

## Observation of Magnetic Level Repulsion in Fe6:Li Molecular Antiferromagnetic Rings

M. Affronte,<sup>1</sup> A. Cornia,<sup>2</sup> A. Lascialfari,<sup>3</sup> F. Borsa,<sup>3,4</sup> D. Gatteschi,<sup>5</sup> J. Hinderer,<sup>6</sup>  
M. Horvatić,<sup>6</sup> A. G. M. Jansen,<sup>6</sup> and M.-H. Julien<sup>7</sup>

<sup>1</sup>*I.N.F.M. and Dipartimento di Fisica, Università di Modena e Reggio Emilia, via G. Campi 213/A, I-41100 Modena, Italy*

<sup>2</sup>*I.N.S.T.M. and Dipartimento di Chimica, Università di Modena e Reggio Emilia, via G. Campi 183, I-41100 Modena, Italy*

<sup>3</sup>*I.N.F.M. and Dipartimento di Fisica "A.Volta," Università di Pavia, Via Bassi 6, I-27100 Pavia, Italy*

<sup>4</sup>*Department of Physics and Astronomy, Ames Laboratory, Iowa State University, Ames, Iowa 50011*

<sup>5</sup>*I.N.S.T.M. and Dipartimento di Chimica, Università di Firenze, via Lastruccia, 5 Sesto Fiorentino, I-50019 Firenze, Italy*

<sup>6</sup>*Grenoble High Magnetic Field Laboratory, MPI-FKF and CNRS, BP 166, F-38042 Grenoble, France*

<sup>7</sup>*Laboratoire de Spectrométrie Physique, Université J.Fourier, BP 87, F-38402, Saint Martin d'Hères, France*

(Received 2 November 2001; published 3 April 2002)

Heat capacity ( $C$ ), magnetic torque, and proton NMR relaxation rate ( $1/T_1$ ) measurements were performed on Fe6:Li single crystals in order to study the crossings between  $S = 0$  and  $S = 1$  and between  $S = 1$  and  $S = 2$  magnetic states of the molecular rings, at magnetic fields  $B_{c1} = 11.7$  T and  $B_{c2} = 22.4$  T, respectively.  $C$  vs  $B$  data at 0.78 K show that the energy gap between two states remains finite at  $B_c$ 's ( $\Delta_1/k_B = 0.86$  K and  $\Delta_2/k_B = 2.36$  K) thus proving that levels repel each other. The large  $\Delta_1$  value may also explain the anomalously large width of the peak in  $1/T_1$  vs  $B$ , around  $B_{c1}$ . This anticrossing, unexpected in a centrosymmetric system, requires a revision of the Hamiltonian.

DOI: 10.1103/PhysRevLett.88.167201

PACS numbers: 75.50.Xx, 75.40.Cx, 76.60.Es

In multilevel magnetic systems, the application of an external magnetic field makes levels with different magnetic features cross each other. The system becomes nearly degenerate for certain values  $B_c$ 's of the external magnetic field and, close to the level crossing (LC) condition, the structure of the magnetic energy levels can be affected by even small perturbations and can display new and interesting dynamical phenomena. A new class of iron-based molecular clusters with a planar ring shape, the so-called "ferric wheels" [1,2], presents a simple pattern of energy levels (see Fig. 1) that can be derived from the spin Hamiltonian of one wheel:

$$\mathcal{H} = \left[ J \sum_{i=1}^{N-1} \mathbf{s}_i \cdot \mathbf{s}_{i+1} + J \mathbf{s}_N \cdot \mathbf{s}_1 \right] + g \mu_B \mathbf{S} \cdot \mathbf{B} + \mathcal{H}', \quad (1)$$

where  $N$  is the number of  $\mathbf{s}_i$  spins and  $\mathbf{S}$  is the total spin of the ring. The first and second terms in Eq. (1) describe nearest-neighbor (NN) Heisenberg and Zeeman interactions, respectively, while  $\mathcal{H}'$  may include single-ion anisotropies, intramolecular dipolar contributions, hyperfine couplings, as well as Dzyaloshinski-Moriya interaction, or higher-order exchange and Zeeman terms. Antiferromagnetic Heisenberg interaction between NN Fe<sup>+3</sup> ( $s_i = 5/2$ ) ions usually represents the dominant term in Eq. (1) and, in zero magnetic field, the ground state is nonmagnetic ( $S = 0$ ). When a strong magnetic field  $B$  is applied, Zeeman interaction leads to successive LC's involving the lowest-lying spin states, hereafter labeled with the spin quantum numbers  $S$  and  $M$ , namely,  $|S, M\rangle$  (Fig. 1) [1]. Since the zero-field energies approximately follow Landé's interval rule  $E_S = 2JS(S + 1)/N$  [1], the ground state changes from  $|0, 0\rangle$  to  $|1, -1\rangle$ , from  $|1, -1\rangle$  to

$|2, -2\rangle$ , etc., at equally spaced magnetic field values  $B_{c1}$ ,  $B_{c2}$ , etc. In these systems,  $J/k_B$  typically ranges from 10 to 30 K and the  $B_c$ 's are consequently readily achievable in the laboratory (typically 4 to 20 T). Additional interest has been recently addressed to the ferric wheels by Loss and co-workers [3] who proposed that quantum coherence can be observed at macroscopic scale in this class of antiferromagnetic molecular nanomagnets. In their model, the energy separation between the lowest-lying levels can be viewed as the tunnel splitting between two degenerate states of the Néel vector [3]. It is thus crucial to follow experimentally the evolution of energy levels as a function of the magnetic field in ring-shaped molecular antiferromagnets. General symmetry arguments show that, in a centrosymmetric cluster and for any perturbation  $\mathcal{H}'$ , the energy separation  $\Delta$  between the two lowest-lying

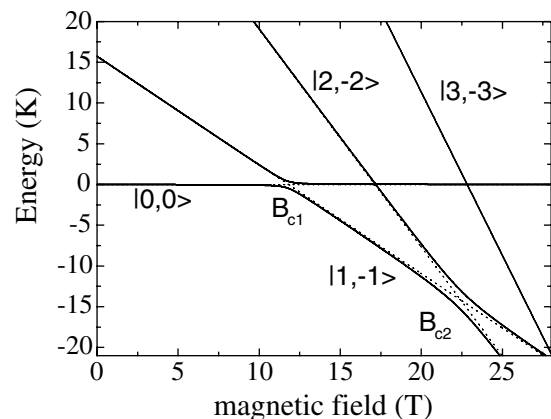


FIG. 1. Lowest-lying energy levels of Fe6:Li as determined from heat capacity data at 0.78 K (solid lines). The dotted lines simulate the LC mechanism.

states must vanish at  $B_{c1}$ ,  $B_{c2}$ , etc., i.e., true LC must be observed (Fig. 1) [4]. Several calculations of energy levels in ferric wheels indeed found true level crossings between  $|S, -S\rangle$  and  $|(S+1), -(S+1)\rangle$  levels [1,3,5]. However, in noncentrosymmetric rings, terms in  $\mathcal{H}'$  (such as Dzyaloshinski-Moriya interaction)—which have been usually neglected so far—are able to mix these states, thus leading to level anticrossings (LAC). The anomalous width of magnetization or torque steps at low temperature [6] can be considered as a possible hint for LAC in an antiferromagnetic ring. We demonstrate in this Letter that heat capacity measurements are a new, more powerful, tool to establish the existence of LAC.

$[\text{LiFe}_6(\text{OCH}_3)_{12}(\text{dbm})_6]\text{B}(\text{C}_6\text{H}_5)_4 \cdot 5\text{CH}_2\text{Cl}_2$  (Fe6:Li in short) single crystals were prepared and characterized as described in Ref. [7]. In all the experiments, the  $a^*$  axis of the selected single crystal (typically  $2.0 \times 1.5 \times 0.3 \text{ mm}^3$ ) was aligned along the external magnetic field  $\mathbf{B}$ . In this way the angle between  $\mathbf{B}$  and the normal to the molecular plane is about  $25^\circ$ . Torque and heat capacity measurements were performed by using a  $^3\text{He}$  cryostat in a 28 T magnet. Microcalorimeters were made of  $4 \times 4 \text{ mm}^2$  Si or sapphire substrates and a Lake Shore Cernox 1030 bare chip thermometer was directly glued to the  $bc$  face of the single crystal. The calorimeters were mounted on top of a CuBe cantilever [6] in order to perform heat capacity and torque measurements simultaneously on the same crystal. Since the quantity of interest was the relative change of the heat capacity  $\Delta C$  at fixed  $T$  and variable  $B$  (for the absolute value of the heat capacity, see Ref. [8]), the  $ac$  method was used at low frequency  $f$  ( $\sim 1 \text{ Hz}$ ) and  $\Delta C$  was simply estimated from the expression  $\Delta C \sim P/(fT_{ac})$ , where  $P$  is the power dissipated by the heater and  $T_{ac}$  is the amplitude of the temperature  $ac$  response.  $^1\text{H}$  NMR measurements were performed at  $T = 1.5$  and  $3.0 \text{ K}$  as a function of magnetic field. The nuclear spin-lattice relaxation rate ( $1/T_1$ ) was measured by monitoring the recovery of the nuclear magnetization with a sequence of  $90^\circ$ – $180^\circ$  reading pulses after saturation with a comb of four ( $90^\circ$ ) pulses. The recovery of the nuclear magnetization  $M_N$  was found to be nonexponential at all fields. However, the exponential behavior was always verified for values  $n(t) = 1 - M_N(t)/M_N(\infty) > k = 0.3$  (far from the crossing field  $k = 0.05$  or lower). So, from the slope of  $n(t)$  for  $t \rightarrow 0$  we were able to extract an average spin-lattice relaxation rate which we called  $1/T_1$ .

Figure 2 shows the torque signal ( $\tau$ ) as a function of  $B$  and its derivative ( $d\tau/dB$ ) measured at  $0.78 \text{ K}$ . The step-like  $\tau$  vs  $B$  curve as well as the peaks in  $d\tau/dB$  indicate that levels cross each other at magnetic field values  $B_{c1} \approx 11.7 \text{ T}$  and  $B_{c2} \approx 22.4 \text{ T}$  [6,9]. No time-dependent phenomena were observed for sweeping rates up to  $0.06 \text{ T/s}$ . The two  $d\tau/dB$  peaks have quite different full width at half maximum (FWHM), namely,  $2.47 \pm 0.01$  and  $3.04 \pm 0.02 \text{ T}$  at  $B_{c1}$  and  $B_{c2}$ , respectively. Note that the measured FWHM is larger than the expected thermal width ( $2.05 \text{ T}$ )

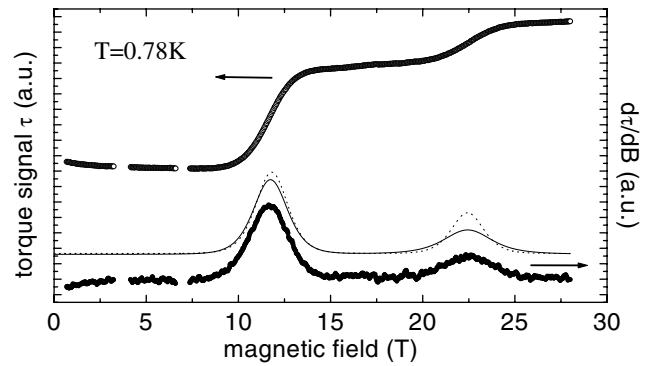


FIG. 2. Torque data  $\tau$  (open circles) and their derivative ( $d\tau/dB$ ) (solid circles) measured at  $0.78 \text{ K}$  on a Fe6:Li single crystal. Calculated derivative  $d\tau/dB$  with (without) LAC is shown as a solid (dotted) line.

at  $0.78 \text{ K}$  [6]. Since this discrepancy was systematically found in other crystals of the same and similar molecular clusters [6,10], *nonthermal broadening* is clearly present.

Heat capacity measurements are shown in Fig. 3. At  $0.78 \text{ K}$ , two pronounced peaks are observed at  $10.4$  and  $13.0 \text{ T}$ , with a relative minimum at  $B_{c1} \approx 11.7 \text{ T}$  while a single broad peak is present at about  $B_{c2} \approx 22.4 \text{ T}$ . The observed behavior can be understood by recalling that a two-level Schottky anomaly  $C_S = (\Delta/k_B T)^2 \times \exp(\Delta/k_B T) [1 + \exp(\Delta/k_B T)]^{-2}$  is expected to reach a maximum when  $\Delta \approx 2.5k_B T$ . Near  $B_{cn}$  the energy separation between the two lowest-lying states is approximately given by  $\Delta(B) = g\mu_B |B_{cn} - B|$  and two peaks must arise at  $B \approx B_{cn} \pm 2.5k_B T/g\mu_B$ , while, most importantly,  $C_S$  must vanish at  $B_{cn}$  if the two levels are degenerate ( $\Delta = 0$ ). The peak positions predicted by this model agree with experimental data but the measured heat capacity *does not vanish* at either  $B_{c1}$  or  $B_{c2}$ . We first check whether this effect can be extrinsic, i.e., due to unavoidable sample inhomogeneity and/or crystal mosaicity which lead to a possible distribution of  $B_{cn}$  values within the specimen. We have simulated this effect by using a

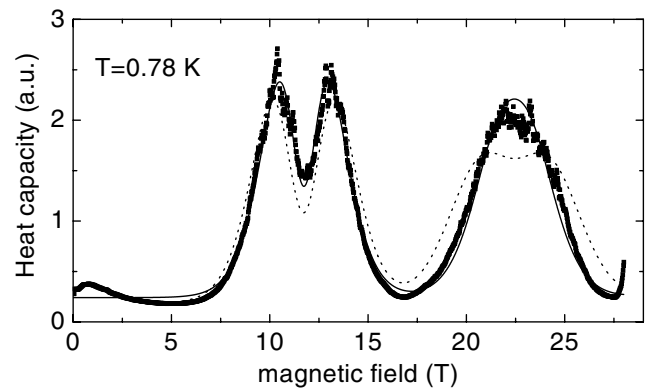


FIG. 3. Heat capacity of Fe6:Li measured at  $0.78 \text{ K}$ . Calculated  $\Delta C$  vs  $B$  with LAC is shown as a solid line. The dotted line provides the best fit to experimental data by assuming a Gaussian distribution of  $B_{cn}$  (see text).

simple four-state model with  $S$  up to 3 and by assuming Gaussian distributions of  $B_{c1}$  and  $B_{c2}$  around central values  $B_{c1}(0)$  and  $B_{c2}(0)$  with standard deviations  $\sigma_1$  and  $\sigma_2$ , respectively [11]. The  $\Delta C$  vs  $B$  data were fitted by treating  $B_{cn}(0)$  and  $\sigma_n$  as adjustable parameters, obtaining  $B_{c1}(0) = 11.72 \pm 0.02$  T,  $B_{c2}(0) = 22.46 \pm 0.04$  T,  $\sigma_1 = 0.62 \pm 0.02$  T, and  $\sigma_2 = 1.14 \pm 0.05$  T with an overall scale factor (Fig. 3). This model actually predicts nonzero heat capacity at  $B_{cn}$ , but does not fit well the high-field behavior (see Fig. 3). Moreover the  $\sigma_1$  and  $\sigma_2$  values required to justify the finite  $\Delta C$  value at  $B_{cn}$  are larger than what we expect from torque data [6,10]. Thus, although extrinsic factors may have some effects at  $B_{cn}$ , we believe that the origin of such a large  $\Delta C$  value at  $B_{cn}$  must be substantially intrinsic and in the following we discuss the effects of LAC to support this conjecture. In the simplest case, the energy gap varies as  $\Delta(B) = \{[g\mu_B(B_{cn} - B)]^2 + 4K_n^2\}^{1/2}$ , where  $K_n$  is the matrix element connecting the two states involved and the minimum energy gap  $\Delta_n = 2K_n$  is reached at  $B_{cn}$ . This model is able to reproduce the experimental behavior in the whole field range (solid line in Fig. 3) with the following best-fit parameters:  $B_{c1} = 11.81 \pm 0.01$  T,  $B_{c2} = 22.43 \pm 0.01$  T,  $K_1 = \langle 1, -1 | \mathcal{H}' | 0, 0 \rangle = 0.43$  K ( $0.299 \pm 0.003$  cm $^{-1}$ ), and  $K_2 = \langle 2, -2 | \mathcal{H}' | 1, -1 \rangle = 1.18$  K ( $0.820 \pm 0.005$  cm $^{-1}$ ) at  $T = 0.78$  K. The pattern of spin levels resulting from these parameters is depicted in Fig. 1 (solid lines). Note that the energy gap  $\Delta_n = 2K_n$  values are strikingly large, being 0.86 and 2.36 K at  $B_{c1}$  and  $B_{c2}$ , respectively. It is worthwhile to stress that with the same set of parameters we can also reproduce the experimental FWHM's of  $d\tau/dB$  curves in Fig. 2, in agreement with the LAC model. Because of the difficulty of these experiments, it was not possible to carry out a systematic angular and temperature dependence of the energy gap. We just mention that, with increasing temperature the  $\Delta_1$  value changes very little ( $\Delta_1/k_B = 0.94$  K at 1.20 K), while  $\Delta_2$  diminishes ( $\Delta_2/k_B = 1.32$  K at 1.20 K). The variation of  $\Delta_2$  is not explained at this point.

The proton spin-lattice relaxation rate ( $1/T_1$ ) as a function of the magnetic field at 1.5 and 3 K is shown in Fig. 4. A pronounced maximum of  $1/T_1$  is observed at about 11.7 T as the ground state changes from  $S = 0$  to  $S = 1$ . The FWHM of the bell-shaped curve is about 1.3 T at 1.5 K and is essentially the same at 3 K, while  $1/T_1$  increases by a factor of  $\sim 3.5$  from 1.5 to 3 K. In the presence of true LC ( $\Delta_1 = 0$ ), there are two magnetic field values for which the tunnel splitting  $\Delta = g\mu_B|(B_{c1} - B)|$  matches the  $^1\text{H}$  Zeeman energy  $\hbar\omega_L$ . At these two field values, one expects a large enhancement of  $1/T_1$  due to cross relaxation between the electronic and nuclear reservoirs [12]. Experimentally we observe only a single broad maximum of  $1/T_1$  instead of the two sharp maxima (separated by about 0.035 T) expected in the hypothesis of true LC. One could argue that the two maxima are present but not resolved because of the large width of the  $1/T_1$  peak.

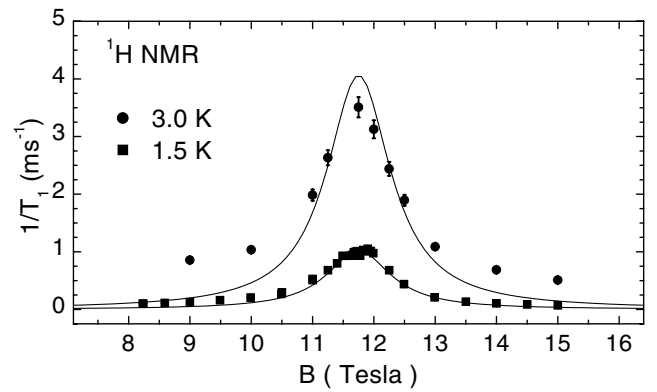


FIG. 4. Proton spin-lattice relaxation rate as a function of magnetic field at two temperatures. The curves are the results of fits (circles,  $T = 3$  K; squares,  $T = 1.5$  K) with the phenomenological model described in the text.

Among possible origins of broadening are lifetime effects due to spin-phonon coupling and intermolecular dipolar and/or hyperfine interactions. The former can be ruled out because the FWHM is  $T$  independent. The latter are estimated to yield a broadening of about 0.2 T, which is much less than the observed one of 1.3 T (Fig. 4). Moreover, inhomogeneous broadening due to a distribution of LC fields is strongly reduced in single crystals as compared with powders [12] and cannot account for the observed width. Clearly, the width and the  $T$  dependence of  $1/T_1$  vs  $B$  in a Fe6:Li single crystal cannot be reconciled with the simple picture of cross relaxation proposed for Fe10 [12].

On the other hand, a simple scenario based on LAC may explain the data. In this case, we expect that the fluctuations of the magnetization between the two adjacent magnetic states will drive the relaxation which can generally be expressed as  $1/T_1 = A^2 J(\omega_L)$ , where  $J(\omega_L)$  is the spectral density of the fluctuations at the nuclear Larmor frequency and  $A$  is an average hyperfine coupling constant [13]. In a phenomenological model, we assume  $J(\omega_L) = \Gamma / [\Gamma^2 + (\hbar\omega_L - \Delta)^2]$ , where  $\Gamma$  is a  $T$ -dependent damping factor associated with level broadening. We write  $\Delta = \{[g\mu_B(B_{c1} - B)]^2 + \Delta_1^2\}^{1/2}$ , where  $B_{c1} = 11.81$  T and  $\Delta_1/k_B = 0.86$  K from heat capacity data. In the absence of detailed knowledge of the spin-lattice relaxation mechanisms as a function of  $T$ , it is difficult to predict the  $T$  range in which the chosen  $J(\omega)$  may be correct. Its low  $\omega$  part should, however, provide a reasonable parametrization of the data close to  $B_{c1}$  even for  $T$  somewhat above  $\Delta_1$ , because the next excited state lies 10 K above the crossing (see Fig. 1). This phenomenological model gives a reasonable fit of  $1/T_1$  data around the maximum (see Fig. 4) by choosing  $A = 8.5 \times 10^7$  rad s $^{-1}$  and a damping factor varying quadratically with temperature  $\Gamma \propto T^2$  [14]. It is noted that the  $T$ -dependent broadening  $\Gamma$  of the magnetic levels is small ( $\Gamma = 0.26$  T at 3 K) and thus it affects only the magnitude of  $1/T_1$ , while the width of the  $1/T_1$  peak is determined by the gap  $\Delta_1$ . The proton relaxation in the

vicinity of  $B_{c1}$  can thus be explained with a phenomenological model based on a direct relaxation process whereby the fluctuations of the local hyperfine field are dominated by an effective frequency which is related to the splitting of the magnetic levels at LAC plus a small damping factor  $\Gamma$ . According to Meier and Loss,  $\Delta_1$  is the tunneling frequency of the Néel vector. It would be interesting in the future to investigate the possible relationship between the decoherence factor and our  $\Gamma$  [3].

In conclusion, specific heat measurements in Fe6:Li under magnetic field show the presence of level anticrossings in the ground state. Torque and NMR measurements can be explained using the minimum gap energy extracted from specific heat data. The presence of LAC cannot be reconciled with the centrosymmetric structure of the cluster as determined from single-crystal x-ray diffraction at 193 K. So we need to assume a distorted molecule at 1 K. One may wonder, for instance, whether ring-shaped clusters are thermodynamically unstable with respect to spin-Peierls-like distortions which eventually lead, at low temperature, to alternating coupling constants. For a distorted molecule, terms in  $\mathcal{H}'$  (such as Dzyaloshinski-Moriya interaction) are able to mix spin states  $|S, -S\rangle$  and  $|S + 1, -(S + 1)\rangle$ .

Thanks are due to A. Campana for help in NMR measurements. This work was carried out within the framework of the Progetto di Ricerca Avanzata MESMAG supported by the Istituto Nazionale per la Fisica della Materia. Experiments at the Grenoble High Magnetic Field Laboratory were supported within the framework of the Human Potential Programme of the European Union under Contract No. UPRI-1999-CT-00030.

- 
- [1] G. L. Abbati *et al.*, Chem. Eur. J. **7**, 1796 (2001); A. Caneschi *et al.*, Chem. Eur. J. **2**, 1379 (1996); K. L. Taft *et al.*, J. Am. Chem. Soc. **116**, 823 (1994).  
 [2] R. W. Saalfrank *et al.*, Angew. Chem., Int. Ed. Engl. **36**, 2482 (1997).

- [3] F. Meier and D. Loss, Phys. Rev. Lett. **86**, 5373 (2001); A. Chiolero and D. Loss, Phys. Rev. Lett. **80**, 169 (1998).  
 [4] C. K. Majumdar and D. K. Ghosh, J. Math. Phys. **10**, 1388 (1969).  
 [5] B. Normand *et al.*, Phys. Rev. B **63**, 184409 (2001).  
 [6] A. Cornia *et al.*, Angew. Chem., Int. Ed. Engl. **38**, 2264 (1999); A. Cornia *et al.*, Phys. Rev. B **60**, 12 177 (1999).  
 [7] Reaction of Hdbm (10 mmol), LiOCH<sub>3</sub> (40 mmol), and FeCl<sub>3</sub> (10 mmol) in anhydrous CH<sub>3</sub>OH (120 mL) gave an orange-yellow precipitate which was collected by filtration, washed with CH<sub>3</sub>OH, and dried under vacuum (2.8 g). The solid (0.7 g) and LiB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> · 3(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>) (0.22 g) were dissolved in 75 mL of CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (3:1) by slow evaporation; the filtered solution gave deep-red crystals in 2–3 days (85% yield based on Fe). The millimeter-sized samples used for the experiments were obtained by additional recrystallization from CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (4:1) mixtures. Crystal data at 193 K:  $a = 14.396(2)$  Å,  $b = 16.945(3)$  Å,  $c = 17.033(3)$  Å,  $\alpha = 61.21(1)^\circ$ ,  $\beta = 69.99(1)^\circ$ ,  $\gamma = 85.93(1)^\circ$ ,  $V = 3399.1(1.1)$  Å<sup>3</sup>, space group P-1,  $Z = 1$ . The crystal lattice comprises centrosymmetric [LiFe<sub>6</sub>(OCH<sub>3</sub>)<sub>12</sub>(dbm)<sub>6</sub>]<sup>+</sup> cations, B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup> anions (disordered over two positions related by an inversion center) and disordered CH<sub>2</sub>Cl<sub>2</sub> molecules. Crystallographic data have been deposited with the Crystallographic Data Centre as supplementary publication No. CCDC 179786.  
 [8] M. Affronte *et al.*, Eur. Phys. J. B **15**, 633 (2000).  
 [9] O. Waldmann *et al.*, Inorg. Chem. **38**, 5879 (1999); O. Waldmann *et al.*, Inorg. Chem. **40**, 2986 (2001).  
 [10] M. Affronte, A. Cornia, and A. G. M. Jansen (unpublished).  
 [11] As  $B_{c3}$  lies far outside the explored magnetic field range, the constraint  $B_{c3} = B_{c1}(0) + B_{c2}(0)$  was applied and the distribution of  $B_{c3}$  values was neglected. This corresponds to assuming  $E_3 = 2E_2$ , i.e., a Landé interval rule for the  $S = 2$  and  $S = 3$  states. A field-independent offset was added to account for heat capacity contributions from the lattice and from the addenda.  
 [12] M.-H. Julien *et al.*, Phys. Rev. Lett. **83**, 227 (1999).  
 [13] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1992).  
 [14]  $1/T_1$  varies as  $T^2$  between 1.5 and 10 K, probably reflecting the variation of population of the  $|2, -2\rangle$  level. This source of relaxation is not taken explicitly into account in our model, but is incorporated into the effective  $\Gamma$ .