

## Spin decoherence in an iron-based magnetic cluster

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### ABSTRACT

Continuous wave (cw) and pulsed high frequency electron paramagnetic resonance (HF-EPR) measurements were performed on an Fe-based magnetic cluster:  $\text{Fe}_7\text{O}_4(\text{O}_2\text{CPh})_{11}(\text{dmem})_2$ , abbreviated  $\text{Fe}_7$ . The cw EPR results show that two different molecular species exist in the crystal, with slightly different zero-field-splitting parameters. The spin decoherence time,  $T_2$ , was measured at high magnetic fields and low temperatures, which makes it possible to obtain high spin polarization and to significantly reduce decoherence due to electron spin flip-flop processes. Theoretical fitting of  $T_2$  versus temperature shows that, for crystalline samples of this molecule, spin flip-flop fluctuations represent the main source of spin decoherence at low temperatures, as reported also for the  $\text{Fe}_8$  single-molecule magnet [Phys. Rev. Lett. 102 (2009) 087603]. Moreover, it is found that  $T_2$  is position dependent within the EPR line, a model for which is given. We also note that this is the third example of an Fe-based cluster that exhibits a measurable decoherence time, and only the second involving a crystal.

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## 1. Introduction

An important aspect of the study of single-molecule magnets is the spin dynamics. For applications like molecular memory [1], it is the relaxation of the magnetization that is of crucial importance and which can in some cases be as long as 40 h [2]. This magnetization relaxation time, typically the relaxation between the ground  $\pm m_S$  states, can usually be described by a combination of tunneling processes and thermal excitations to higher lying spin sublevels through allowed  $\Delta m_S = \pm 1$  transitions. These can be parameterized with a tunneling rate and the spin–lattice relaxation time ( $T_1$ ), respectively.

For applications like quantum computing on the other hand [3,4], the spin–spin relaxation time or spin-memory time  $T_2$  is the important parameter, as it determines how long the phase of a superposition of states remains well defined. In this context  $T_2$  is often referred to as the dephasing time or decoherence time. While magnetization relaxation and tunneling rates can be measured through magnetization and AC susceptibility of single crystals of molecular magnets, it has proven difficult to measure  $T_1$  and  $T_2$  relaxation directly, because the  $T_2$  in single crystalline sys-

tems is too short to obtain an echo in pulsed EPR measurements. One approach is to dilute the molecular magnet spin system [5–8], but this usually can only be achieved by making a glass, which introduces a wide distribution of orientations and surroundings. Recently, however,  $T_1$  and  $T_2$  of the well-known  $\text{Fe}_8$   $S = 10$  single-molecule magnet were reported in a pure single crystal [9]. This study showed that in the limit where the spin splitting is much larger than the temperature ( $h\nu \gg kT$ ), the  $T_2$  relaxation due to the surrounding electron spin bath can be strongly suppressed. This is due to the suppression of electron spin flip-flop transitions of the surrounding molecules when the spin polarization is high.

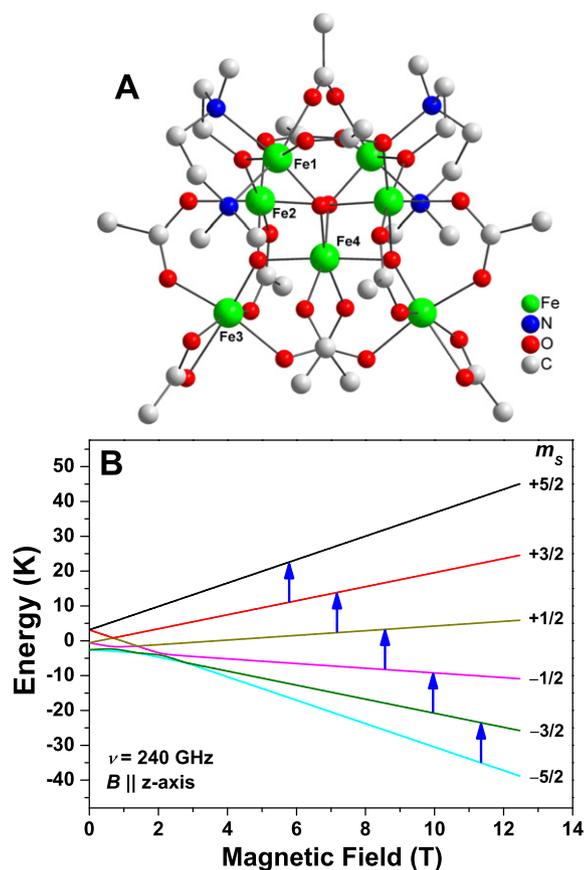
Here we report a study of the  $T_2$  relaxation time in a single crystal of another iron based magnetic cluster:  $\text{Fe}_7\text{O}_4(\text{O}_2\text{CPh})_{11}(\text{dmem})_2$ , abbreviated  $\text{Fe}_7$  (Fig. 1A), which has a spin ground state  $S = 5/2$ . As in the case of the  $\text{Fe}_8$  [9], we have found a strong temperature dependence of  $T_2$ , indicating a suppression of electron spin flip-flop transitions at low temperatures. While this system is not strictly a single-molecule magnet, as the zero-field splitting parameter is positive, it provides an additional example of the suppression of the spin–spin relaxation due to the spin bath in a crystalline magnetic molecular complex.

## 2. Experimental details

Single crystals of  $\text{Fe}_7$  were grown as described previously [10]. The single crystals used for the pulsed EPR study had dimensions

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**Fig. 1.** (A) Labeled representation of the structure of the  $\text{Fe}_7$  molecule, with the phenyl rings of the benzoate ligands omitted for clarity. (B) Calculated Zeeman diagram with  $B \parallel z$ , obtained via diagonalization of the Hamiltonian of Eq. (1), with  $g = 2.00$ ,  $D = +0.62 \text{ cm}^{-1}$  and  $E = 0.067 \text{ cm}^{-1}$ .

of  $0.5 \times 0.5 \times 1.0 \text{ mm}$ . High frequency EPR measurements were performed on a locally developed superheterodyne quasi-optical pulsed/cw EPR spectrometer which is located at the National High Magnetic Field Laboratory in Tallahassee, FL, USA. The spectrometer operates at 120, 240 and 336 GHz. It employs Schottky diode mixer/detectors and a superconducting magnet (Oxford Instruments) capable of reaching a field of 12.5 T. Temperature variation was accomplished using a continuous helium flow cryostat, capable of accessing the range from 1.3 to 400 K with a precision of 0.1 K [11,12].

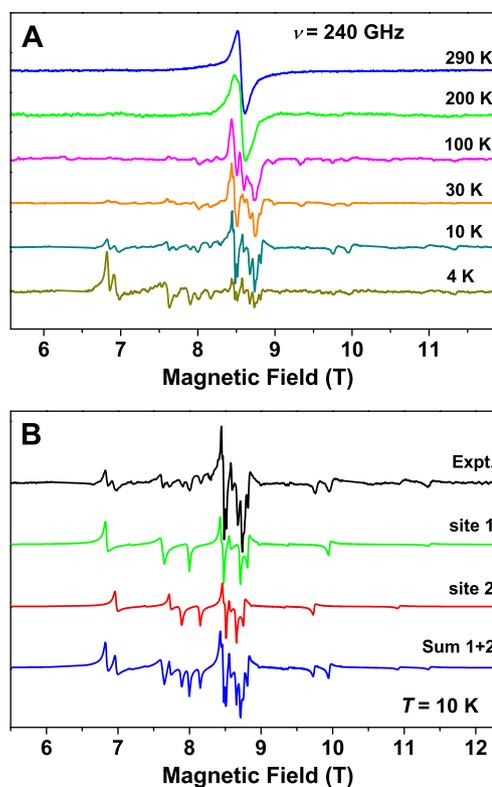
### 3. Data and discussion

A labeled representation of the  $\text{Fe}_7$  molecule is shown in Fig. 1A. The complex crystallizes in the monoclinic space group  $C2/c$  with the  $\text{Fe}_7$  molecule lying on a crystallographic  $C_2$  axis passing through the central Fe atom. All of the molecules in the crystal are nominally identically aligned, which simplifies interpretation of the EPR spectra. The seven Fe ions all have the oxidation state of 3+, and magnetization measurements show the dominance of antiferromagnetic interactions within the core, resulting in a spin  $S = 5/2$  ground state [10].

The magnetic properties of the  $S = 5/2$   $\text{Fe}_7$  cluster can be described via the following effective spin Hamiltonian:

$$\hat{H} = g\beta\vec{B} \cdot \hat{S} + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2), \quad (1)$$

with  $g = 2.00$ ,  $D = +0.62 \text{ cm}^{-1}$  and an estimated  $E \geq 0.067 \text{ cm}^{-1}$  [10]. These parameters imply a non-axiality of the zero-field

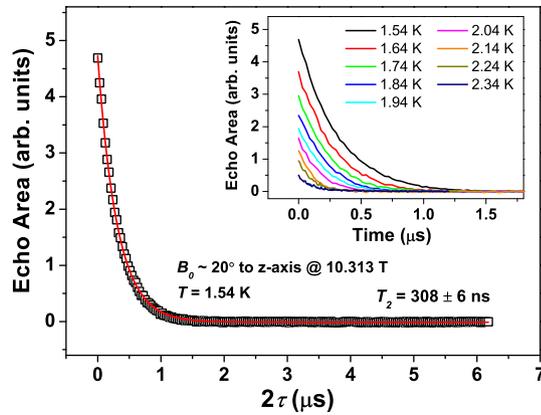


**Fig. 2.** (A) Temperature dependence of the cw EPR spectra at 240 GHz. (B) The cw EPR spectrum at 240 and 10 K (top) with simulations (below – see legend). The employed spin Hamiltonian parameters are: (site 1)  $S = 5/2$ ,  $g = 2.0023$ ,  $D = 0.65 \text{ cm}^{-1}$ ,  $\Delta D = 0.01 \text{ cm}^{-1}$ ,  $E = 0.06 \text{ cm}^{-1}$ ,  $\Delta E = 0.003 \text{ cm}^{-1}$ ; (site 2)  $S = 5/2$ ,  $g = 2.0023$ ,  $D = 0.55 \text{ cm}^{-1}$ ,  $\Delta D = 0.01 \text{ cm}^{-1}$ ,  $E = 0.07 \text{ cm}^{-1}$ ,  $\Delta E = 0.003 \text{ cm}^{-1}$ . The spectrum labeled “Sum 1+2” is obtained by adding the spectra for sites 1 and 2 in equal proportion. The  $\Delta D$  and  $\Delta E$  represent the FWHM of the Lorentzian distributions of  $D$  and  $E$ , which contribute to the broadening of the transitions with higher  $m_S$  values [13,14].

splitting (ZFS) tensor, which is not unexpected given the low symmetry of the molecule. Fig. 1B shows the Zeeman energy level diagram for a spin  $S = 5/2$  system, with the above parameters, and with the field applied parallel to the  $z$ -axis of the molecule. It can be seen that, at high fields and low temperatures, the  $m_S = -5/2$  level will be preferentially populated. As a consequence, the molecular (electronic) spin system will be strongly polarized and, hence, decoherence due to spin fluctuations should be strongly suppressed [9].

Fig. 2A shows the temperature dependence of cw EPR spectra for a polycrystalline sample at 240 GHz. The room temperature spectrum consists of a single peak with an approximately Lorentzian lineshape, which can be interpreted as an exchange narrowed line due to the individual Fe(III) ions. The spectra then develop clear fine structures (ZFS) as the temperature is reduced to the point where  $k_B T$  is comparable to, or lower than the exchange coupling within the molecule. As reported previously [10], the low temperature spectra cannot be fit with a single set of spin Hamiltonian parameters. However, a reasonably good simulation is obtained by assuming that there are two  $S = 5/2$  molecular species in the crystal with slightly different ZFS parameters. This is likely due to disorder associated with ligand or solvent molecules, as has been found from studies of numerous other SMMs [15].

The temperature dependence of  $T_2$  was investigated using pulsed EPR at 240 GHz using a non-resonating sample holder [11,12]; measurements were performed with the magnetic field applied approximately along each of the three principal magnetic



**Fig. 3.** Echo area as a function of  $\tau$  measured by a Hahn echo sequence, with the magnetic field  $\sim 20^\circ$  away from the z-axis. The solid line is a fit to a single exponential. The inset shows the echo decay at different temperatures.

axes, in the temperature range from 1.4 to 2.6 K. A typical Hahn echo sequence ( $\pi/2 \rightarrow \tau \rightarrow \pi \rightarrow \tau \rightarrow \text{echo}$ , Fig. 4A) was utilized, with the delay time  $\tau$  varied during the measurements. The widths of the pulses were adjusted to maximize the echo signals and were typically between 100 and 150 ns. Fig. 3 shows the echo area as a function of  $\tau$  at 1.54 K and 10.313 T, with the magnetic field  $\sim 20^\circ$  away from the z-axis. At these temperatures and fields, only the  $m_S = -5/2$  level has appreciable population. Consequently, only the  $-5/2 \rightarrow -3/2$  transition is observed. The decay can be fit by a single exponential function ( $\exp(-2\tau/T_2)$ ) with  $T_2 = 308 \pm 6$  ns. The inset to Fig. 3 shows the echo decay at different temperatures. It can clearly be seen that the echo decays faster with increasing temperature.

Fig. 4 shows the temperature dependence of  $T_2$  at 240 GHz, for magnetic fields along each of the three principal axes of the ZFS tensor. The strong temperature dependence of  $T_2$  suggests that, like  $\text{Fe}_8$ , the main decoherence mechanism in this temperatures range is due to dipolar coupling to fluctuating neighboring molecular spins. To test this hypothesis, we have fit the  $T_2$  data with a spin flip-flop model using Eq. (2) [9,16,17]:

$$\frac{1}{T_2} = A \sum_{m_S=-5/2}^{3/2} W(m_S) P_{m_S} P_{m_S+1} + \Gamma_{\text{res}}, \quad (2)$$

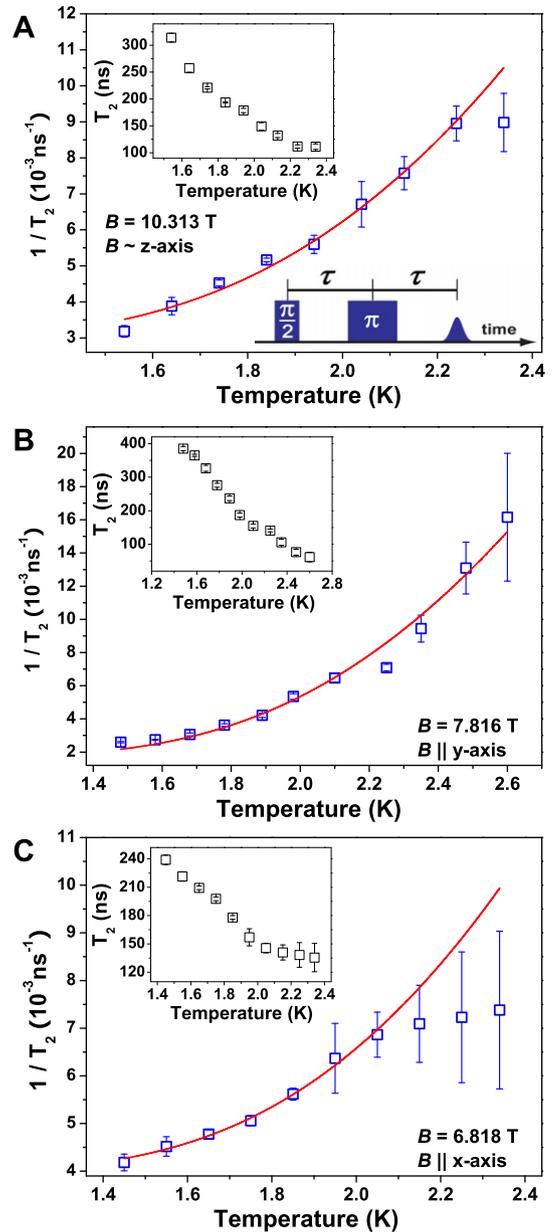
with  $P_{m_S}$  given by,

$$P_{m_S} = \frac{e^{-E(m_S)/(k_B T)}}{Z}, \quad (3)$$

where  $A$  is a temperature independent adjustable parameter,  $Z$  is the partition function for the  $\text{Fe}_7$   $S = 5/2$  spin system, and  $\Gamma_{\text{res}}$  is a residual relaxation rate due to other temperature independent decoherence sources. The flip-flop transition probability for two spins,  $W(m_S)$ , is given by

$$W(m_S) = |\langle m_S + 1, m_S | S_1^+ S_2^- | m_S, m_S + 1 \rangle|^2 + |\langle m_S, m_S + 1 | S_1^+ S_2^- | m_S + 1, m_S \rangle|^2. \quad (4)$$

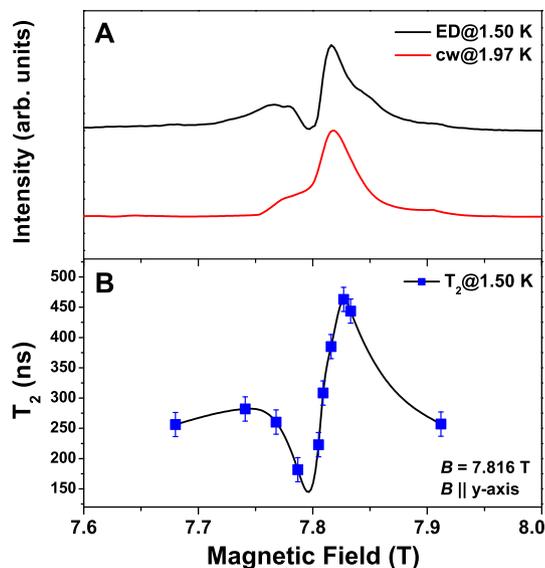
The solid lines in Fig. 4 are the fits to Eq. (2) for the three field orientations. It is seen that the experimental data fit well with the proposed model, confirming that the primary decoherence mechanism for  $\text{Fe}_7$  in this temperature range involves electron spin bath fluctuations. The best agreement is obtained with  $\Gamma_{\text{res}} = 4.0, 1.7$  and  $2.9 \times 10^{-3} \text{ ns}^{-1}$ , for the x-, y- and z-directions, respectively, which correspond to residual decoherence times of  $T_2 = 250, 590$



**Fig. 4.** Spin-spin relaxation rates ( $1/T_2$ ) as a function of temperature at 240 GHz with: (A)  $B \sim 20^\circ$  away from the z-axis; (B)  $B \parallel y$ ; and (C)  $B \parallel x$ . The solid lines are fits to Eq. (2), and the insets show the corresponding temperature dependences of  $T_2$ .

and 340 ns. These values are shorter than those for  $\text{Fe}_8$  (1  $\mu\text{s}$ ), though of the same order of magnitude [9].

We also observed an interesting phenomenon when comparing the echo-detected (ED) and cw EPR spectra, as shown in Fig. 5A: it is seen that the resonance fields and line shapes do not match very well. This is believed to be due to a field dependence of  $T_2$ , which is confirmed by the measurements displayed in Fig. 5B. A similar behavior was seen when the magnetic field was aligned along all three principal axes of the ZFS tensor. The effect has also been observed in single crystals of the  $\text{Fe}_8$  SMM [9,18]. This is likely related to the reduced spectral density associated with the edges of the resonance line, leading to a reduced spin flip-flop rate because fewer neighboring spins are in resonance with each other. In addition, re-absorption of the echo might play a role in reducing the intensity at the center of the EPR line.



**Fig. 5.** (A) echo-detected (ED) and integrated cw EPR spectra with  $B \parallel y$ . (B) Position dependence of  $T_2$  at 1.50 K. The solid line in (B) is a guide to the eye.

#### 4. Conclusion

cw EPR studies of  $\text{Fe}_7$  reveal two distinct molecular species with slightly different ZFS parameters. A high spin polarization may be achieved at high magnetic fields and low temperatures, resulting in a strong suppression of decoherence due to spin flip-flop processes. The residual  $T_2$  values are of the order of 250–590 ns (at 0 K), likely resulting from electron-nuclear hyperfine interactions, or spin diffusion processes. We also find that the decoherence time depends on the position within the inhomogeneously broadened resonance line.

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