipolar interaction. The μ^+SR measurements were performed at ISIS pulsed muon facility (Rutherford Appleton Laboratory) on MUSR beam line. The spin-lattice relaxation rate λ was obtained from the stretched exponential decay $[\exp(-(\lambda t)_\beta)]$ of the muon polarization which indicates the presence of a distribution of muon sites. Details about both NMR and μSR methods of measurement and a critical discussion of the parameters measured have been reported in a previous publication [15].

A complete set of relaxation data for both NMR and μSR are shown in Fig. 2. Both NMR and μSR relaxation show a similar enhancement at $T < 100$ K. The μSR relaxation goes through a field dependent maximum at $T < 50$ K except that for the $H = 0$ data. The NMR relaxation time at low frequency becomes so short below 50 K that the signal is lost. It is measurable again at very low T (<5 K) where T_1 and T_2 become sufficiently long (see the NMR data at 4.2 and 3 K in Fig. 2). Thus, it can be inferred that a maximum similar to the one observed in μSR is present. Another broad and structured maximum can be observed at relatively high temperature in the NMR high frequency data at 87 MHz and 200 MHz reported previously [15]. Since we are interested in the fluctuations of the magnetization in the $S_T = 10$ ground state, we consider here only the low T and low H data for both μSR and NMR.

We consider the Mn12 cluster in its magnetic ground state characterized by 21 energy levels labeled by the magnetic quantum number m [14] which, neglecting small transverse fourth order terms, can be expressed as $E_m = -Dm^2 - Bm^4 - hm\cos\theta$, where the anisotropy parameters are $D = 0.556$ K, $B = 1.1 \times 10^{-3}$ K, $h = g\mu_B H = 1.33H$ (K/T), and θ is the angle between the tetragonal z axis and the external magnetic field. Muon (nuclear) spin-lattice relaxation involves the exchange of the small quantum of Zeeman energy with the "lattice" and is thus possible only if a lifetime broadening of the magnetic molecular levels is present. In the framework of the weak collision approximation [16] the above "scattering" process can be described in terms of the correlation function of the transverse component $h_\pm(t)$ of the time dependent transverse hyperfine field at the

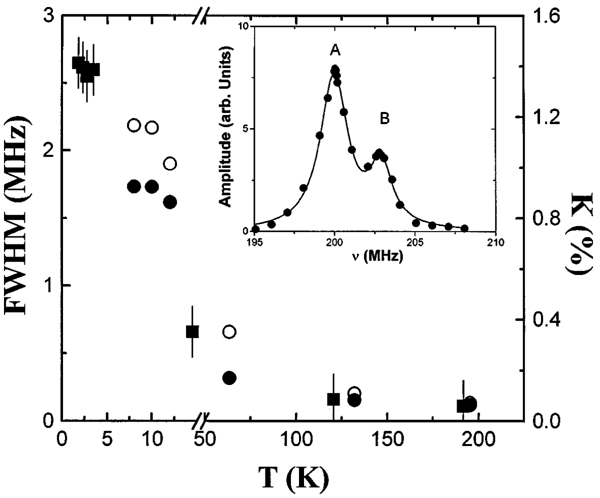

FIG. 1. Proton NMR, shift of the line B (■), and full width at half maximum of line A (○) and of line B (●) versus temperature at 4.7 T. The inset shows the proton NMR spectrum at 8 K and 4.7 T.

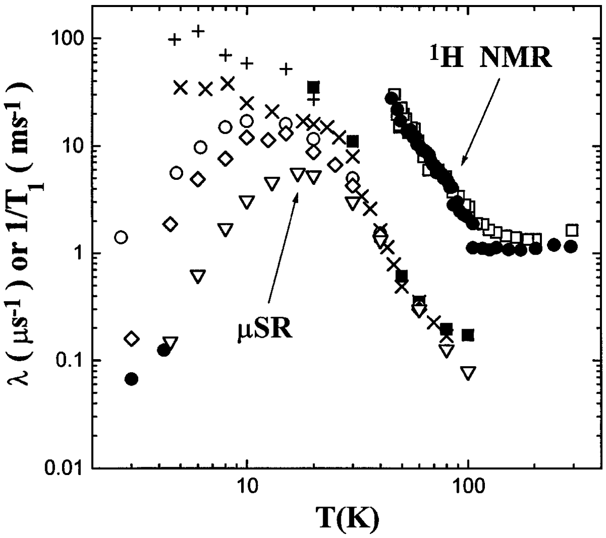

FIG. 2. Longitudinal spin-lattice relaxation rate for protons (T_1^{-1}) and muons (λ) plotted versus temperature for different applied magnetic fields. NMR: (□) 0.33 T (●) 0.73 T; μSR: (■) zero field, (+) 0.025 T, (×) 0.1 T, (○) 0.15 T, (◇) 0.2 T, (▽) 0.37 T.

muon (nuclear) site. If $\Delta h_\pm$ is the hyperfine field change when the magnetization of the molecule changes orientation (i.e., $\Delta m = \pm 1$ transitions) and if we assume an exponential correlation function with correlation time τ_m (corresponding to a Lorentzian broadening of the m sublevels) then we can write:

$$\langle h_\pm(t)h_\pm(0)\rangle = \sum_{m=+10}^{-10} \langle \Delta h_\pm^2 \rangle \exp\left(-\frac{t}{\tau_m}\right)\frac{\exp(-E_m/kT)}{Z}, \tag{1}$$

where Z is the partition function. The lifetime τ_m can be expressed in terms of the spin-phonon transition probabilities $p_{m\to m'}$ for a transition $m \to m'$:

$$\frac{1}{\tau_m} = p_{m\to m-1} + p_{m\to m+1}; \tag{2}$$

where according to Villain *et al.* [5,11,17],

$$\begin{aligned} p_{m\to m-1} &= C\,\frac{(E_{m-1}-E_m)^3}{e^{(E_{m-1}-E_m)/kT}-1}, \quad \text{and} \\ p_{m\to m+1} &= C\,\frac{(E_m-E_{m+1})^3}{1-e^{-(E_m-E_{m+1})/kT}}, \quad \text{for } m > 0 \end{aligned} \tag{3}$$

while for $m < 0$ one has to replace $m-1$ with $m+1$ in the first part of Eq. (3) and replace $m+1$ with $m-1$ in the second part of Eq. (3).

In Eq. (3) the parameter $C = (3/2\pi\rho v^5\hbar^4)|\langle m|V|m\pm 1\rangle|^2$, with v the phonon velocity, depends on the matrix element of the spin-phonon interaction. Thus we can write for the NSLR or μSR relaxation [16]

$$\begin{aligned} \frac{1}{T_1}\,(\text{or } \lambda) &= \frac{1}{2}\,\gamma_N^2 \int \langle h_\pm(t)h_\pm(0)\rangle \exp(i\omega_L t)\,dt \\ &= \frac{A}{Z}\sum_{m=+10}^{-10} \frac{e^{-E_m/kT}\tau_m}{1+\omega_L^2\tau_m^2}, \end{aligned} \tag{4}$$

where $A = \gamma_N^2\langle\Delta h_\pm^2\rangle$, γ_N is the nuclear (muon) gyromagnetic ratio and ω_L is the Larmor frequency.

The experimental μSR relaxation rates are compared with the theoretical calculation [Eq. (4)] in Fig. 3. The adjustable parameters are A and C which are chosen to yield a reasonable fit for all the curves in Fig. 3:

$$A_{\mu\mathrm{SR}} = 6\times 10^{15}\ (\mathrm{rad/sec^{-2}}) \quad \text{and}$$

$$C = \frac{3|V_{m,m\pm 1}|^2}{2\pi\hbar^4\rho v^5} = 0.9\times 10^5\ (\mathrm{Hz/K^3}).$$

An uncertainty of ±25% can be assigned to the values of the parameters A, C from a comparison of the theoretical curves with the experimental data for different values of the parameters. The value $C = 0.9\times 10^5$ Hz/K^3 falls in the range $\sim 10^3$–10^5 which is typical of simple magnetic ions [14,17].

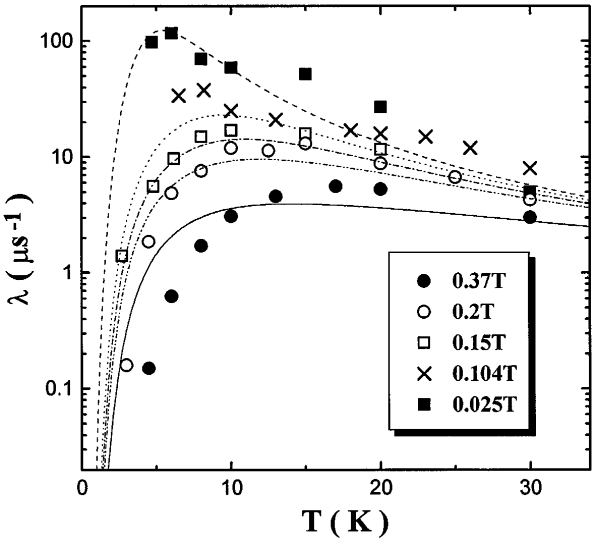

FIG. 3. Muon relaxation rates versus temperature for different applied magnetic fields. The curves are theoretical fits according to Eq. (4) with the choice of parameters discussed in the text.

Since the low H, low T maximum in the NMR SLR cannot be measured due to short relaxation times (see Fig. 2), we checked the validity of Eq. (4) by measuring the NMR relaxation at $T = 4.2$ K and $T = 3$ K as a function of external magnetic field (resonance frequency) as shown in Fig. 4. Both sets of experimental data in Fig. 4 can be fitted with Eq. (4) using the same C value used in the μSR fit (Fig. 3) and $A_{\mathrm{NMR}} = 0.4\times 10^{12}$ (rad/sec^{-2}). The value of $A_{\mathrm{NMR}} = 0.4\times 10^{12}$ (rad/sec^{-2}) corresponds to a root mean square hyperfine field $\frac{\gamma}{2\pi}\sqrt{\langle\Delta h_\pm^2\rangle} = \sqrt{A_{\mathrm{NMR}}}/2\pi = 100$ KHz which is of the correct order of magnitude being a fraction of the inhomogeneous width of the NMR spectrum (see Fig. 1). The ratio $\sqrt{A_{\mu\mathrm{SR}}\gamma_N^2/A_{\mathrm{NMR}}\gamma_\mu^2} = \sqrt{\langle\Delta h_\pm^2\rangle_{\mu\mathrm{SR}}/\langle\Delta h_\pm^2\rangle_{\mathrm{NMR}}} = 38$ is surprisingly high, suggesting that the muon location in the Mn12-acetate molecule is on an oxygen bridging the

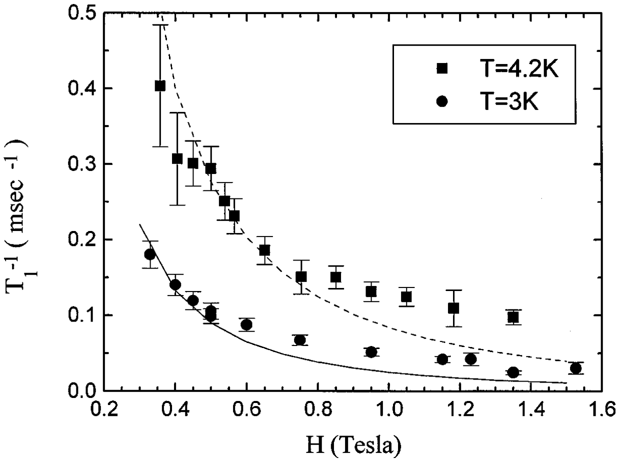

FIG. 4. Proton spin-lattice relaxation rate versus applied magnetic field at 4.2 and at 3 K. The curves are the fits according to Eq. (4) with fitting parameters discussed in the text.

Mn ions and is thus subjected to a much larger hyperfine field than the protons.

At the values of the field H corresponding to level crossings the macroscopic relaxation of the cluster magnetization was found [9] to speed up as a result of increased macroscopic quantum tunneling. A decrease of the lifetime τ_m due to tunneling effects should give rise to an enhancement of the proton T_1^{-1} with respect to the value calculated from Eq. (4) on the basis of thermal fluctuations alone. The deviation of T_1^{-1} in Fig. (4) from the calculated curves could be due to tunneling since it occurs most prominently in the range of field values for which level crossings are expected. In fact, from the formula for the energy levels E_m adopted here [14] the first order level crossings range from $H = 0.58$ T for the $m = -10$ to $m = 9$ crossing to $H = 0.43$ T for the $m = -1$ to $m = 0$ crossing. The second order crossings would be at twice those fields.

In conclusion, the effects of fluctuations in thermal equilibrium of the orientation of the magnetization in Mn12 molecule have been detected in both NMR and μSR experiments. The lifetimes τ_m of each given orientation of the magnetization m, due to spin-phonon coupling [5,11,17], are derived from the experimental data. These values should be useful in describing the macroscopic relaxation time τ of the magnetization in the framework of a mixed quantum-thermal relaxation mechanism [14]. Only marginal evidence for macroscopic quantum tunneling could be seen in the nuclear relaxation data, suggesting the need for specifically designed NMR or μSR experiments to study the phenomenon more quantitatively.

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