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Isotope substitution effects on spin dynamics of the molecular nanomagnet Fe8 cluster studied by NMR

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Abstract

We have carried out ^{1}H NMR at $T = 1.5$ K in both ^{57}Fe-enriched Fe8 cluster and non-enriched Fe8 cluster to investigate isotope substitution effects on magnetic properties. The 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. The absence of a difference of the magnetic field dependence of $1/T_1$ between the two systems indicates that the spin–phonon coupling constant is not affected by the change of mass of the isotopes in the Fe8 cluster.

Keywords: Fe8; Nuclear magnetic resonance; Quantum tunneling

1. 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,

$$H = DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B SH \qquad (1)$$

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 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 ~360 mK, while the relaxation time shows no large difference by the substitutions above 1.5 K where the spin–phonon coupling is considered to dominate the relaxation time.

In order to investigate the isotope substitution effects on magnetic properties of Fe8 clusters from a microscopic point of view, we have carried out proton nuclear magnetic resonance (NMR) in an isotropically substituted Fe8 cluster in which ^{56}Fe is replaced with ^{57}Fe isotopes. The results are compared with the case of non-enriched Fe8 clusters to discuss the influence of isotope substitutions on the spin dynamics in the Fe8 cluster systems.

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2. Experimental

The powder samples of $[Fe_8(tacn)_6O_2(OH)_{12}]\cdot[Br_8\cdot 9H_2O]$ where tacn is the organic ligand 1,4,7-triazacyclonane were prepared by the method reported in the literature [5]. As for the preparation of the ^{57}Fe-enriched sample, we used 96% enriched ^{57}Fe-oxides to prepare a Fe(tacn)Cl_3 precursor and the precursor was used to synthesis ^{57}Fe-enriched Fe8 cluster following the same method. In the following the non-enriched Fe8 (standard) and the ^{57}Fe enriched Fe8 will be referred to as stFe8 and ^{57}Fe8, respectively. NMR was carried out utilizing a phase-coherent pulse spectrometer. The external magnetic field for our experiments is always applied along the easy-axis in the Fe8 clusters. Nuclear spin-lattice relaxation rates $1/T_1$ were measured at Lamor field using the saturation recovery method. The nuclear magnetization recovery was nonexponential so that $1/T_1$ was determined from the initial slope of the recovery curve.

3. Results and discussions

Fig. 1(a) shows the ^{1}H NMR spectrum measured at 178 MHz and $T = 1.5$ K in the ^{57}Fe8 cluster. The observed spectrum is completely the same one observed in the stFe8 cluster measured at 198 MHz as shown in the Fig. 1(b). The structure of the spectrum is originated from the existence of many protons in the clusters and static internal fields at the proton sites due to the freezing of the Fe^{3+} ($s = 5/2$) spin moments in the total $S = 10$ magnetic state [6].

The static internal field at proton sites in Fe8 is expressed by a sum of dipolar hyperfine and contact hyperfine fields [6]. The dipolar field is due to the local magnetic moments of Fe^{3+} ions and the contact hyperfine field is originated from the overlap of the wave function at the proton sites with the d electrons (Fe^{3+}) wave function. Thus no difference between ^{1}H NMR spectrum in ^{57}Fe8 and stFe8 indicates that static magnetic properties for both spin moments of each Fe^{3+} ions and spin structure of the cluster are not affected by the isotope substitutions.

In order to investigate dynamical magnetic properties of ^{57}Fe8 cluster, we have carried out ^{1}H-$1/T_1$ measurements as a function of the external field which is applied parallel to the easy-axis of the cluster. The external magnetic field dependence of $1/T_1$ of protons in ^{57}Fe8 at $T = 1.5$ K is shown in Fig. 2, together with the results for stFe8 measured at the same temperature.

As can be seen in the figure, $1/T_1$ decreases largely with increasing the magnetic field and the magnetic field dependence of $1/T_1$ of protons in ^{57}Fe8 does not show any difference from those in stFe8 at 1.5 K within our experimental uncertainty.

As have been reported, the external magnetic field dependence of $1/T_1$ of protons in stFe8 cluster can be explained by the model in terms of the thermal fluctuations of the total spin $S = 10$ of the cluster originating from the spin–phonon interactions. In this case, $1/T_1$ is given by [6,7]

$$1/T_1 = \frac{1}{2}\gamma_N^2 \int \langle h_\pm(t)h_\pm(0)\rangle \exp(i\omega_L t)\mathrm{d}t = \frac{A}{Z}\sum_{m=+10}^{-10} \frac{\tau_m \exp(-E_m/k_B T)}{1+\omega_L^2\tau_m^2} \qquad (2)$$

where 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.

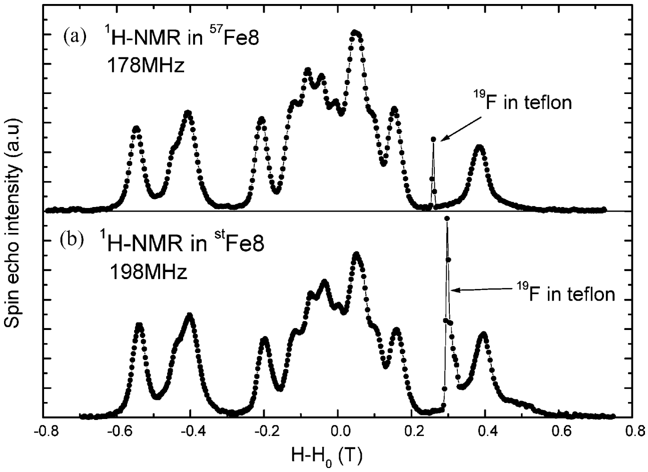

Fig. 1. Comparison of ^{1}H NMR spectrum in ^{57}Fe8 cluster with ^{1}H NMR in stFe8 cluster at $T = 1.5$ K. The horizontal axis is shifted by Lamor field H_0 for the comparison ($H_0 = 4.18$ T for ^{57}Fe8 and $H_0 = 4.65$ T for stFe8).

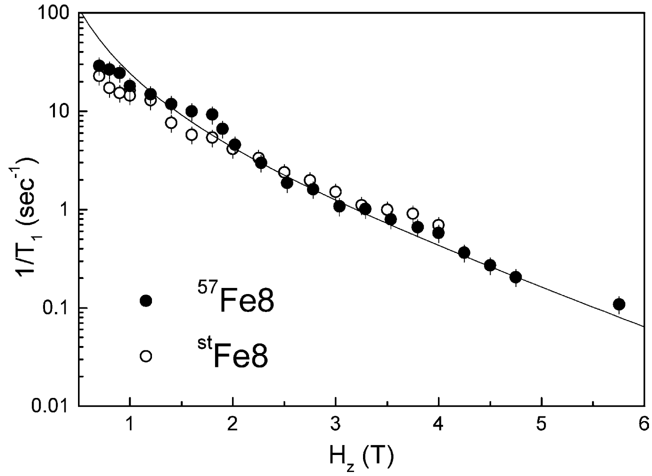

Fig. 2. External field dependences of $1/T_1$ in ^{57}Fe8 and stFe8 powders measured at $T = 1.5$ K. A solid line is theoretical estimation calculated by a simple model, eq. (3) with a set of parameters: $C = 31$ Hz K^{-3} and $A = 0.21 \times 10^{12}$ (rad s^{-1})^2.

τ_m is the life time broadening of the magnetic m-th sublevels originating from the spin–phonon interactions, which are expressed as $1/\tau_m = P_{m\to m+1} + P_{m\to m-1} + P_{m\to m+2} + P_{m\to m-2}$ for each individual m state. The transition probabilities due to the spin–phonon interactions can be expressed by [8] $P_{m->m\pm1} = Cs_{\pm1}(E_{m\pm1}-E_m)^3/(\exp\{(E_{m\pm1}-E_m)/k_BT\}-1)$ and $P_{m->m\pm2} = 1.06Cs_{\pm2}(E_{m\pm2}-E_m)^3/(\exp\{(E_{m\pm2}-E_m)/k_BT\}-1)$, 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 magnetic field are well reproduced by the equation (3) with a set of parameters of $A = 0.21\times10^{12}$ (rad s^{-1})^2 and $C = 31$ Hz K^{-3} as shown in the Fig. 2 by a solid line. Thus the magnetic field dependence of $1/T_1$ at the measured temperature is well explained by the model in terms of the thermal fluctuations of the total spin $S = 10$ of the cluster originating from the spin–phonon interactions. Therefore, the absence of a difference of $1/T_1$ between the two systems indicates that the spin–phonon coupling parameter C is not changed appreciably by the substitution of ^{57}Fe for ^{56}Fe 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.

On the other hand, the absence of appreciable change of the spin–phonon coupling can not explain for the large influence to the relaxation time of the magnetization by the isotope substitutions below 360 mK. Since the magnetization is considered to relax through a pure tunneling process at low temperature below 360 mK, 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].

4. Conclusion

We have investigated isotope substitution effects on magnetic properties on Fe8 cluster in its $S = 10$ ground state by ^{1}H NMR measurements utilizing ^{57}Fe-enriched Fe8 and non-enriched Fe8 clusters. ^{1}H NMR spectrum shows no difference between ^{57}Fe-enriched Fe8 and non-enriched Fe8 clusters, suggesting the local spin moments on Fe^{3+} ($s = 5/2$) and spin structure does not change by the substitutions. From the comparison of the magnetic field dependence of $1/T_1$ in both systems, the spin–phonon coupling constant is revealed to be not affected by the change of mass of the isotopes in the Fe8 cluster.

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