

Proton NMR for Measuring Quantum Level Crossing in the Magnetic Molecular Ring Fe10

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The proton nuclear spin-lattice relaxation rate $1/T_1$ has been measured as a function of temperature and magnetic field (up to 15 T) in the molecular magnetic ring $\text{Fe}_{10}(\text{OCH}_3)_{20}(\text{O}_2\text{CCH}_2\text{Cl})_{10}$ (Fe10). Striking enhancement of $1/T_1$ is observed around magnetic field values corresponding to a crossing between the ground state and the excited states of the molecule. We propose that this is due to a cross-relaxation effect between the nuclear Zeeman reservoir and the reservoir of the Zeeman levels of the molecule. This effect provides a powerful tool to investigate quantum dynamical phenomena at level crossing.

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The magnetic properties of metal ion clusters incorporated in large molecules attract considerable interest for the new physics involved and for the potential applications [1,2]. At low temperatures, these molecules act as individual quantum nanomagnets, enabling to probe, at the macroscopic scale, the crossover between quantum and classical physics [3]. Of fundamental interest is the situation of (near) degeneracy of two magnetic levels, where quantum mechanical phenomena such as tunneling or coherence can occur. These effects have been intensively explored in the recent years, mostly in the high-spin ($S = 10$) molecules Mn12 and Fe8 [4], or in the ferritin protein [5]. Another interesting system is the molecule $[\text{Fe}_{10}(\text{OCH}_3)_{20}(\text{O}_2\text{CCH}_2\text{Cl})_{10}]$ (in short Fe10), where the ten Fe^{3+} ions ($s = 5/2$) are coupled in a ring configuration by an antiferromagnetic exchange $J/k_B \approx 13.8$ K [6,7]. Unlike Mn12 or Fe8, the ground state of Fe10 is nonmagnetic (total spin $S = 0$). The energies E of the excited states are given approximately by Landé's rule,

$$E(S) = \frac{P}{2} S(S+1), \quad (1)$$

where S is the total spin value and $P = 4J/N$, with $N = 10$ the number of magnetic ions in the ring. In zero magnetic field, the first excited state is $S = 1$, the second $S = 2$, etc. (see Fig. 1). This picture is modified by an external magnetic field, which lifts the degeneracy of the magnetic states. A sufficiently strong field can induce level crossings between the ground state and the excited states, as shown in Fig. 1. In other words, the ground state of the molecule can be changed by the field, from $S = 0$ to $S = 1$, then from $S = 1$ to $S = 2$, etc. Owing to the relatively low value of the magnetic exchange coupling in Fe10, this field-induced transition can be observed experimentally in conventional magnetic fields, for instance, through steps of the magnetization [6,8].

The situation of degeneracy between levels raises fundamental problems of quantum dynamics [9,10] (specific calculations for Fe10 can be found in [11]). A crucial is-

ssue is the role played by the coupling between magnetic molecular levels and the environment such as phonons and/or nuclear spins [9]. Clearly, essential information on this problem should be accessed through measurements of the nuclear spin-lattice relaxation rate $1/T_1$ since the nuclei (here protons) probe the fluctuations of the local field induced at the nuclear site by the localized magnetic moments.

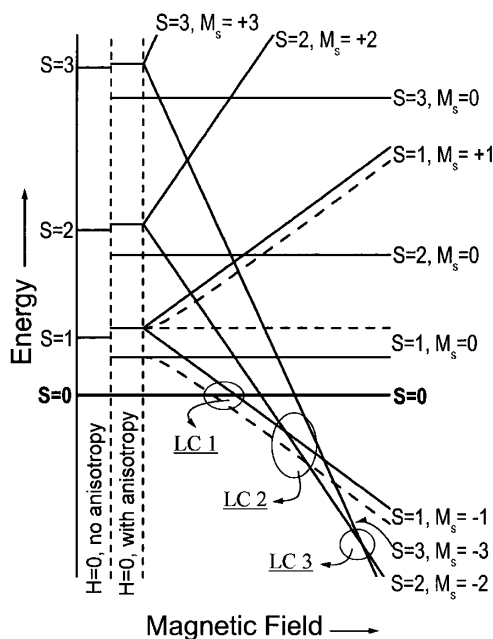


FIG. 1. Energy levels vs magnetic field for the lower four manifolds ($S = 0$ to $S = 3$) in Fe10. The zero-field splitting due to magnetic anisotropy is included only for the levels relevant to level crossing effects. Dashed lines are energy levels for $\theta = 90^\circ$ ($S = 1$ case). All the other energy levels are for $\theta = 0^\circ$. Note that the labels of magnetic levels refer to the solid lines only. LC1, LC2, and LC3 refer to the three level crossings evidenced in this work through proton spin-lattice relaxation.

The physics of level crossings is almost not documented experimentally, due to the rarity of systems in which the observation is possible. A situation which has some analogy with the one reported here is the crossover from antiferromagnetic to ferromagnetic phase in 1D chains, where a divergence of the one-magnon density of states generates an enhancement in the nuclear spin-lattice relaxation rate [12]. A closer situation of level crossing between singlet and triplet states can be observed in 1D gapped quantum magnets [13], but the physical context and the continuum of excited states make the situation certainly not comparable to that in finite-size magnets. In this respect, the mesoscopic ring Fe10 constitutes a model system since magnetic levels are sharp and well defined in energy, due to the finite size of the system.

Previous ^1H NMR relaxation measurements in Fe10 have concerned magnetic fields much lower than the expected energy gap $E(1) \sim 6$ K [Eq. (1)] [14,15].

Here, we present new proton T_1 measurements in Fe10, as a function of the magnetic field up to 15 T, and in the temperature range $1.3 \leq T \leq 4.2$ K. Our main result is the observation of a dramatic enhancement of $1/T_1$ when the magnetic field reaches the critical values for which the magnetic levels become degenerate (level crossing) [16]. Although broadening effects due to the use of a powder sample prevent yet a quantitative interpretation of the data, it is pointed out that the cross-relaxation effect between (proton) nuclear and molecular levels, discovered here, should provide a powerful method to investigate the physics of level crossing if large enough single crystals become available.

The powder samples were synthesized as described elsewhere [6]. High-field ($H \geq 8$ T) NMR measurements were performed at the Grenoble High Magnetic Field Laboratory in a 17 T variable field superconducting magnet. All measurements were performed with home-built pulsed NMR spectrometers.

The proton NMR spectrum is featureless, except for an asymmetry related to the orientation distribution of the grains and to the superposition of resonances from inequivalent proton sites in each molecule. The width of the spectrum is both temperature and field dependent due to an inhomogeneous component, i.e., a distribution of hyperfine (dipolar) fields from Fe moments [14]. At low field ($H = 0.33$ T), the full width at half maximum (FWHM) is about 25 kHz at room temperature; it increases to a maximum of about 70 kHz at about 30 K and it decreases again at low temperature reflecting the collapse of the spin susceptibility when the Fe10 molecular states condense into the $S = 0$ ground state. In the temperature range investigated here (1.3–4.2 K), there is a residual field-dependent inhomogeneous broadening of the proton NMR line, which is due to the Fe moments in the $S = 1$ excited state. At 1.3 K the FWHM varies from 25 kHz at $H = 0.33$ T to 1.8 MHz at 14.65 T.

T_1 was extracted from the recovery of the spin-echo amplitude following a sequence of saturating radio frequency pulses. Both $(\frac{\pi}{2})_x - (\frac{\pi}{2})_y$ (solid echo) and $(\frac{\pi}{2})_x - (\pi)_y$ (Hahn echo) sequences were used with similar results. The recovery of the nuclear magnetization was found to be non-exponential at all fields. For low fields ($H \leq 1$ T), the NMR line is sufficiently narrow to be completely saturated by the radio frequency pulses. In this case, the non-exponential recovery is solely related to the distribution of relaxation rates, due to the superposition of inequivalent proton sites, and to the orientation distribution in the powder. At higher fields, the line becomes too broad to be completely saturated and thus the initial recovery is affected by spectral diffusion effects. Therefore, in order to measure a relaxation parameter consistently we chose to define T_1 as the time at which the nuclear magnetization has recovered half of the equilibrium value, after removal of the initial fast recovery due to spectral diffusion. This criterion is insensitive to the spectral diffusion, the strength of which depends on hardly controllable experimental parameters. The criterion also makes the T_1 value insensitive to slight modifications of the recovery law that were sometimes observed for the very long time delays. Otherwise, the shape of the recovery law was found to be field and T independent. T_1 was also checked to be the same at different positions on the line.

The magnetic field dependence of proton $1/T_1$ is reported in Fig. 2. For technical reasons, experiments between 8 and 15 T were performed at $T = 1.3$ K, while those at lower fields were at $T = 1.5$ – 1.7 K. The difference is minor and, as will be seen later, T_1 is basically T independent in most of the field range. So, Fig. 2 can be regarded as the field dependence of T_1 at fixed temperature. $1/T_1$ shows three very well-defined peaks centered around the critical field values: 4.7, 9.6, and 14 T. These values correspond very closely to the fields for which steps were observed in the magnetization [6,8].

At low fields ($H < 1.5$ T), the T dependence of $1/T_1$ is almost exponential (Fig. 3). This implies that the proton relaxation is dominated by the singlet-triplet gap and the

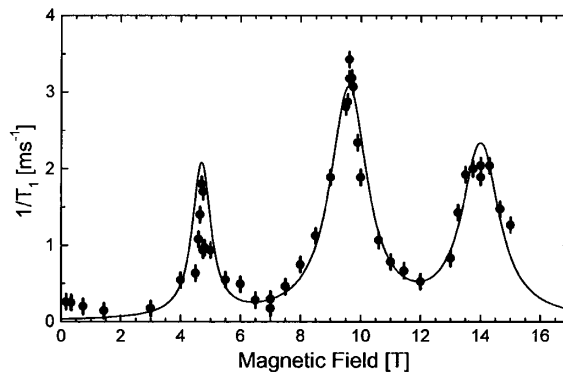


FIG. 2. Magnetic field dependence of proton $1/T_1$ at 1.3–1.7 K. The line is a theoretical fit according to Eq. (4) with the choice of parameters discussed in the text.

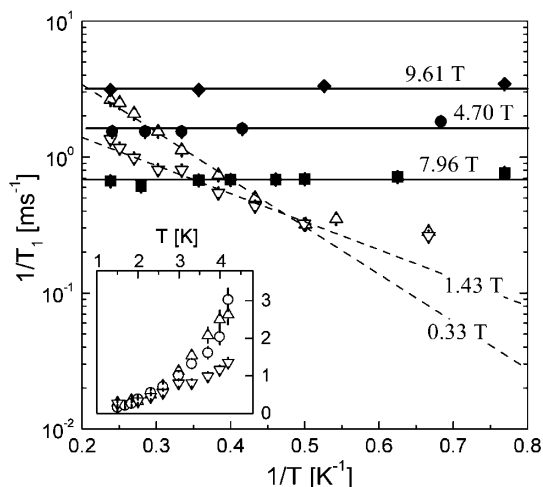


FIG. 3. (Main panel) proton $1/T_1$ vs inverse temperature; activated behavior at low fields: 0.33 and 1.43 T, and constant at 4.7, 7.96, and 9.61 T. (Inset) activated behavior of $1/T_1$ in linear scales; 0.33 T (Δ), 0.75 T (\circ), and 1.43 T (∇).

finite lifetime of the $S = 1$ excited state which generates fluctuations in the local hyperfine field at the proton site [13,17]. The exponential T dependence is a consequence of the Boltzmann distribution of the $S = 1$ population.

However, as shown in Fig. 3, $1/T_1$ at a higher magnetic field appears to be temperature independent both at level crossings (4.7 and 9.61 T) and in between them (7.96 T). Thus, the strong enhancement around level crossing requires a new description of the nuclear relaxation, which cannot be based on thermal excitations. Near the critical field for level crossing, the coupled system nuclei plus molecular magnetic moments can undergo flip-flop energy conserving transitions, resulting in a transfer of energy from the nuclear system to the molecular magnet which depends on the matching of energy levels and not on temperature. Thus, we propose that the peaks in $1/T_1$ vs magnetic field are the result of a cross-relaxation effect between the nuclear Zeeman levels and the magnetic molecular levels. In fact, since the magnetic molecules are strongly coupled to the "lattice," the cross relaxation becomes a very effective channel for spin-lattice relaxation.

It is emphasized that cross relaxation, here in the sense of the matching of energy levels, is observed between two nuclear reservoirs [18] or between two electron reservoirs [19]. Strictly speaking the cross relaxation occurs only when the condition $\hbar\omega_n = \hbar\gamma_n H = g\mu_B|H - H_c|$ is met. However, the broadening of both the NMR line and of the molecular energy levels can allow the energy conserving condition to be met over a wide field interval. Furthermore, broadening effects are expected for a powder sample.

In order to analyze the data quantitatively, it is necessary to have a precise description of the magnetic level diagram for Fe10. For the triplet state, the energy levels are obtained from the diagonalization of the

Hamiltonian,

$$\mathcal{H} = \vec{S}\hat{D}\vec{S} + g\mu_B\vec{B} \cdot \vec{S} + P, \quad (2)$$

which yields a secular equation for energy E ,

$$\begin{aligned} & \left(P - \frac{2}{3}D_1 - E\right)\left(P + \frac{1}{3}D_1 - E\right)^2 \\ & - \left(P - \frac{2}{3}D_1 - E\right)g^2\mu_B^2B^2\cos^2\theta \\ & - \left(P + \frac{1}{3}D_1 - E\right)g^2\mu_B^2B^2\sin^2\theta = 0, \quad (3) \end{aligned}$$

where we have assumed a diagonal, traceless, axial tensor for the zero-field splitting $[-(1/3)D_1, -(1/3)D_1, (2/3)D_1]$. The axis perpendicular to the Fe10 ring plane is a hard axis, i.e., $D_1 > 0$. The values $P = 6.5$ K and $D_1 = 3.23$ K are obtained from recent torque magnetometry measurements [8]. As shown in Fig. 1, the critical field H_c for the first level crossing depends on the angle θ between the crystal field axis and the magnetic field: H_c varies from 4.33 T for $\theta = 90^\circ$ up to 5.6 T for $\theta = 0^\circ$ [8]. This implies a powder distribution of relaxation rates which should contribute to the width of the first peak at 4.7 T. The calculation of the level distribution for $S \geq 2$ is more complex, making a quantitative analysis of the second and third crossings beyond the scope of the present paper.

It is very interesting to point out the differences between the three peaks in $1/T_1$. At the first level crossing ($H_c = 4.7$ T), there is a very steep increase of $1/T_1$ occurring in an extremely narrow field interval (about 0.1 T). This is very suggestive of a resonant process in the relaxation. The two other peaks have a more regular shape but the third peak is smaller than the second one. Of course, we speculate that these differences are related to the different spin values involved in each level crossing. In particular, the first crossing involves the nonmagnetic level $S = 0$.

We tentatively describe the results in Fig. 2 as a sum of Lorentzian functions of width Γ_α with $\alpha = 1, 2, 3$ for the three level crossing conditions,

$$\frac{1}{T_1} \propto \sum_{\alpha=1}^3 A_\alpha \left[\frac{\Gamma_\alpha}{\Gamma_\alpha^2 + (\gamma_n H - \frac{1}{\hbar} g\mu_B |H - H_c|)^2} \right]. \quad (4)$$

This expression fits the data reasonably well with the choice of parameters: $A_1 \approx 0.3A_2 \approx 0.5A_3 = 4\pi \times 10^{13} \text{ rad s}^{-2}$ (≈ 0.36 T) and $\Gamma_1 \approx 0.5\Gamma_2 \approx 0.5\Gamma_3 = 2\pi \times 10^{10} \text{ rad s}^{-1}$, and critical fields $H_{c1} = 4.7$, $H_{c2} = 9.6$, and $H_{c3} = 14.0$ T. The physical meaning of the coupling constant A_α is not clear without a quantitative theory for the cross-relaxation effect. The width of each peak is most likely related to the distribution of level crossing fields due to the distribution of angles between the magnetic field and the crystalline axis in our powder sample. Thermal broadening is also expected since 1.3 K is equivalent to ~ 1 T.

In summary we have presented an investigation of the proton spin-lattice relaxation rate $1/T_1$ at low temperature in the Fe10 molecular magnetic ring. $1/T_1$ at low fields is dominated by the thermal fluctuations in the triplet excited state. At high magnetic fields we have reported a dramatic enhancement of the $1/T_1$ in correspondence to the critical fields for which the lowest lying molecular energy levels become almost degenerate. The effect can be explained by a T -independent resonant cross-relaxation effect where thermal fluctuations mediated by phonons do not seem to play a role. Thus, the magnetic transitions between nearly degenerate $\Delta S = 1$ states become possible, presumably because of the coupling with the nuclear spins [20,21].

The most promising perspective opened by these results concerns the possibility of studying dynamical effects of quantum mechanical origin that are expected in the vicinity of the level crossing conditions. Enhanced transfer of population between two levels is possible, through a mechanism of quantum tunneling. We have shown here that the dynamics of nearly degenerate molecular levels is coupled to the dynamics of nuclear spins. This has to be taken into account in future theoretical works on Fe10, and at the same time the coupling between nuclei and molecular levels makes such NMR experiments a privileged tool for detailed studies when large enough single crystals become available.

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[1] D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, *Science* **265**, 1055 (1994); D. Gatteschi, A. Caneschi, R. Sessoli, and A. Cornia, *Chem. Soc. Rev.* 101 (1996).

[2] D. D. Awschalom and D. P. DiVincenzo, *Phys. Today* **48**, No. 4, 43 (1995), and references therein.

[3] P. C. E. Stamp, *Nature (London)* **383**, 125 (1996); B. Swartzschild, *Phys. Today* **50**, No. 1, 19 (1997).

[4] See references cited in the most recent works of R. Caciuffo *et al.*, *Phys. Rev. Lett.* **81**, 4744 (1998); J. R. Friedman, M. P. Sarachik, and R. Ziolo, *Phys. Rev. B* **58**, R14 729 (1998).

[5] S. Gider *et al.*, *Science* **268**, 77 (1995).

[6] K. L. Taft *et al.*, *J. Am. Chem. Soc.* **116**, 823 (1994).

[7] Z. Zeng, Y. Duan, and D. Guenzburger, *Phys. Rev. B* **55**, 12 522 (1997).

[8] A. Cornia *et al.* (unpublished).

[9] P. C. E. Stamp, cond-mat/9810353, and references therein.

[10] S. Miyashita, K. Saito, and H. De Raedt, *Phys. Rev. Lett.* **80**, 1525 (1998).

[11] A. Chiolero and D. Loss, *Phys. Rev. Lett.* **80**, 169 (1998).

[12] L. J. Azevedo, A. Narath, P. M. Richards, and Z. G. Soos, *Phys. Rev. B* **21**, 2871 (1980).

[13] For NMR studies, see M. Chiba *et al.*, *J. Phys. Soc. Jpn.* **57**, 3178 (1988); G. Chaboussant *et al.*, *Phys. Rev. Lett.* **80**, 2713 (1998); M. Chiba *et al.*, *Physica (Amsterdam)* **246B & 247B**, 576 (1998).

[14] A. Lascialfari, D. Gatteschi, F. Borsa, and A. Cornia, *Phys. Rev. B* **55**, 14 341 (1997).

[15] A. Lascialfari, Z. H. Jang, F. Borsa, D. Gatteschi, and A. Cornia, *J. Appl. Phys.* **83**, 6946 (1998).

[16] Throughout this paper, we shall use the term "level crossing." Actually, levels may cross or anticross (level repulsion) depending on details of the magnetic Hamiltonian (see, for instance, Ref. [21]).

[17] A. Lascialfari *et al.*, *Phys. Rev. Lett.* **81**, 3773 (1998).

[18] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1992).

[19] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970).

[20] A. Cornia, A. Fort, M. G. Pini, and A. Rettori (private communication).

[21] For example, R. F. Kiefl, *Hyperfine Interact.* **32**, 707 (1986); E. Roduner, I. D. Reid, M. Ricc6, and R. De Renzi, *Ber. Bunsen-Ges. Phys. Chem.* **93**, 1194 (1989).