Spin freezing in geometrically frustrated magnetic molecule Fe$_{30}$ revealed by NMR

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Abstract. Static and dynamical properties of Fe$^{3+}$ ($3d^5; S = 5/2$) spins in geometrically frustrated magnetic molecule Fe$_{30}$ have been investigated by nuclear magnetic resonance (NMR) in the temperature range $T = 0.1 - 300$ K. From a measurement of nuclear spin-lattice relaxation rates as a function of temperature, the fluctuation frequency of Fe$^{3+}$ spins is found to decrease with decreasing temperature, indicating spin freezing at low temperatures.

1. Introduction
Magnetic properties of geometrically frustrated antiferromagnets have attracted a great deal of interest, due to pronounced quantum phenomena, such as the suppression of the magnetic ordering and unconventional spin state like e.g. spin liquid or spin freezing [1]. Recent success in synthesizing nanoscale molecular magnets offers the opportunity to investigate the effects of spin frustration at a quasi-zero dimensional level [2,3]. Molecular magnets are composed of a core of strongly interacting spins localized on transition metal ions surrounded by large organic ligands, so that the intermolecular magnetic interaction between neighboring molecular magnets is very small and the observed magnetic properties of the bulk samples are considered to originate from intramolecular magnetic properties only [2].

The compound [Mo$_{72}$Fe$_{30}$O$_{252}$(Mo$_2$O$_7$H$_2$O)$_2$(Mo$_2$O$_6$H$_2$O)$_2$(CH$_3$COO)$_{12}$(H$_2$O)$_{91}$]$_{150}$H$_2$O (in short Fe$_{30}$) is one of the largest molecular paramagnets prepared to date and has 30 Fe$^{3+}$ ($S = 5/2$) ions occupying the 30 vertices of an icosidodecahedron, resulting in a closed spherical structure of 2.5 nm
diameter [4]. This polyhedron contains 20 corner-sharing Fe\textsuperscript{3+} triangles with antiferromagnetic (AF) exchange coupling ($J/k_B \sim 1.57 \text{ K}$) between Fe spins [4,5].

The compound shows a simple paramagnetic behavior down to ~20 K where the magnetic susceptibility departs from a simple Curie-Weiss law. The magnetic susceptibility shows a broad peak around 2 K and almost constant below 1 K down to 0.12 K [4]. No three dimensional magnetic ordering down to 60 mK was reported from magnetization measurements [6]. In our previous $^1$H-NMR spectrum measurements [7], we reported a sudden increase of spectrum line width below ~600 mK, which indicates cross over from paramagnetic behavior to a frozen spin configuration.

In this paper, we have carried out further $^1$H-NMR measurements at low temperatures down to 0.05 K in order to investigate static and dynamical properties of Fe\textsuperscript{3+} spins in Fe\textsubscript{30}. From a measurement of nuclear spin-lattice relaxation rates as a function of temperature, fluctuation frequency of Fe\textsuperscript{3+} spins is found to become slower on lowering temperature, which leads to spin freezing state at lowest temperatures.

2. Experimental

A polycrystalline samples of $[\text{Mo}_7\text{Fe}_{30}\text{O}_{252}(\text{Mo}_2\text{O}_7(\text{H}_2\text{O}))_2(\text{Mo}_2\text{O}_8\text{H}_2(\text{H}_2\text{O}))(\text{CH}_3\text{COO})_{12}(\text{H}_2\text{O})_{91}]$ \textsubscript{150} H\textsubscript{2}O was prepared as described elsewhere [8] and was also used in our previous NMR studies [6]. Temperature dependence of the magnetic susceptibility was measured at $H = 0.1 \text{ T}$ in a temperature range of 1.8-300 K using a superconducting quantum interface device (SQUID) magnetometer (Quantum design MPMS-7T). NMR measurements were conducted using pulsed NMR techniques on $^1$H (nuclear spin $I = \frac{1}{2}$ and gyromagnetic ratio $\gamma_{N}/2\pi = 42.5759 \text{ MHz}/T$) nuclei in the temperature range of 0.05 K $\leq T \leq 300$ K using a $^3$He-$^4$He dilution refrigerator. The $^1$H-NMR spectra were obtained by sweeping the external magnetic field at constant frequency. The nuclear spin-lattice relaxation time $T_1$ was measured by the saturation method at the highest peak position in $^1$H-NMR spectrum. The nuclear magnetization recovery was found to be nonexponential in most measurements, which is due to the existence of protons with inequivalent spatial locations. Such a non-exponential behavior in $^1$H-NMR in the Fe\textsubscript{30} was already reported by Lago et al [9]. $T_1$ values were determined from the initial slope of the recovery behavior, which corresponds to a weighted average relaxation rate of the nonequivalent protons [10].

![Graph showing temperature dependence of FWHA of $^1$H-NMR spectrum in Fe\textsubscript{30} at $H = 0.61 \text{ T}$ (closed circles) and $H = 0.16 \text{ T}$ (open circles).]

3. Experimental results and discussion

Figure 1(a) shows temperature dependence of FWHA (Full width at half amplitude) of the $^1$H NMR spectrum at frequency of $f = 26 \text{ MHz}$ ($H = 0.61 \text{ T}$), together with data at $f = 7.03 \text{ MHz}$ ($H = 0.16 \text{ T}$) reported previously [7]. A dramatic broadening of the spectrum is clearly observed at ~600 mK for both magnetic fields. Fig. 1(b) shows $^1$H-NMR spectra at $f = 7.03 \text{ MHz}$ for several temperatures. The
FWHA is almost independent of magnetic field below 600 mK, which indicates freezing state of Fe$^{3+}$ spins. As can be seen in the figure, $^1$H-NMR signal at $T = 0.1$ and 0.19 K can be observed at $H = 0$ T, which is also direct evidence of very slow fluctuations of the Fe spin moments. Almost no signal was observed around 1 K due to a shortening of nuclear spin-spin relaxation time $T_2$ which follows a corresponding shortening of the nuclear spin-lattice relaxation time $T_1$.

To investigate the dynamical properties of the Fe$^{3+}$ spins, we have carried out proton $T_1$ measurements in a wide temperature range of $T = 0.1$-300 K. Figure 2(a) shows temperature-dependence of $1/T_1$ under two magnetic fields. With decreasing temperature, $1/T_1$ for $H = 0.75$ T decreases gradually and starts to increase around 20 K, then shows a peak around 2 K. Similar temperature dependence of $1/T_1$ was reported by Lago et al. [9] and the peak of $1/T_1$ is found to increase in magnitude and moves toward to low temperature by decreasing magnetic field. $T$-dependence of $1/T_1$ at $H = 0.16$ T is also plotted in the figure where $1/T_1$ could not be measured between 0.6 K and 1.5 K because of shortening of $T_2$ (i.e., $T_1$).

In general, $1/T_1$ is expressed by the Fourier transform of the time correlation function of the transverse fluctuating local field at nuclear sites as [11]

$$\frac{1}{T_1} = \frac{1}{2} \gamma^2 \chi \int \langle h_x(t) h_x(0) \rangle e^{i\omega t} dt,$$  \hspace{1cm} (1)

with $\gamma$ the nuclear gyromagnetic ratio and $\omega$ the Larmor frequency. When the time correlation function is assumed to decay as $\exp(-\Gamma t)$, the $1/T_1$ can be written as [12]

$$\frac{1}{T_1} = A \chi T \frac{\Gamma}{\Gamma^2 + \omega^2},$$  \hspace{1cm} (2)

where $A$ is a parameter related to the hyperfine field and $\Gamma$ corresponds to the inverse of the correlation time of the fluctuating hyperfine fields at proton sites due to the Fe$^{3+}$ spins.

To analyze the $T$-dependence of $1/T_1$ by using Eq. (2), it is useful to re-plot the data by changing the vertical axis from $1/T_1$ to $1/T_1 T\chi$ as shown in Fig. 2(b), where the $\chi T\chi$ values for $T = 0.1$-2 K are obtained from $\chi$ data reported by Müller [4] and for $T = 1.8$-300 K we used our data. If $\Gamma$ is independent of temperature, $1/T_1 T\chi$ should be constant which is in fact observed above 30 K in Fig. 2(b). This indicates that the nuclear spin relaxation above ~30 K is explained by the paramagnetic fluctuations of the Fe$^{3+}$ spins whereby the spins fluctuate almost independently from each other. On
the other hand, below 30 K $1/T_1 T\chi$ shows increase with decreasing temperature. This indicates the simple paramagnetic fluctuations model cannot explain the $T$-dependence of $1/T_1 T\chi$.

According to Eq. (2), $1/T_1 T\chi$ is proportional to $1/\Gamma$ when $\Gamma >> \omega_L$ (fast-motion regime), while $1/T_1 T\chi$ is proportional to $\Gamma^2/\omega_L^2$ in the case of $\Gamma << \omega_L$ (slow-motion regime). When $\Gamma = \omega_L$, $1/T_1 T\chi$ shows a peak. Assuming $A = 1.7 \times 10^{11}$ (rad$^2 \cdot$ K$ \cdot$ emu/mol/s$^2$) and $\Gamma = 1.34 \times 10^7$ T$^4$ (rad/s), the experimental results at low temperature regions below 4 K are qualitatively reproduced by Eq. (2), as shown in Fig. 2(b) by solid lines for different magnetic fields. These results indicate that the peak observed in $T$-dependence of $1/T_1 T\chi$ originates from a crossover between the fast-motion regime and the slow-motion regime, whereby the fluctuation frequency of Fe$^{3+}$ spins below the peak temperature is less than the NMR frequency range which is of the order of MHz.

To see the $T$-dependence of fluctuation frequency of Fe$^{3+}$ spins for a wide temperature region, we extract temperature dependence of $\Gamma$ from the temperature dependence of $1/T_1 T\chi$ assuming Eq. (2) is valid for all temperature region. The estimated $T$-dependencies of $\Gamma$ for the two different magnetic fields are shown in Fig. 3(c). This log-log plot shows very clearly that $\Gamma$ has the power low behavior $(T^4)$ at low temperatures below ~ 1 K and shows almost constant of $3 \times 10^9$ Hz at high temperatures. At low enough temperature Fe$^{3+}$ spins can fluctuate with low frequency which is less than NMR frequency of the order of MHz. Such a slow spin dynamics is consistent with the observation of broadening of NMR spectrum below 600 mK. The origin of the spin freezing in Fe$_{30}$ is pointed out to be intramolecular exchange disorder by recent theoretical studies using Monte Carlo simulation [7].

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