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Spin Dynamics of the Molecular Nanomagnet Fe8 Studied by ^{1}H-NMR

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The proton nuclear spin-lattice relaxation rate $1/T_1$ has been measured as a function of temperature (T=1.4-4.2K) and magnetic field (H=0.6-5T) in the Fe8 cluster in its high spin S=10 ground state. The strong temperature and field dependence of $1/T_1$ can be fitted well by using a simple model in terms of the thermal fluctuations of the total spin S=10 of the cluster originating from the spin-phonon interactions. $1/T_1$ data of protons in a partially deuterated Fe8 cluster is also reported. The results indicate that the spin phonon coupling constant is not affected by the change of mass of the isotopes in the Fe8 cluster.

Keywords: Nanomagnet; Fe8 cluster; nuclear magnetic resonance

INTRODUCTION

The recent observation of resonant quantum tunneling of magnetization in molecular nanomagnet $[Fe_8(N_3C_6H_{15})_6O_2(OH)_{12}]\cdot[Br_8\cdot 9H_2O]$ (in short, Fe8) has generated great interest[1,2]. The magnetic core of the

Fe8 cluster is made up of eight Fe^{3+} (s=5/2) ions. The strong antiferromagnetic couplings between Fe^{3+} spins give rise to a high total spin S=10 ground state at low temperature. The magnetic ground state of the Fe8 cluster can be described by a simple spin Hamiltonian,

$$H=DS_z^2+E(S_x^2-S_y^2)+g\mu_B\mathbf{S}\cdot\mathbf{H} \quad (1)$$

where D=−0.27 K and E=0.046 K are anisotropy constants[3] and last term is the Zeeman energy associated from the external magnetic field. The negative crystal field anisotropy introduces an energy barrier to the reorientation of the total spin, which generates spectacular superparamagnetic relaxation phenomena[3] and quantum tunneling effects[1,2] at low temperature.

For proper description of the quantum dynamical effects in the high spin ground state, one has to take into account for the environmental effects represented by spin-phonon coupling, intermolecular magnetic interactions and hyperfine interactions with nuclei. This was recently demonstrated by the influence of nuclear spins in the quantum tunneling of magnetization in isotopically substituted Fe8 samples[4]. The relaxation time of the magnetization is reported to be largely influenced by the isotope substitutions below ~360mK, while the relaxation time shows no large difference by the substitutions above 1.5K where the spin-phonon coupling is considered to dominate the relaxation time.

In order to shed light on the spin dynamics of Fe8 cluster from a microscopic point of view, we have measured proton spin-lattice relaxation rates (T_1^{-1}) as a function of the external magnetic field (along to the easy-axis) and as a function of temperature in molecular nanomagnet Fe8. We have also carried out ^{1}H-NMR in partially deuterated Fe8 cluster to investigate the influence of isotope substitutions on the spin dynamics of the Fe8 cluster.

RESULTS AND DISCUSSIONS

The powder samples of $[Fe_8(tacn)_6O_2(OH)_{12}]^{8+}\cdot[Br_8\cdot 9H_2O]^{8-}$ where *tacn* is the organic ligand 1,4,7-triazacyclonane were prepared by the

method reported in the literature[5]. The partially deuterated Fe8 sample was crystallized from pyridine-d_5 and D_2O (99%) under an inert atmosphere at 5 °C by using a nondeuterated $Fe(tacn)Cl_3$ precursor. The details of the sample preparation were described elesewhere[6]. In the following the standard non-deuterated Fe8 and the deuterated Fe8 will be referred to as stFe8 and ^{D}Fe8 respectively. The nuclear magnetic resonance (NMR) was curried out utilizing a phase-coherent pulse spectromenter. Nuclear spin-lattice relaxation rates T_1^{-1} were measured by the saturation recovery method. The nuclear magnetization recovery was nonexponential so that T_1^{-1} was determined from the initial slope of the recovery curve.

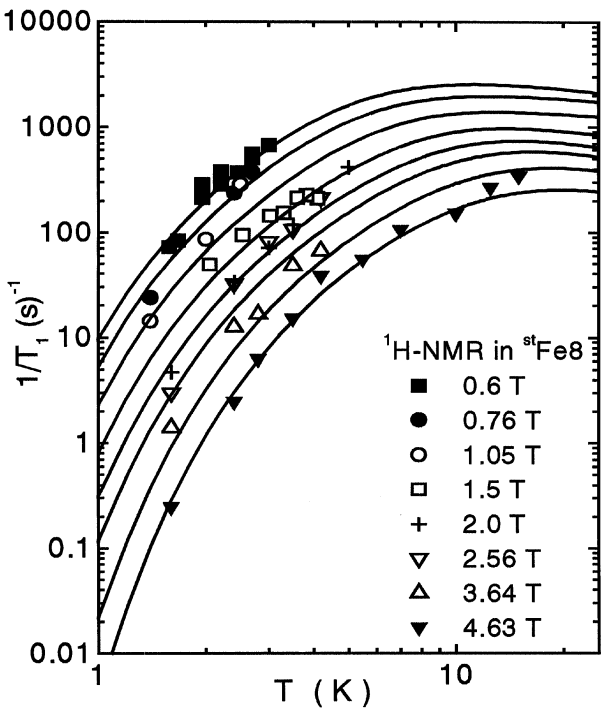

FIGURE 1 Temperature dependence of T_1^{-1} of Fe8 powders at different fields compared with the theoretical estimations (solid lines) calculated by a simple model, eq. (2). All curves are obtained with the same set of parameters : C = 31 Hz/K^3 and A= 1.02×10^{12} (rad/sec)^2.

Figure 1 shows the temperature (T) dependence of T_1^{-1} of proton NMR in stFe8 under various external magnetic fields where the magnetic field is applied parallel to the easy-axis. T_1^{-1} exhibits a remarkable decrease with decreasing temperature down to 1.5K and increasing magnetic fields. As have been pointed out[6], by considering the system in the S=10 spin, T_1^{-1} is given by

$$1/T_1 = \frac{1}{2}\gamma_N^2 \int < h_{\pm}(t)h_{\pm}(0) > \exp(i\omega_L t)dt$$

$$= \frac{A}{Z}\sum_{m=+10}^{-10} \frac{\tau_m \exp\left(-\frac{E_m}{k_B T}\right)}{1+\omega_L^2 \tau_m^2} \qquad (2)$$

where τ_m is the life time broadening of the magnetic m-th sublevels originating from the spin-phonon interactions. γ_N is gyromagnetic ratio of proton, ω_L is Lamor frequency, Z is the partition function and A is a parameter related to the hyperfine coupling constants. The life-time τ_m for each individual m state is determined by $1/\tau_m = P_{m\to m+1} + P_{m\to m-1} + P_{m\to m+2} + P_{m\to m-2}$. The transition probabilities due to the spin phonon interactions can be expressed by[7]

$$P_{m->m\pm1} = C\, s_{\pm1}(E_{m\pm1}-E_m)/\{\exp(E_{m\pm1}-E_m)/k_B T-1\}),$$
$$P_{m->m\pm2} = 1.06 C s_{\pm2}(E_{m\pm2}-E_m)/\{\exp(E_{m\pm2}-E_m)/k_B T-1\}),$$

where $s_{\pm1} = (S \mp m)(S \pm m+1)(2m+1)^2$ and $s_{\pm2} = (S \mp m)(S \pm m+1)$ $(S \mp m+1)$ $(S \pm m+2)$ and C is the spin-phonon coupling constant and E_m is an energy level for m-th sublevel which can be calculated from the eq. (1).

The experimental data as a function of temperature under different magnetic fields are well reproduced by the equation (2) with a set of parameters of $A=1.02\times10^{12}$ (rad/sec)^2 and C=31 Hz/K^3 as shown in the Figure 1 by solid lines. Thus, it turns out that the strong field and temperature dependence of T_1^{-1} can be well understood by the model in terms of the thermal fluctuations of the total spin S=10 of the cluster originating from the spin-phonon interactions.

Figure 2 shows the temperature dependencies of T_1^{-1} of protons in ^{D}Fe8 under two different magnetic fields together with the results for stFe8 measured at the same magnetic fields. T_1^{-1} of protons in ^{D}Fe8 does not show any difference from those in stFe8 above 1.4K within our experimental uncertainty. Since the dependence of T_1^{-1} on both H and T in the measured region is well explained by the model originated from the spin-phonon interactions, the result indicates that the spin-phonon coupling parameter C is not changed appreciably by the substitution of ^{2}D for ^{1}H in the Fe8 cluster. This can explain the results of relaxation measurements of the magnetization which does not change in both samples above 1.5 K where spin-phonon coupling dominates the relaxation rates. It would be worth to point out that no-appreciable change of the spin phonon coupling is not responsible for the large influence to the relaxation time of the magnetization by the isotopes substitutions below 360mK where the magnetization relaxes through a pure tunneling process. Thus we may consider that nuclear spins play an important role for the mechanism of QTM as has been pointed out by Wernsdorfer et al.[4].

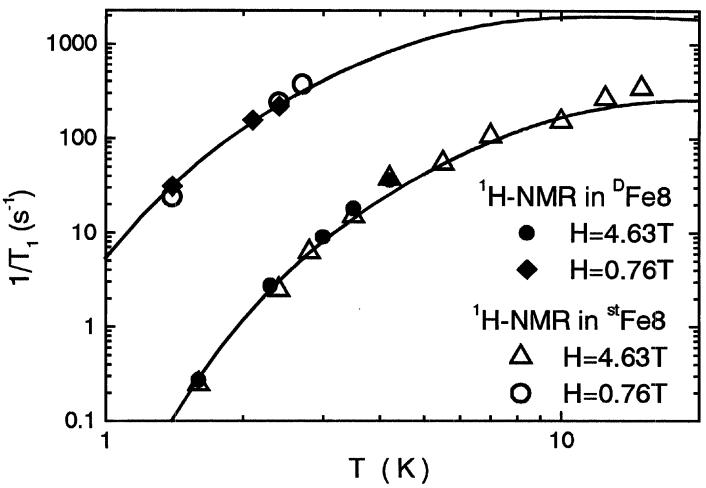

FIGURE 2 Temperature dependence of T_1^{-1} of protons in ^{D}Fe8 at two different magnetic fields. T_1^{-1} of protons in stFe8 at the same magnetic fields is also plotted for the comparison. Solid lines are same curves plotted in Figure 1 for corresponding magnetic fields.

CONCLUSIONS

We have investigated the spin dynamics of Fe8 cluster in its S=10 ground state by ^1H nuclear spin-lattice relaxation rates (T_1^{-1}) measurements as a function of temperature and as a function of applied magnetic field. The strong temperature and field dependence of T_1^{-1} can be fitted well by using a simple model in which the time dependence of the hyperfine field at the nuclear site is due to the fluctuations of the local magnetic moment of the Fe(III) as a result of the intrawell transitions which insure the establishment of thermal equilibrium. From the comparison of T_1^{-1} of protons in normal and deuterated Fe8, it is found that the spin-phonon coupling constant is not affected by the change of mass of the isotopes in the Fe8 cluster.

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