Huge Transverse Magnetization in the Field-Induced Phase of the Antiferromagnetic Molecular Wheel CsFe$_8$

L. Schnelzer, O. Waldmann, M. Horvatić, S. T. Ochenbein, S. Krämer, C. Berthier, H. U. Güdel and B. Pilawa

$^1$Physikalisches Institut, Universität Karlsruhe (TH), 76128 Karlsruhe, Germany
$^2$Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland
$^3$Grenoble High Magnetic Field Laboratory, CNRS, BP 166, 38042 Grenoble Cedex 9, France
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The $^1$H-NMR spectrum and nuclear relaxation rate $T_1^{-1}$ in the antiferromagnetic wheel CsFe$_8$ were measured to characterize the previously observed magnetic field-induced low-temperature phase around the level crossing at 8 T. The data show that the phase is characterized by a huge staggered transverse polarization of the electronic Fe spins, and the opening of a gap, providing microscopic evidence for the interpretation of the phase as a field-induced magneto-elastic instability.

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Molecular magnetic clusters of nanometer size have received enormous attention recently because of their spectacular quantum phenomena [1]. A peculiar class of magnetic cluster is the antiferromagnetic (AFM) molecular wheel, in which magnetic metal ions are assembled in a ring-like structure [inset to Fig. 1(a)] [2]. Strong AFM Heisenberg interactions between the metal ions lead to a nonmagnetic $S = 0$ ground state and a first excited $S = 1$ state in zero magnetic field. In a field the Zeeman splitting lifts the degeneracy of the $S = 1$ level, such that a sufficiently strong field induces a level crossing (LC), where the ground state of the molecule changes from $S = 0$, $M = 0$ to $S = 1$, $M = -1$ [inset to Fig. 1(b)] [2, 3]. Due to the quasi degeneracy near the LC, the magnetism of the molecule is sensitive to weak interactions with the environment, such as the lattice vibrations or the surrounding magnetic molecules. Studying the LCs in AFM wheels is hence of broad interest as it provides experimental insight into the interplay of a mesoscopic quantum system with its environment.

The molecule $[\text{CsFe}_8\{\text{N}$(\text{CH}_2\text{CH}_2\text{O})_3\}_6]\text{Cl}$, or CsFe$_8$ in short [3], which realizes a ring of eight spin-5/2 Fe(III) ions, is particularly interesting as it is the only AFM wheel system in which magnetic torque studies revealed a phase transition below a temperature $T_c$ of about 0.7 K and in a field range of about $\pm 1.5$ T around the LC, between fields $B_{c1}$ and $B_{c2}$ [the phase diagram is sketched in the inset to Fig. 1(b)] [2, 4]. This could be a field-induced magnetic phase transition, similar to the weakly-interacting dimer compounds, such as TiCuCl$_2$, where a Bose-Einstein condensation of magnons occurs [3]. However, the prerequisite magnetic interactions between clusters are negligible in CsFe$_8$, as evidenced by the crystal structure and other arguments [2]. The novel scenario of a field-induced magneto-elastic instability, or spin Jahn-Teller effect was hence proposed [3, 4], which explained the torque data well.

In order to obtain microscopic insight into this phase, we performed a proton nuclear magnetic resonance (NMR) study of CsFe$_8$ single crystals. The $^1$H-NMR spectrum and $T_1^{-1}$ relaxation rate allow one to investigate the local spin configuration and spin dynamics, respectively, of the Fe spins in a wheel [11, 12]. The data provide the first strong experimental evidence for

FIG. 1: (color online) (a) Field dependence at $T = 105$ mK and (b) temperature dependence at $B = 8$ T of the $^1$H-NMR spectrum of CsFe$_8$. The inset in (a) shows the structure of CsFe$_8$, the left inset in (b) the energy spectrum, and the right inset in (b) the phase diagram near the level crossing; crosses indicate the $(B, T)$ values for which spectra are shown.
Crystals of CsFe₈·5CHCl₃·0.5H₂O were synthesized following [3]. The space group is P2₁/n; the molecules exhibit approximate C₄ symmetry along the wheel or crystal c axis. The NMR measurements were performed at the Grenoble High Magnetic Field Laboratory. The single-crystal samples were mounted in the mixing chamber at the Grenoble High Magnetic Field Laboratory. The crystals of CsFe₈ exhibit approximate C₄ symmetry along the wheel or crystal c axis. The NMR measurements were performed at the Grenoble High Magnetic Field Laboratory. The single-crystal samples were mounted in the mixing chamber at the Grenoble High Magnetic Field Laboratory. The crystals of CsFe₈ exhibit approximate C₄ symmetry along the wheel or crystal c axis. The NMR measurements were performed at the Grenoble High Magnetic Field Laboratory. The single-crystal samples were mounted in the mixing chamber at the Grenoble High Magnetic Field Laboratory.

The dipolar coupling of the 96 nuclear ¹H spins and the 8 electronic Fe spins in a CsFe₈ molecule is described by the Hamiltonian [13]

\[ \mathcal{H}_{NMR} = - \sum_k \hbar \nu B \cdot \mathbf{I}_k + \sum_{k,i} \mathbf{D}_{ki} \cdot \mathbf{S}_i, \]

where \( k \) refers to the protons and \( i \) to the Fe ions, and \( \nu, \mu = x, y, z \). The first, dominant term is the nuclear Zeeman energy. The second term represents the dipolar coupling between the ¹H nuclear spins \( \mathbf{I}_k \) and Fe spins \( \mathbf{S}_i \), where \( \mathbf{R}_{ki} \) denotes the distance vector between the two spins, which is known from the crystal structure. The chemical shift at each proton site can be omitted as it is completely negligible compared to the huge spectral broadening in the field-induced phase. Also, the \( a \) priori unknown transferred hyperfine coupling has been neglected; we will come back to this later in the discussion.

In a strong magnetic field, and at zero temperature, the resonance frequency of the \( k \)th proton is shifted with respect to \( \nu_0 \) by

\[ \delta \nu_k = - \sum_i D_{ki}^z \langle B|\hat{S}_{iz}|B \rangle - \sum_i D_{ki}^x \langle B|\hat{S}_{ix}|B \rangle. \]

Here, \( z \) denotes the magnetic field direction, and \( |B \rangle \) the (field-dependent) ground state of CsFe₈. The \( x \) and \( y \) directions were chosen such that \( \langle B|\hat{S}_{iy}|0 \rangle = 0 \). The first term in Eq. (3) reflects the shift due to a longitudinal magnetic polarization, and the second one that due to a transverse polarization. It is noted that the spin polarization detected by NMR is static on the time scale of the NMR experiment [13].

At low fields, CsFe₈ is non-magnetic and the shifts \( \delta \nu_k \) are zero. At high fields, the molecule is in the \( S = 1 \) state, which is characterized by a uniform longitudinal polarization of size \( 1/8 \mu_B \) on each Fe ion, i.e., \( \langle B|\hat{S}_{iz}|B \rangle = -1/8 \) and \( \langle B|\hat{S}_{ix}|B \rangle = 0 \). The smallest distance between a proton and an Fe ion in CsFe₈ is 3.05 Å; the shift by the longitudinal polarization is thus bounded above by 0.7 MHz, in perfect accordance with the experiment at high fields. The bound, however, implies that the ten times broader NMR spectra observed in the field-induced phase cannot be accounted for by a magnetic contribution; therefore, the large transverse polarization has to be staggered, consistent with AFM interactions in the wheel.

The proposed field-induced magneto-elastic instability in CsFe₈.

In the following we focus on the unprecedentedly large broadening of the ¹H-NMR spectrum in the regime of the field-induced phase. It will be shown that it is a direct signature of a huge transverse magnetic polarization of the CsFe₈ molecule. Since the broadening is symmetric, the transverse polarization has to be staggered, consistent with AFM interactions in the wheel.

Figure 1 presents the ¹H-NMR spectra at 105 mK and 8 T and the deduced gap \( \Delta_0 \) (symbols), respectively, as well as the theoretical expectation (lines).

FIG. 1: (color online) ¹H-NMR spectrum at 105 mK and 8 T and the simulation. The left and right insets show the broadening of the spectrum and the deduced gap \( \Delta_0 \) (symbols), respectively, as well as the theoretical expectation (lines).

FIG. 2: (color online) ¹H-NMR spectrum at 105 mK and 8 T and the simulation. The left and right insets show the broadening of the spectrum and the deduced gap \( \Delta_0 \) (symbols), respectively, as well as the theoretical expectation (lines).
for by a longitudinal polarization. A transverse polarization is hence considered. This component can be indeed obtained by a mixing of the two states at the LC, which will be denoted as $|0\rangle$ and $|1\rangle$, see left inset to Fig. 3(b). We write $|B\rangle = \alpha |0\rangle + \beta |1\rangle$, with $\alpha^2 + \beta^2 = 1$. At zero temperature the longitudinal polarization is then $\langle B | \hat{S}_{iz} | B \rangle = \beta^2 \langle 1 | \hat{S}_{iz} | 1 \rangle$. The mixing, however, also induces a transverse polarization $\langle B | \hat{S}_{iz} | B \rangle = 2\alpha\beta \langle 0 | \hat{S}_{iz} | 1 \rangle$.

The matrix elements were evaluated as follows. First, for $\langle 1 | \hat{S}_{iz} | 1 \rangle$ and $\langle 0 | \hat{S}_{iz} | 1 \rangle$ one has to solve the (electric) spin Hamiltonian of CsFe$_2$, $\hat{\mathcal{H}} = -J \sum_i \hat{S}_i \cdot \hat{S}_{i+1} + D \sum_i \hat{S}_i^2 + \mu_B \mathbf{B} \cdot \mathbf{S}$, which consists of the AFM nearest-neighbor Heisenberg interactions in the wheel $(J = -21.5 \text{ K})$, the easy-axis single-ion anisotropy $(D = -0.55 \text{ K})$, and the electronic Zeeman term $(\mathbf{S} = \sum_i \hat{S}_i)$ [14]. This was achieved by numerical diagonalization of $\hat{\mathcal{H}}$ in the two-sublattice approximation (which works excellently for the states relevant here) [14], for given field $B$ and orientation $\varphi$. Then, the local spin matrix elements were evaluated for given $\alpha, \beta$. In order to mimic the field-induced phase, the mixing was chosen such that $\beta^2$ is zero for fields below $B_{c1}$, increases linearly with field from 0 to 1 in the range $B_{c1}$ to $B_{c2}$, and is 1 above $B_{c2}$. This ensures that outside the range $[B_{c1}, B_{c2}]$ the mixing (and transverse polarization) is zero. The linear increase between $B_{c1}$ and $B_{c2}$ is suggested by the experimentally observed linear increase of the magnetization in the field-induced phase, i.e., of $-\langle B | \hat{S}_z | B \rangle = -\beta^2 \sum_i \langle 1 | \hat{S}_{iz} | 1 \rangle$. At exactly the LC field, $\beta^2 = 1/2$ and mixing is maximal.

The upper panels in Fig. 3 present the calculated contributions of the longitudinal and transverse polarizations to the NMR shifts $\delta\nu_k$. The curves in the lower panels of Fig. 3 were obtained from the data in the upper panels by convolution with a Gaussian to account for the NMR line width. For the longitudinal polarization, the calculation yields asymmetric shifts of at most 0.6 MHz, in accordance with the above bound. In the low-field regime, the spectrum consists of a narrow peak. With increasing field the central line is slightly shifted and a weak shoulder develops, in very good agreement with the experiments outside the field-induced phase. As regards the transverse polarization, the calculation reveals very large shifts of up to 7 MHz, which build up quickly even for small mixing. For comparison with experiment, the shifts produced by the longitudinal and transverse polarization have to be added. The result at the LC field, after convolution with a Gaussian, is shown in Fig. 3.

The comparison of experiment and simulation in Fig. 3 shows an excellent agreement, providing a reliable proof of the spin configuration in the field-induced phase. It is noted that the central peak in the experimental spectra is mostly due to the protons in the solvent (outside the ring molecules), which were omitted in the simulation. We want to stress that the calculations did not involve any free parameter, besides assuming $\alpha = \beta$, which is certainly reasonable at the LC. The calculated transverse polarization is staggered with a magnitude of 1.7 per Fe center (in units of $g\mu_B$). This is a stunning 27 times larger than the longitudinal polarization of $\beta^2/8 = 1/16$. Roughly speaking, the transverse component is built up by almost the complete spin (5/2) at each site, while the longitudinal component comes from $S = 1 \times (3\beta^2)$ distributed over 8 sites. For comparison, in spin-1/2 dimer systems such as TiCuCl$_3$, in which also a $S = 0$ and $S = 1$ level mix, but because of very different physics [9], the transverse polarization is at most 0.35, a mere 1.4 times larger than the longitudinal polarization of $0.25 \times [10]$. Interestingly, also for $D = 0$ a large transversal magnetization of 1.1 per Fe is calculated. Hence, the essential factor in the huge broadening of the NMR spectrum is not $D$, but the mixing of the $|0\rangle$ and $|1\rangle$ levels. However, the magnetic anisotropy is the key element in a field-induced magneto-elastic instability [6], and the size of $D$ may be the crucial factor for the existence of the field-induced phase in CsFe$_2$ in the first place.

Some discrepancies between the observed and simulated spectra can be noted in Fig. 3. One possible reason could be a transferred hyperfine coupling, which was neglected in Eq. 1. This coupling is isotropic, and its transverse component hence zero. Therefore, it does not contribute to the dominating transverse component of the calculated NMR spectrum [shown in Fig. 3(d)]. It will, however, contribute to the much smaller longitudinal component [shown in Fig. 3(c)], and thus may slightly modify the details of the final calculated spectrum. A second reason could be the (implicit) assumption of a structurally symmetric wheel in the spin Hamiltonian $\hat{\mathcal{H}}$. Some weak distortion of the real molecule, either due
We now turn to the temperature dependence of the $^1$H nuclear $T_1^{-1}$ relaxation rate. The $T_1^{-1}$ rate is mainly driven by the fluctuations of the Fe spins [11, 12], somewhat modified (homogenized) by the nuclear spin diffusion mechanism [13]. The $T_1^{-1}$ data measured at the LC field are shown in Fig. 4. One set of data points was recorded at the central line at 340.15 MHz. Three different regimes can be identified. Above $T_c$, $T_1^{-1}$ is almost constant, with a small decrease towards lower temperatures, as expected for any high-temperature regime. At $T_c$, the relaxation rate drops significantly, indicating the transition to the field-induced phase. The drop is enhanced by a strong reduction of the nuclear spin diffusion due to the huge broadening of the NMR spectrum. Below about $0.5T_c$, the $T_1^{-1}$ rate shows a thermally activated behavior, $T_1^{-1} \propto \exp[-E_A/(kB T)]$, with an activation energy of $E_A = 2.0(1)$ K.

In order to confirm that the $T_1^{-1}$ data at the central peak represent the field-induced phase well, some control values were measured at 337.40 MHz, i.e., in the wing of the NMR spectrum, which exists only in the field-induced phase. The same temperature dependence was well reproduced by an effective two-level Hamiltonian, which includes the important non-diagonal magneto-elastic couplings [6, 8]. The key prediction of this model is a mixing of the two levels and a concomitant opening of an energy gap in the field-induced phase. The observed huge broadening of the NMR spectrum was shown in the above to be directly related to a strong transverse polarization due to a mixing of the two lowest spin states. These measurements hence provide a direct microscopic confirmation of the level mixing in the field-induced phase. Furthermore, the model predicts a thermally activated behavior at low temperatures, with an activation barrier equal to the energy gap. At the LC, the model predicts a gap of $\Delta_{\text{max}} = g\mu_B(B_{c2} - B_{c1})/2$. For our sample this implies a gap of 2.2 K, which is in excellent agreement with the activation energy $E_A = 2.0$ K deduced from the $T_1^{-1}$ measurement.

Either one of the features: broadening, transverse polarization, or mixing may be considered as the order parameter of the phase transition. Within a two-level Hamiltonian description, these features are related to a gap parameter $\Delta_0 = 2(0)\hbar/\{1\}$, which is most conveniently taken as the order parameter. The field dependence of the broadening of the NMR spectra at 105 mK, and the $\Delta_0$ determined from it, are presented in the insets to Fig. 2. They show how the field-induced phase develops as a function of field, in very good agreement with the model predictions. Furthermore, the model provides a (rough) estimate of $T_c$, $k_B T_c = \Delta_{\text{max}}^2/2$, which is also consistent with experiment. It is remarked that an energy gap at the LC of 2 K represents a rather strong effect on the magnetic degrees of freedom in CsFe$_8$; this value should be compared to the gap of 6 K in zero field [inset to Fig. 1(b)].

In summary, we studied the field and temperature dependence of the $^1$H-NMR spectrum and $T_1^{-1}$ relaxation rate in a single crystal of the molecular wheel CsFe$_8$ in the field-induced low-temperature phase around the level crossing at 8.0 T. The NMR data unambiguously demonstrated that this phase is characterized by (i) a huge broadening of the $^1$H-NMR spectra due to a huge staggered transverse polarization of the Fe spins, and (ii) an energy gap of 2.0 K at the level crossing. These findings provide strong microscopic evidence for the previously proposed model of a field-induced magneto-elastic instability. Future work should attempt the direct measurement of structural distortions and determination of the relevant vibration modes and spin-phonon coupling constants. Also, a microscopic theory is lacking.

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