# A hysteresis phenomenon in NMR spectra of molecular nanomagnets Fe8: a resonant quantum tunneling system

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**Abstract**

A molecular nanomagnet Fe8 with a total spin $S = 10$ in the ground state attracts much attention as a substance which exhibits the quantum tunneling of magnetization below 300 mK. We performed $^1$H NMR measurements for a single crystal of Fe8 in temperature range between 20 and 800 mK. The spectra below 300 mK strongly depend on the sequence of the applied field and those in the positive and negative fields are not symmetric about zero field, while they are symmetric above 300 mK. We discuss the origin of this hysteresis phenomenon, relating to the initial spin state of molecules, the resonant quantum tunneling and the nuclear spin relaxation process.

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

As a result of recent progress of chemical synthesis techniques, it becomes to be possible to obtain high quality molecular nanomagnets, which are magnetically isolated molecules with the identical size and orientation. The molecules comprise several number of magnetic ions and have the ground states with a composite spin at low temperatures due to the strong intramolecule magnetic interactions. [1]

One of the most attractive features in such molecular nanomagnets is the resonant quantum tunneling of magnetization (QTM) observed in Mn12 and Fe8. [2–5] The triclinic molecular crystal $[(C_6H_{15}N_3)_6Fe_8O_2(OH)_{12}]Br_7(H_2O)Br \cdot 8H_2O$, abbreviated Fe8, has eight $Fe^{3+}$ ions with spins $s = 5/2$ in each molecule. At low temperatures, the ground state has a total spin $S = 10$, where six spins are parallel to each other and antiparallel to the rest of two spins. [6] The system in a field $\boldsymbol{H}$ is described by the Hamiltonian $\mathcal{H} = -DS_z^2 - E(S_x^2 - S_y^2) + g\mu_B \boldsymbol{H} \cdot \boldsymbol{S}$, where $D = 0.27$ K and $E = 0.046$ K. [3,7] When the applied field is parallel to the easy axis, the 21 discrete energy levels denoted by the magnetic quantum number $M$ cross at fields of $H_c = 0.21n$ T ($n = 0, \pm1, \pm2, \ldots, \pm10$) as shown in Fig. 1. It has been observed that the spin state of Fe8 tunnels from the $M$ state to the $M'$ state with a probability $P_{M,M'}$ below 300 mK at the energy level crossing fields. [3–5]

We performed $^1$H NMR measurements for a single crystal of Fe8 in temperature range between 20 and 800 mK, applying the magnetic field along the easy axis, to investigate QTM.

The spectra above 3 K have a sharp peak, while they gradually become to be broad and to have structures below 3 K. These structures are caused by the existence of a lot of $^1$H sites with different internal fields due to the Fe spin freezing. Figure 2 shows a spectrum at 150 mK, which was measured with increasing the field from $-3$ to $+3$ T at a rate of 0.5 T/min after field cooling at $-3$ T from 800 mK. It is characteristic that the spectra in the positive and negative fields are not symmetric about zero field, though a symmetric one is expected if Fe magnetization follows the field. The expected symmetric spectrum was observed above 300 mK for the rate of 0.01 T/min. This suggests that the thermal relaxation is dominant and that the electron spin system is in the thermal equilibrium above 300 mK. The spectra at 150 mK and 500 mK in the

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negative field are essentially identical, which indicates that the Fe state is in the $M = 10$ state in the negative field at both temperatures. On the other hand, the spectrum in the positive field at 150 mK, shown in Fig.2, reflects QTM rather than the thermal relaxation and is considered to be the superposition of signals from $^1$H nuclei in Fe8 molecules in the $M = 10$ state and those in the $M = -10$ state. As shown in Fig. 1, once the Fe spin changes its state at the level crossing points between the states with different signs due to the tunneling, it immediately relax to the states with the same sign following the Boltzmann distribution. [5] Thus, the $M = \pm 10$ states contribute the spectrum in the above field sweep at low temperatures.

After measuring the spectrum shown in Fig. 2, we consecutively measured spectra with increasing the field from $-3$ to $+3$ T again, which is shown in Fig. 3. Comparing the spectrum in Fig. 3 with that in Fig. 2, the structures in the positive field are exactly same, implying that both the Fe spin and the $^1$H nuclear spin states are identical due to the relaxation of $^1$H spins induced by the fluctuations accompanied with the quantum tunneling of the Fe spins. On the other hand, spectra in the negative field have same peak positions but have quite different intensities. This implies that the Fe spin states are both in the $M = 10$ state though the $^1$H nuclear spin states are occupied differently due to the long spin-lattice relaxation time over 100 s. [5]

We also measured the spectrum at the sweep rate of 0.01 T/min on the same condition as Fig. 2. It was revealed that the spectrum in the negative field is independent of the field sweep rate, which is consistent with the fact that the $M = 10$ state has no level crossing points in the negative field. In the positive field, however, the signal intensities measured at 0.01 T/min are much larger than those at 0.5 T/min. This is interpreted by the sweep-rate dependence of the Landau-Zener tunneling probability [8]. Further experiments and analyses are in progress.

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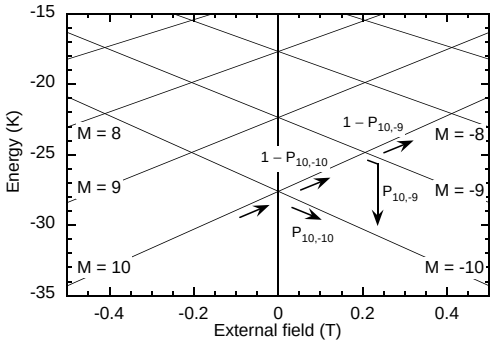


Fig. 1. An energy diagram of Fe8 in the field along the easy axis. The arrows indicate the transitions of Fe spin states by QTM during the field-sweep experiment.

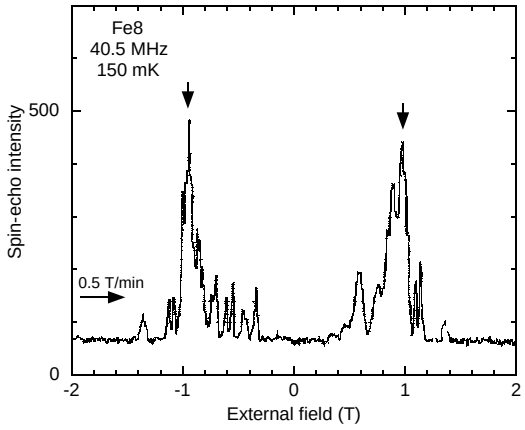


Fig. 2. $^1$H NMR spectrum at 150 mK measured with increasing the field from $-3$ to $+3$ T at the rate of 0.5 T/min after field cooling at $-3$ T from 800 mK. The vertical arrows indicate the zero shift position of $^1$H nuclei.

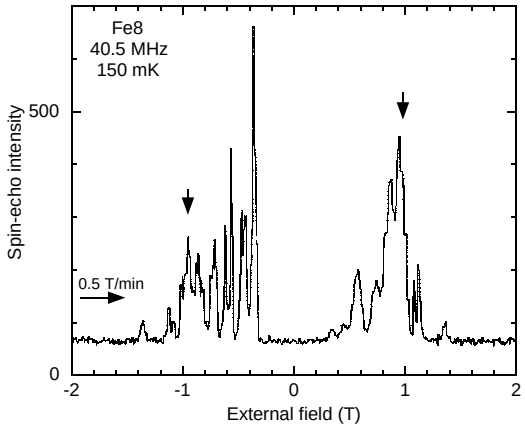


Fig. 3. $^1$H NMR spectrum at 150 mK measured with increasing the field from $-3$ to $+3$ T at the rate of 0.5 T/min after measuring the spectrum shown in Fig. 2. The vertical arrows indicate the zero shift position of $^1$H nuclei.