TITLE:
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CITATION:
Ueda, M ...[et al]. Proton spin relaxation induced by quantum tunneling in Fe8 molecular nanomagnet. PHYSICAL REVIEW B 2002, 66(7): 073309.

ISSUE DATE:
2002-08-15

URL:
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Proton spin relaxation induced by quantum tunneling in Fe8 molecular nanomagnet

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(Received 19 April 2002; published 26 August 2002)

The spin-lattice relaxation rate $T_1^{-1}$ and NMR spectra of $^1$H in single crystal of molecular magnets Fe8 have been measured down to 15 mK. The relaxation rate $T_1^{-1}$ shows a strong temperature dependence down to 400 mK. The relaxation is well explained in terms of the thermal transition of the iron state between the discreet energy levels of the total spin $S=10$. The relaxation time $T_1$ becomes temperature independent below 300 mK and is longer than 100 s. In this temperature region stepwise recovery of the $^1$H-NMR signal after saturation was observed depending on the return field of the sweep field. This phenomenon is attributed to the resonant quantum tunneling at the fields where levels cross and is discussed in terms of the Landau-Zener transition.

DOI: 10.1103/PhysRevB.66.073309 PACS number(s): 76.60.-k, 75.45.+j

Recently, molecular nanomagnets have attracted much attention to study quantum mechanical phenomena in the macroscopic system owing to their identical size, the well-defined structure and a well-characterized energy structure.\(^1\)\(^-\)\(^3\) The molecular magnet $[(\mathrm{C}_6\mathrm{H}_{15}\mathrm{N}_3)_6\mathrm{Fe}_8\mathrm{O}_2(\mathrm{OH})_{12}]\mathrm{Br}_8(\mathrm{H}_2\mathrm{O})\mathrm{Br}\cdot 8\mathrm{H}_2\mathrm{O}$, abbreviated Fe8, is a representative compound in which quantum tunneling of magnetization (QTM) has been observed as the temperature-independent recovery of magnetization below 400 mK.\(^4\)\(^-\)\(^7\)

The molecular magnet Fe8 consists of eight Fe\(^{3+}\) ions with spin $s=5/2$ in each molecule. The magnetic interactions between the spins in the molecule are antiferromagnetic and their magnitudes are 22–170 K,\(^8\) while the magnetic interactions between the molecules are negligibly small. The magnetic properties of this compound at low temperatures have been described by a total spin of 10.\(^8\)\(^-\)\(^9\) The spin Hamiltonian in the field $\mathbf{H}$ is expressed by

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

where $D$ and $E$ are the easy axis and the in-plane anisotropy, respectively.\(^4\) We have determined the values of $D = -0.276$ K and $E = -0.035$ K by magnetization measurement on a single crystal.\(^7\) When there is no magnetic field, the anisotropy stabilizes the degenerate spin states of $m = \pm 10$ at low temperatures. These states correspond to opposite directions of the magnetization in the classical sense. The energy barrier caused by the anisotropy for reversal of the magnetization between $m = \pm 10$ is reported to be 25 K.\(^4\)

Quantum tunneling of magnetization in Fe8 has been observed only by magnetization measurements.\(^4\)\(^-\)\(^7\) In order to study the spin dynamics in Fe8 from a microscopic point of view, we performed NMR experiments and found a stepwise recovery of the $^1$H spin echo signal due to resonant quantum tunneling at the level crossing fields.

We synthesized single crystals of Fe8, following the method reported previously.\(^10\) The sizes of the crystals used for the experiments were about 4×2×1 mm\(^3\). The NMR spectrum and the spin-lattice relaxation rate $T_1^{-1}$ of $^1$H in Fe8 were measured by the coherent pulsed NMR method in external magnetic fields up to 5.4 T. The spectra were obtained by measuring the spin-echo intensity with sweeping the field at a fixed frequency. The relaxation rate was obtained by measuring the recovery of the spin echo intensity as a function of the time after saturation of the $^1$H spins using comb pulses. The experimental temperature was lowered down to 15 mK using a $^3$He-$^4$He dilution refrigerator. The samples were sealed with $^3$He gas in a cell made of PCTFE plastic(polychlorotrifluoroethylene). The cell was set in the mixing chamber of the dilution refrigerator.

The NMR spectrum at room temperature is narrow with the width smaller than 50 Oe, while the spectrum becomes broader and shows structure at lower temperatures. The structure is caused by freezing of the iron magnetization and the existence of many $^1$H sites.

Figure 1 shows the temperature dependence of the relaxation rate $T_1^{-1}$. The rate $T_1^{-1}$ decreases steeply over six decades with lowering the temperature from 10 K to 400 mK, and decreases with increasing field. Below 300 mK $T_1^{-1}$ is almost temperature independent and has a strong site dependence, as is found in Fig. 1.

Figure 2 shows NMR spectra of the single crystal at 150 mK. The field was applied so as to make an angle $\theta$ of 50° from the easy axis and to be within the $ab$ plane. In this experiment, we first saturated the $^1$H spin system by the comb pulses at a fixed frequency, sweeping the field up and down between 0.1 and 1.5 T for more than three times, until there was no observation of the echo signals. Then the field was decreased to a certain field $H_r$ with a constant sweep rate $dH/dt$. Immediately after arriving at $H_r$, the field was increased with the same sweep rate and the spectrum was taken at a fixed repetition time. No signals were expected to be observed, because the returning duration after the saturation was planned to be enough shorter than the relaxation time that is longer than 100 s. Indeed no signals except from
$^{19}$F in the material of the sample cell and $^3$He in the mixing chamber were observed when the field was returned at 0.05 T, as shown in the lowest spectrum in Fig. 2. However, signals were observed when the return fields were negative.

FIG. 2. NMR spectra of single crystal Fe8, which were taken with increasing the field from $H_r$ after the saturation, $T=150$ mK, $f=29$ MHz, $dH/dt=0.9$ T/min, and $\theta=50^\circ$. Broken lines show the level crossing fields.

FIG. 3. Return field $H_r$ dependence of echo intensity at field of (a) 0.45 T, $\theta=50^\circ$ and (b) 0.60 T, $\theta=0^\circ$. Broken lines show calculated level crossing fields. The echo intensity at 60 mK in (a) is normalized with that for 150 mK at $H_r=−2.0$ T.

FIG. 4. Sweep rate $dH/dt$ dependence of echo intensity at 0.60 T when (a) $H_r=−0.1$ T and (b) $H_r=−0.3$ T. The field is applied parallel to the easy axis. The solid and broken lines show calculated values by Eqs. (8) and (9), respectively.
The intensities of the signals increased with decreasing return field.

Figures 3(a) and 3(b) show the return field dependence of the echo intensity. Figure 3(a) was obtained in the case when the field was applied with \( \theta = 50^\circ \) within the \( ab \) plane. Figure 3(b) is the case when the field was parallel to the easy axis (\( \theta = 0^\circ \)). The echo intensities were picked up at fields of 0.45 and 0.60 T for Figs. 3(a) and 3(b), respectively. The intensity increases sharply with steps at 0, -0.31, -0.63, and -1.00 T for Fig. 3(a), while for Fig. 3(b) the steps are at +0.02 and -0.20 T. The increase in the intensity at the steps cannot be explained by recovery due to the spin-lattice relaxation time shown in Fig. 1. Moreover the intensity is dependent on the sweep rate of the field, but independent on temperature. Figure 4 shows the sweep rate dependence of the intensity at a field of 0.60 T when the field was applied parallel to the easy axis and the return fields were -0.1 T and -0.3 T. The intensity is large when the sweep rate is slow.

First we analyze the relaxation rate. The temperature dependent relaxation rates of a molecular magnet Mn12 were first discussed by Lascialfari et al.\(^{11}\) In general \( T_1^{-1} \) is given by the Fourier transform of the correlation function for fluctuating transverse local fields \( h_z(t) \) at nuclear sites, and is expressed as

\[
\frac{1}{T_1} = \frac{\gamma_N^2}{2} \int \langle \{ h_z(t) h_z(0) \} \rangle e^{-i\omega t} dt, \tag{2}
\]

where \( \gamma_N \) is the nuclear gyromagnetic ratio and \( \omega_L \) is the Larmor frequency. When the correlation is assumed to be described by an exponential function with a lifetime \( \tau_m \) in the \( m \) state, the correlation can be expressed as

\[
\langle \{ h_z(t) h_z(0) \} \rangle = \sum_{m=-10}^{+10} \langle \Delta h_z^2 \rangle e^{-t/\tau_m} e^{-E_m/k_B T} Z, \tag{3}
\]

where \( E_m \) is the energy of the eigenstate \( m \) and \( Z \) is the partition function. The lifetime \( \tau_m \) for the \( m \) state is governed by the spin-phonon interaction \( \mathcal{H}_{sp} \) and is expressed by the probabilities \( p_{m-m-1} \) for the transition from the \( m \) to the \( m-1 \) state and \( p_{m-m+1} \) for that from the \( m \) to the \( m+1 \) state, as follows:\(^{12}\)

\[
\frac{1}{\tau_m} = p_{m-m-1} + p_{m-m+1} + \begin{cases} \frac{C \Delta E_m^3}{e^{\Delta E_m/k_B T} - 1} + \frac{C \Delta E_{m+1}^3}{1 - e^{-\Delta E_{m+1}/k_B T}} & (\text{for } m > 0), \\ \frac{C \Delta E_m^3}{1 - e^{-\Delta E_m/k_B T}} + \frac{C \Delta E_{m-1}^3}{e^{\Delta E_{m-1}/k_B T} - 1} & (\text{for } m < 0), \end{cases} \tag{4}
\]

where \( \Delta E_m = |E_{m-1} - E_m| \). The parameter \( C \) is given by

\[
C = \frac{3}{2\pi \rho v^2 h^4} |\langle m|\mathcal{H}_{sp}|m \pm 1 \rangle|^2, \tag{5}
\]

where \( \rho \) is the spin-phonon coupling constant and \( v \) is the phonon velocity. The probability from the \( m \) state to the \( m' \) state in this case is expressed\(^{13-15}\) as

\[
P_{m,m'} = 1 - \exp \left( -\frac{\pi \Delta_{m,m'}^2}{2h g \mu_B |m-m'| dH/dt} \right), \tag{7}
\]
where $\Delta_{n,m'}$ is the tunneling gap at the level crossing. These transitions would induce fluctuations of the local field at proton sites and cause extra relaxation of the nuclear spins.

After quantum tunneling, the spin state rapidly relaxes to the lower energy levels, following the Boltzmann distribution. The lifetime $\tau_m$ below 300 mK estimated is to be less than $10^{-7}$ sec from the measured relaxation time and Eq. (6). It should be noted that these thermal transitions can occur only between states with the same sign of $m$, while quantum tunneling occurs between states with opposite sign of $m$.

The measured period of the stepwise behavior for $\theta=50^\circ$ was 0.32 T, while that for $\theta=0^\circ$ was 0.22 T. The period of level crossing fields is expressed approximately as $\Delta H = D/tg \mu_B \cos \theta$ and the values are 0.31 and 0.21 T for $\theta=50^\circ$ and $0^\circ$, respectively. The values coincide fairly well with the experimental results. These results clearly indicate that the sudden recovery of the $^1H$ spins is caused by resonant quantum tunneling of the iron magnetization at the level crossing fields.

When the iron spin state in a certain molecule changes through tunneling, the $^1H$ spins in the molecule would be rapidly relaxed. The iron spins which have tunneled in zero or negative fields arrive at the $m=10$ state and have possibility to tunnel again in the zero or positive fields. If it is assumed that the iron spins which have experienced tunneling once at least contribute to the proton relaxation, the echo intensities $I_o$ at the monitoring field after the field returning would be expressed as

$$I_o = I_{10}(1 - (1 - P_{10,10})^2), \quad (8)$$

for $H_{-10,0} < H < 0$, and

$$I_o = I_{02}(1 - (1 - P_{10,10})^2(1 - P_{10,9})^2), \quad (9)$$

for $H_{-10,0} < H < H_{-10,0}$, where $H_{m,m'}$ is the crossing field of the states $m$ and $m'$. The measured sweep rate dependence of echo intensities was fitted to Eqs. (8) and (9) with Eq. (7), $\Delta_{-10,10} = 3.52 \times 10^{-7}$ K and $\Delta_{-10,0} = 9.66 \times 10^{-7}$ K, as shown in Fig. 4. The agreement between calculated and experimental values is reasonably good and these values for $\Delta_{-10,10}$ and $\Delta_{-10,0}$ are close to those reported from magnetization measurements. 6,7

As is found in Fig. 3(b), the echo intensities for $H < -0.25$ T at a sweep rate of 0.9 T/min remain constant and smaller than those for $dH/dt = 0.08$ T/min. The stepwise recovery was not observed for the lower crossing fields. An intensity of the signals which were measured at the slow sweep rate of 0.08 T/min with $H_r$ less than $-0.6$ T corresponds to the intensity of the signal which recovered completely. This intensity was obtained for the fast rate of 0.9 T/min by sweeping the field up and down three times between $-0.1$ and $-0.6$ T. However, the intensity after sweeping up and down three times at lower fields between $-0.6$ and $-1.0$ T with $dH/dt = 0.9$ T/min remained small. This suggests that tunneling does not occur at fields lower than $-0.6$ T, though the reason is not clear.

In conclusion, the proton relaxation rate $T_1^{-1}$ of Fe8 above 400 mK is dominated by the thermal fluctuation of the iron magnetization with spin $S=10$. The transition of magnetization between the states split by $D_S^2$ is caused by the spin-phonon interaction, and induces the fluctuation at nuclear sites. The rate becomes temperature independent below 300 mK. In this temperature region the stepwise recovery of the echo intensity caused by quantum tunneling at the level crossing fields was observed in the $^1H$-NMR spectrum. This indicates that the internal field at proton sites fluctuates due to the resonant quantum tunneling of iron spins, which is described by the Landau-Zener transition. The temperature independent relaxation rates themselves measured below 300 mK are governed by the temperature independent correlation times possibly related to the quantum effect, however, this quantum process is another one than the resonant quantum tunneling.

We would like to thank Prof. S. Miyashita and Dr. K. Saito for valuable discussions. We also thank Dr. H. Miyasaka and Dr. H.-C. Chang for their helpful advice on synthesis of the samples.

1D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, Science 265, 1054 (1994).
2L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) 383, 145 (1996).
3J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. 76, 3830 (1996).
4C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. 78, 4645 (1997).
5T. Ohm, C. Sangregorio, and C. Paulsen, J. Low Temp. Phys. 113, 1141 (1998).
6W. Wernsdorfer, R. Sessoli, A. Caneschi, D. Gatteschi, and A. Cornia, Europhys. Lett. 50, 552 (2000).
7W. Wernsdorfer and R. Sessoli, Science 284, 133 (1999).
8C. Delfs, D. Gatteschi, L. Pardi, R. Sessoli, K. Wieghardt, and D. Hanke, Inorg. Chem. 32, 3099 (1993).
9M. Ueda, S. Maegawa, H. Miyasaka, and S. Kitagawa, J. Phys. Soc. Jpn. 70, 3084 (2001).
10K. Wieghardt, K. Pohl, I. Jibril, and G. Huttner, Angew. Chem. Int. Ed. Engl. 23, 77 (1984).
11A. Lascialfari, Z.H. Jang, F. Borsa, P. Carretta, and D. Gatteschi, Phys. Rev. Lett. 81, 3773 (1998).
12J. Villain, F. H-Boutron, R. Sessoli, and A. Rettori, Europhys. Lett. 27, 159 (1994).
13L. Landau, Phys. Z. Sowjetunion 2, 46 (1932).
14C. Zener, Proc. R. Soc. London, Ser. A 137, 696 (1932).
15S. Miyashita, J. Phys. Soc. Jpn. 64, 3207 (1995).