Field-induced magnetoelastic instabilities in antiferromagnetic molecular wheels

O. Waldmann,1,2 C. Dobe,1 S. T. Ochsenbein,1 H. U. Güdel,1 and I. Sheikin2

1Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland
2Grenoble High Magnetic Field Laboratory, CNRS, 38002 Grenoble, France

(Dated: March 23, 2022)

The magnetic torque of the antiferromagnetic molecular wheel CsFe₈ was studied down to 50 mK and in fields up to 28 T. Below ca. 0.5 K phase transitions were observed at the field-induced level-crossings (LCs). Intermolecular magnetic interactions are very weak excluding an explanation in terms of field-induced magnetic ordering. A magneto-elastic coupling was considered. A generic model shows that the wheel structure is unconditionally unstable at the LCs, and the predicted torque curves explain the essential features of the data well.

PACS numbers: 33.15.Kr, 71.70.-d, 75.10.Jm

Antiferromagnetic (AF) molecular wheels attracted huge attention recently because of their peculiar quantum properties. These molecules are characterized by a ring-like arrangement of magnetic metal ions; the ferric wheel [CsFe₈(N(CH₂)₂CH₂O)₈]Cl, or CsFe₈, studied in this work is shown in Fig. 1(a). The ions within a wheel experience AF nearest-neighbor Heisenberg interactions, and the molecule’s ground state at zero magnetic field is nonmagnetic with total spin $S = 0$. The next higher lying states belong to $S = 1, 2$, etc. In a magnetic field these states split due to the Zeeman interaction, leading to a series of level crossings (LCs) at characteristic fields at which the ground state changes from the $S = 0, M = 0$ level to the $S = 1, M = -1$ level, the $S = 2, M = -2$ level, and so on, see inset of Fig. 1(b). The magnetization curve at low temperatures thus exhibits a staircase-like field dependence, with a step at each LC. In this work we report field-dependent measurements of the magnetic torque on CsFe₈, which show clear indications of phase transitions at the LCs at low temperatures.

The observed anomalies at the LCs could be due to weak magnetic interactions between the molecules in the sample (intermolecular interactions). Since at low temperatures AF wheels behave like dimers, this would place CsFe₈ in the context of weakly-interacting dimer compounds, such as TlCuCl₃, which may exhibit Bose-Einstein condensation of magnons. Observation of such phenomena in a crystal of molecular wheels would be of great interest, but in CsFe₈ intermolecular interactions are very weak excluding such a scenario.

The degeneracy at the LCs suggests a Spin-Peierls type of effect as an alternative, in which the degeneracy is lifted due to a coupling of the spin system to the lattice. CsFe₈ is well described by the spin Hamiltonian

$$\hat{H} = -J \left( \sum_{i=1}^{7} \hat{S}_i \cdot \hat{S}_{i+1} + \hat{S}_8 \cdot \hat{S}_1 \right) + g \mu_B \hat{S} \cdot \hat{B} + \hat{H}_A,$$

which includes the Heisenberg and Zeeman terms ($J = -20.6$ K, $g = 2$), and a term $\hat{H}_A$ describing a weak uniaxial magnetic anisotropy, mostly due to ligand-field and dipolar interactions (the magnetic anisotropy is well described by a term $D \sum_{i=1}^{8} \hat{S}_i^2 = D = -0.56$ K and the wheel axis $z$). $\hat{S}_i$ is the spin operator of the $i$th ion with spin $s = 5/2$. Recent theoretical studies on isotropic AF spin rings ($\hat{H}_A = 0$) yielded a magneto-elastic (ME) instability in zero field for sufficiently small elastic constants, but only for rings with $s = 1/2$ [12, 13]. These conclusions hold also with applied magnetic fields since a modulation of the exchange constants along the ring cannot lift the

FIG. 1: a) Torque vs. field, $\tau(B)$, for a single crystal of 2 at 55, 100, 200, 300, and 400 mK (online colors: black, red, blue, green, magenta) ($\varphi = -3.3^\circ$). The right inset shows $d\tau/dB$ at the first LC, arrows indicate the onset of anomalies. The left inset shows the structure of CsFe₈. b) $\tau(B)$ for a single crystal of 1 at 60 and 700 mK (online colors: black, red) ($\varphi = 93.6^\circ$). The right inset shows the data as $d\tau/dB$. The left inset shows a calculated energy spectrum as function of field neglecting magnetic anisotropy ($J = -20.6$ K, arrows mark the first two LCs, the involved levels are labeled by $S,M$).
degeneracy at the field-induced LCs. However, as will be shown below, the situation changes markedly in the presence of a magnetic anisotropy, as in CsFe₈. A simple, generic model is introduced, which demonstrates that at the LCs the ring structure is unstable against distortions for any value of the spin-phonon coupling. The model reproduces the characteristic features of the data well, suggesting a ME origin of the anomalies at the LCs in CsFe₈.

Single crystals of CsFe₈ were prepared as in Ref. [6], but crystallized either from a mixture of CHCl₃ and CH₂Cl₂ by pentane vapor diffusion yielding CsFe₈·5CHCl₃·0.5H₂O (1) [14], or from ethanol by diethyl-ether vapor diffusion yielding CsFe₈·8C₂H₅OH (2) [11]. 1 (2) crystallizes in the space group P21/n (P4/n) and the molecules exhibit approximate (crystallographic) C₄ symmetry. The magnetic parameters, J and D, of the molecules are not affected by the solvents [11], but intermolecular exchange interactions, if present, should be strongly affected. The magnetic torque τ was measured with a CuBe cantilever inserted into the M10 magnet at the Grenoble High Magnetic Field Laboratory equipped with an Oxford 3He/4He dilution fridge. Background signals were negligible; only raw data are shown here. In total six single-crystal samples were investigated.

Figure 1 presents the field dependence of the torque τ of CsFe₈ at various temperatures for fields close to the uniaxial axis and almost perpendicular to it (φ denotes the angle between field and uniaxial axis z). At the highest temperatures, the curves exhibit the expected behavior: At the LC fields the torque curves display steps broadened by the effect of, e.g., temperature (a plot dτ/dB vs. B shows Gaussian-like peaks with widths Γ). For CsFe₈, the first three LCs are observed in fields up to 28 T. Normally, the steps become sharper with lower temperatures, corresponding to decreasing widths Γ, but in CsFe₈, in contrast, a very different behavior is observed at low temperatures. For fields close to the uniaxial axis, φ ≈ 0°, a dome-shaped contribution to the torque, centered at the LC fields, appears. This is apparent in Fig. 1a) for the LCs at 18 T and 25.5 T, but also the first LC at 11 T shows the anomaly, as seen in dτ/dB [inset of Fig. 1a)]. Anomalies were also observed for close to perpendicular fields, φ ≈ 90°, Fig. 1b). Here the torque exhibits a linear field dependence at the first LC at 7.7 T, but also at the higher LCs at 16.5 T and 24 T. Anomalous behavior is evident from the inset of Fig. 1b).

Figure 2a) presents dτ/dB near the first LC for φ ≈ 90° as determined from measurements at several temperatures from 55 mK to 1 K. At the higher temperatures, the curves exhibit the usual Gaussian-like field dependence, but below a critical temperature Tc, of about 0.65 K for the shown sample, a plateau corresponding to a linear field dependence in τ(B) emerges. The temperature dependencies of the lower and upper critical fields, as defined by the kinks in dτ/dB, are plotted in Fig. 2b) (the difference will be denoted as ∆B₀). The figure also displays the maximum and half-maximum field values of the Gaussian-like curves for T > Tc.

All investigated crystals showed the anomalies at the LCs, with a variation in Tc (0.35 to 0.65 K) and ∆B₀ (1.5 to 3 T). Smaller ∆B₀ corresponded to smaller Tc and vice versa. One origin for the variation seems to be a dependence of Tc and ∆B₀ on the field orientation indicated by the data. Within experimental resolution, a hysteresis was not detected.

The above torque data clearly demonstrates a phase transition at the LCs in CsFe₈. The similarity of the torque curves in Fig. 1b) with magnetization curves observed for systems exhibiting field-induced magnetic order [7] suggests to assign the anomalies in CsFe₈ to intermolecular magnetic interactions. However, this is an unlikely scenario because i) intermolecular magnetic dipole-dipole interactions are very weak (even optimistic estimates yield values < 10 mK), ii) in the crystal structures of 1 and 2 the individual molecules are well separated and no exchange pathways exist, iii) exchange interactions would strongly depend on the solvent and the details of the crystal packing, in contrast to the observation of similar critical field ranges and temperatures in crystals of 1 and 2, and iv) no indications of intermolecular interactions were found in the comparable systems [NaFe₆{N(CH₂CH₂O₃)₆}Cl·6CHCl₃ down to 0.3 K, [Fe₆{N(CH₂CH₂O₃)₆}·6MeOH down to 0.2 K,
and \([\text{NaFe(OCH}_3\text{)_{12}(C}_{17}\text{H}_{15}\text{O}_4\text{)}_{6}\text{ClO}_4]\) down to 40 mK \cite{19, 20, 21}. Intermolecular interactions on the order of several 100 mK are not apparent in CsFe₈.

In view of the degeneracy at the LCs a ME effect might be suggested. For isotropic AF spin rings such an effect is unrealistic, at least for spins \(> 1/2\) \cite{12, 13}, but, as will be shown below, with an additional magnetic anisotropy the ring structure becomes unconditionally unstable at the LCs: For a distorted ring the magnetic anisotropy allows for a mixing of the levels at a LC, resulting in an avoided LC with a gap \(\Delta\) and hence a lowering of the ground-state energy by \(\Delta/2\), which is proportional to the modulation of the anisotropy constants and thus in first approximation linear in the distortion.

Following Ref. \cite{22}, the low-\(T\) magnetic behavior near a LC is well described by the two-level Hamiltonian

\[
\hat{H}_{S,S+1} = \left( \frac{\epsilon_S}{\Delta/2} \frac{\Delta/2}{\epsilon_{S+1}} \right),
\]

where \(S\) and \(S+1\) index the two levels \(|S, -S\rangle\) and \(|S+1, -S-1\rangle\) involved in the level crossing. Here, a rotated axis system with the quantization axis parallel to the field \(B\) is used, and \(|S, M\rangle\) refers to the labels of the total spin operator in the rotated frame, \(\hat{S}_S^2\) and \(\hat{S}_S^\zeta\). \(\epsilon_S(B, \varphi)\) describes the field and angle dependence of the levels without a mixing. In first order, one obtains \(\epsilon_S(B, \varphi) = -bS + \Delta_S(\varphi)\) with the reduced field \(b = g\mu_B B\), where \(\Delta_S(\varphi)\) accounts for the exchange interactions and the zero-field splittings produced by \(\hat{H}_A\). The LC field is given by \(b_0(\varphi) = \Delta_{S+1} - \Delta_S\). A level mixing at the LC is included in the model via \(\Delta(\varphi)\), which in first order is given by \(\Delta/2 = (S, -S)\hat{H}_A^\prime|S+1, -S-1\rangle\) and is thus independent of the magnetic field (\(\hat{H}_A^\prime = \hat{H}_A\) expressed in the rotated reference frame).

The symmetry of a non-distorted ring (\(C_3\) symmetry of the spin Hamiltonian) prohibits a mixing of the levels, hence \(\Delta = 0\) \cite{16, 17}. A structural distortion induces a modulation of the exchange and anisotropy constants, which affects both \(\Delta_S\) and \(\Delta\) [the ME coupling due to \(\Delta_S(\Delta)\) will be called diagonal (non-diagonal)]. \(\Delta_S\) is not affected in first order by these modulations as it is only sensitive to the average of the exchange and anisotropy constants \cite{11}. Thus, \(\Delta_S\) varies as \(\Delta_S \propto x^2\), where \(x\) is a parameter describing the structural distortion (as usual it has been assumed that the modulation of the parameters is linear in the distortion). This is in accordance with Refs. \cite{12, 13}, and leads to similar conclusions. For the non-diagonal ME coupling, however, since it is sensitive to the amplitude of the modulations, one finds \(\Delta \propto x\) [we write \(\Delta(x) = ax\) with the ME coupling constant \(a\)]. The gain in magnetic energy is now linear in the distortion resulting in an unconditional ME instability \cite{24}. In this model, the microscopic details of the non-diagonal ME coupling are lumped into the parameter \(a\).

![Figure 3](image-url)

**FIG. 3:** Field dependence of a) the order parameter \(\Delta_0\), b) the torque contribution \(\delta\tau_1\), and c) the torque contribution \(\delta\tau_2\) around a LC at \(b_0\) [the plots were normalized to \(\alpha^2/(2k)\), \(\partial\delta\theta_0/\partial\varphi\), and \(-\partial\Delta_0/\partial\varphi\), respectively].

The change in ground-state energy due to an opening of a gap at the LC is easily calculated. Including the elastic energy, the potential \(V(x)\) of the total system is

\[
V(x) = \frac{1}{2}\sqrt{(b-b_0)^2 + \Delta(x)^2} + \frac{1}{2}(b-b_0) + \frac{1}{2}kx^2,
\]

where \(k\) is the spring constant. In the adiabatic approximation, which neglects the kinetic energy of the phonons (the validity of this approach is discussed in Ref. \cite{13}), the equilibrium distortion \(x_0\) is given by the minimum of \(V(x)\), yielding the condition

\[
(b-b_0)^2 + \Delta_0^2 = \frac{\alpha^2}{2k} \tag{4}
\]

with \(\Delta_0 = \Delta(x_0)\). Accordingly, as a function of magnetic field, the order parameter \(\Delta_0\) describes a semi circle of radius \(\alpha^2/(2k)\) around \(b_0\), see Fig. 3(a), and the system exhibits a spontaneous distortion for fields in between \(b_0 + b_c\) with \(b_c = \alpha^2/2k\).

The model permits an analytical calculation of the torque profiles at low temperature. Inserting eq. (4) into eq. (2) of Ref. \cite{22}, the change of the torque \(\delta\tau\) for magnetic fields in the critical region \(b_0 \pm b_c\) is obtained as

\[
\delta\tau(b, \varphi) = \frac{1}{2} \frac{\partial b_0}{\partial \varphi} \left[ 1 + \frac{(b-b_0)}{b_c} \right] - \frac{1}{2} \frac{\partial\Delta_0}{\partial \varphi} \frac{\Delta_0}{b_c}. \tag{5}
\]

The torque signal consists of two contributions. The first term, \(\delta\tau_1\), describes a linear increase of the torque from zero at \(b \leq b_0 - b_c\) to \(\partial\delta\theta_0/\partial\varphi\) at \(b \geq b_0 + b_c\) [Fig. 3(b)], while the second term, \(\delta\tau_2\), is proportional to the square of the order parameter, \(\delta\tau_2 \propto \Delta_0^2\) [Fig. 3(c)]. The relevance with the experimental data is obvious: the dome-shaped torque contribution produced by \(\delta\tau_2\) resembles the behavior at the LCs for \(\varphi \approx 0^\circ\), Fig. 3(a), and the slope-like contribution of \(\delta\tau_1\) that for \(\varphi \approx 90^\circ\), Fig. 3(b).

In general the torque signal in the critical region is a combination of a slope-like and a dome-shaped curve, with angle dependent relative weights. The dependence
of the LC field on $\varphi$ turns out to be $b_0(\varphi) \propto 3 \cos^2 \varphi - 1$ \cite{11}, so that the contribution of the slope-like part to the torque, which is controlled by the factor $\partial b_0 / \partial \varphi$, varies as $\cos \varphi \sin \varphi$. The variation of the contribution of the dome-shaped part with angle is more complex, since the various magnetic anisotropy terms of possible relevance may result in very different angle dependencies of $\Delta_0$. An anisotropy term $\hat{H}_D = \sum D_i (S_i^2 - S_i (S_i + 1)/3)$, for instance, gives rise to $\Delta \propto \sin^2(\varphi) \cos(\varphi)$. A Dzyaloshinskii-Moriya interaction $\hat{H}_{DM} = \sum d_i (\hat{S}_i \times \hat{S}_{i+1})$, on the other hand, is likely to arise in the course of a structural distortion because of the lowered symmetry of the ring \cite{18}, varies as $\sin(\varphi)$, so that $\partial \Delta_0 / \partial \varphi$ is important at small angles but negligible near $90^\circ$. This could explain a dominance of the dome-shaped contribution for parallel fields, and of the slope-like contribution for perpendicular fields, as observed. The details are not yet understood, and more studies are clearly needed. However, the proposed scenario is capable of explaining the different findings for nearly parallel and perpendicular fields, which in our opinion supports the idea of a ME origin of the observed anomalies in CsFe$_8$.

With $k = 10$ N/m (corresponding to a typical phonon frequency of $\omega = 100$ cm$^{-1}$ and a reduced mass $\mu \approx 14$), a $b_0$ of about 1 T implies the reasonable value $\alpha = 3$ meV/Å (in spin-Peierls systems, e.g., the coupling constant is $\approx 10|J|/d_0$ with $d_0 \approx 3.5$ Å). Concerning the stability of the distortions against thermal fluctuations, the critical temperature may be estimated from $1/2(\partial^2 V / \partial x^2)x_0^2 \approx 1/2k_B T_c$, i.e., $k_B T_c \approx b_c/2$. A critical field of about 1 T then suggests $T_c \approx 1$ K, which is on the order of the observed values. Here however it should be noted that for systems, which exhibit unconditionnal lattice instabilities, BCS type of relations between order parameter and $T_c$ are found \cite{18}. Also, strain effects between the molecules in the crystal might result in cooperativity which would help to stabilize the distorted phase \cite{24}. A realistic theory thus might have to include not only the optic but also the acoustic phonons.

In conclusion, we have studied the field dependence of the magnetic torque for the AF molecular wheel CsFe$_8$ and observed anomalies at the level-crossing fields at low temperatures. With respect to their explanation, several mechanisms were considered. Magnetic interactions between different molecules are very weak and are thus unlikely to cause the anomalies. As a second possibility, magneto-elastic instabilities were discussed. Indeed, by introducing a generic model, it has been shown that a non-diagonal magneto-elastic coupling due to a magnetic anisotropy induces structural instabilities at the LCs. The predicted torque curves allowed to explain the generic features of the experimental data, in particular the unusual dome-shaped parts for magnetic fields close to the uniaxial axis. The current work necessarily could not answer all questions, and more advanced work as well as theoretical work is needed. Of most importance would be structural measurements. On the one hand, they would allow a direct test of the above scenario, and on the other hand, would yield information about the relevant distortion modes - a crucial input for any microscopic model to be developed.

For a number of ferric wheels, evidence for gaps at the LCs has been reported \cite{18, 12, 21}. In these works, thermodynamic data were found to be better explained by assuming avoided LCs (with temperature-independent gaps). In this context it is interesting to note that the anomalies observed in CsFe$_8$s below $T_c$ are announced by an excessive broadening of the torque steps above $T_c$, see Fig. 2(b). This mimics avoided LCs, and it will be thus interesting to see whether the earlier reports of avoided LCs were not in fact first hints of the above anomalies.

Financial support by EC-RTN-QUEMOLNA, contract no MRTN-CT-2003-504880, and the Swiss National Science Foundation is acknowledged.

---

* Corresponding author.
E-mail: waldmann@iac.unibe.ch

1. K. L. Taft et al., J. Am. Chem. Soc. 116, 823 (1994).
2. D.Gatteschi et al., Science 265, 1054 (1994).
3. A. Chiovero and D. Loss, Phys. Rev. Lett. 80, 169 (1998).
4. O. Waldmann et al., Phys. Rev. Lett. 91, 237202 (2003).
5. O. Waldmann et al., Phys. Rev. Lett. 95, 057202 (2005).
6. R. W. S~aalfrank et al., Angew. Chem. Int. Ed. Engl. 36, 2482 (1997).
7. A. Cornia et al., Angew. Chem. Int. Ed. Engl. 38, 2264 (1999).
8. O. Waldmann et al., Inorg. Chem. 38, 5879 (1999).
9. T. Nikuni et al., Phys. Rev. Lett. 84, 5868 (2000).
10. C. Rüegg et al., Nature 423, 62 (2003).
11. O. Waldmann et al., Inorg. Chem. 40, 2986 (2001).
12. L. Spanu and A. Parola, Phys. Rev. Lett. 92, 197202 (2004).
13. M. Elhajal and F. Mila, cond-mat/0503017.
14. Details of synthesis and structure will be given elsewhere.
15. Y. Ajiro et al., J. Phys. Soc. Jap. 58, 1021 (1989).
16. F. Meier and D. Loss, Phys. Rev. B 64, 224411 (2001).
17. O. Waldmann, Europhys. Lett. 60, 302 (2002).
18. M. Affronte et al., Phys. Rev. Lett. 88, 167201 (2002).
19. O. Waldmann et al., Phys. Rev. Lett. 89, 246401 (2002).
20. B. Pilawa et al., Phys. Rev. B 71, 184419 (2005).
21. F. Cinti, M. Affronte, and A. G. M. Jansen, Eur. Phys. J. B 30, 461 (2002).
22. O. Waldmann et al., Phys. Rev. Lett. 92, 096403 (2004).
23. A formal analogy of the model with the Jahn-Teller effect should be noted, see e.g. Ref. \cite{24}. This suggests to call it a spin-Jahn-Teller effect.
24. G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. 38, 1 (1975).
25. For CsFe$_8$, because of its rather large $D/J$ ratio, the linear approximation for the field dependence does not provide truly quantitative results (a quadratic field term would have to be included), but the model qualitatively grasps all essential features correctly.