Quantum Tunneling of Magnetization in Molecular Nanomagnet Fe8 Studied by NMR

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Abstract

Magnetization and NMR measurements have been performed for single crystals of molecular magnet Fe8. The field and temperature dependences of magnetization below 25 K are well described in terms of the isolated clusters with the total spin $S = 10$. The stepwise recoveries of ^{1}H-NMR signals at the level crossing fields caused by the resonant quantum tunneling of magnetization were observed below 400 mK. The recovery of the NMR signals are explained by the fluctuation caused by the transition between the energy states of Fe magnetizations governed by Landau-Zener quantum transitions.

Key words: nanomagnet; molecular magnet; quantum tunneling; NMR; magnetization

Molecular nanomagnets have attracted much attention on quantum mechanical phenomena in the mesoscopic magnetic system. [1–3] The molecule $[(C_6H_{15}N_3)_6Fe_8O_2\ (OH)_{12}]Br_7(H_2O)Br\cdot 8H_2O$, abbreviate Fe8, is one of the representative compounds, in which the quantum tunneling of the magnetization has been observed at low temperatures.[4–7] The molecular Fe8 consists of eight Fe^{3+} ions with spin $s = 5/2$ in each molecule. The magnetic properties of this compound at low temperatures have been described by a total spin of $S = 10$ for each molecule. [8] The spin Hamiltonian in the field $\boldsymbol{H}$ is expressed by

$$\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2) + g\mu_{\rm B}\boldsymbol{S}\cdot\boldsymbol{H}, \qquad (1)$$

where D is an easy axis anisotropy and E is an anisotropy within the xy-plane. [4] When there is no magnetic field, the anisotropy stabilizes the degenerate spin states of $m = \pm 10$ at low temperatures, which correspond to opposite directions of the magnetizations with the energy barrier of 25 K for reversal of the magnetization in the classical picture.

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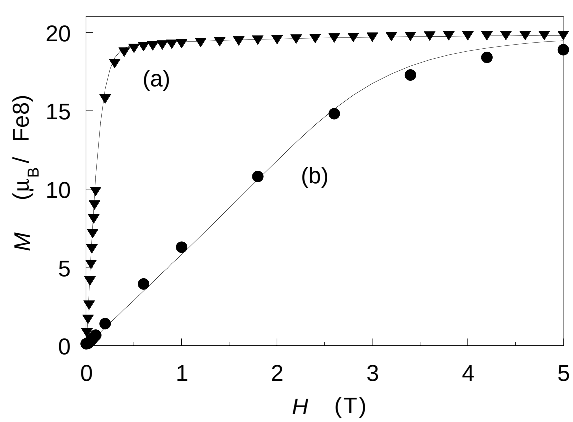

Fig. 1. Magnetization curves (a) $H \parallel a$-axis and (b) $H \perp a$-axis at 2K. Solid lines show the calculated values.

We synthesized single crystals of Fe8, and studied the quantum phenomena by the magnetization and ^{1}H-NMR experiments. The sizes of the crystals used for the experiments were about 3 mm × 2 mm × 1 mm.

Figure 1 shows the field dependence of the magnetizations per molecule in the magnetic field parallel to the a-axis and perpendicular to the a-axis at 2 K. The difference between the two magnetization curves show

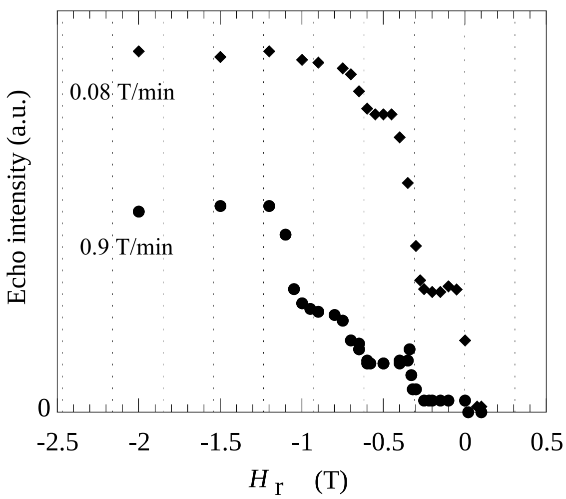

Fig. 2. Return field dependence of the echo intensity after the saturation. The operating frequency is 29 MHz. The sweeping rates of the field are 0.08 T/min and 0.90 T/min. $\theta = 50^\circ$ and the echo intensity is taken at 0.45 T.

the large magnetic anisotropy in this compound. The magnetizations saturate to the value of 20 μ_B/Fe8 in the magnetic fields about 0.5 T and 5 T for $\boldsymbol{H} \| a$-axis and $\boldsymbol{H} \perp a$-axis, respectively. The saturated value of 20 μ_B/Fe8 indicates that the total spin S of the molecule is 10. The temperature dependences of the susceptibilities in $\boldsymbol{H} \| a$-axis and $\boldsymbol{H} \perp a$-axis and the angular dependence of the magnetization were also measured. These experimental results are well reproduced by Hamiltonian eq. (1) with $D = -0.276$ K and $E = -0.035$ K, and the easy axis is found to orient with the angle of 16° from the a-axis in the ab-plane and with an inclination of 0.7° from the ab-plane. [9]

The NMR spectra become to be broad and have structures below 3K due to the freezing of the Fe magnetizations and the existence of the many proton sites. The temperature and magnetic field dependences of the spin-lattice relaxation rates T_1^{-1} were measured by means of the coherent pulse NMR method. The relaxation rates decrease steeply over six decade as lowering the temperature from 10 K down to 400 mK. The relaxations are well described by the fluctuations dominated by the thermal transition of the iron spin states between the discrete energy levels separated by the single ion anisotropy. [7] Below 400 mK the T_1^{-1} becomes to be longer than 100 s and almost temperature independent.

We have observed the quantum tunneling of magnetization by NMR below 300 mK. The experimental method is as follows. We first saturated all ^{1}H spins with comb rf pulses at a fixed frequency in the positive field until no echo signals were observed. Then the field was decreased to the negative fields with a constant sweep rate. Immediately after arriving at a certain field H_r, the field was increased with the same sweep rate and the NMR spectrum was taken at a fixed repetition time. The return field dependence of the echo intensity is shown in Fig. 2, which was obtained in the case when the field was applied with $\theta = 50^\circ$ from the easy axis, and the intensities were taken at +0.45 T. The echo intensities increases sharply at 0, -0.31, -0.63 and -1.00 T. The echo intensities become larger for slower sweep rate. The return field dependence of the intensity with the field parallel to the easy axis ($\theta = 0^\circ$) was also taken and the same sudden increases were observed.

The fields at which the intensity sharply increases coincide well with the crossing fields of the energy levels calculated from the Hamiltonian of eq. (1). The fact indicates that the resonant quantum tunneling of the Fe magnetization occurs at the level crossing fields and the induced fluctuations enhance the proton relaxation. The increase of the echo intensities for slower sweep rate is consistent with the Landau-Zener (LZ) quantum transition model at the energy level crossing fields. The LZ transition probability from the m state to the m' state is expressed as, [10–12]

$$P_{m,m'} = 1 - \exp\left(-\frac{\pi \Delta_{m,m'}^2}{2\hbar g \mu_B |m - m'| dH/dt}\right), \qquad (2)$$

where $\Delta_{m,m'}$ is the tunneling gap at the level crossing and dH/dt is the sweep rate. The measured sweep rate dependence of echo intensities are analyzed by LZ model with the tunneling gaps $\Delta_{-10,10} = 3.52 \times 10^{-7}$ K and $\Delta_{-10,9} = 9.66 \times 10^{-7}$ K. [7]

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