Field-Induced Magnetoelastic Instabilities in Antiferromagnetic Molecular Wheels

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The magnetic torque of the antiferromagnetic molecular wheel $CsFe_8$ was studied down to 50 mK and up to 28 T. Below about 0.5 K phase transitions were observed at the field-induced level crossings (LCs). Intermolecular magnetic interactions are very weak excluding field-induced magnetic ordering. A magnetoelastic 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.

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Antiferromagnetic (AFM) molecular wheels have attracted a huge amount of attention recently because of their peculiar quantum properties [1–5]. These molecules are characterized by a ringlike arrangement of magnetic metal ions; the ferric wheel $[CsFe_8\{N(CH_2CH_2O)_3\}_8]Cl$, or $CsFe_8$ [6], studied in this work is shown in Fig. 1(a). The ions within a wheel experience AFM 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 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) [1,7,8]. The magnetization curve at low temperatures thus exhibits a staircaselike field dependence, with a step at each LC. In this Letter we report field-dependent measurements of the magnetic torque on $CsFe_8$, 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 AFM wheels behave like dimers [4], this would place $CsFe_8$ in the context of weakly interacting dimer compounds, such as $TlCuCl_3$, which may exhibit Bose-Einstein condensation of magnons [9,10]. Observation of such phenomena in a crystal of molecular wheels would be of great interest, but in $CsFe_8$ 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. $CsFe_8$ is well described by the spin Hamiltonian [5,11]

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

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 $D\sum_{i=1}^{8} \hat{S}_{i,z}^2$ with $D = -0.56$ K and the wheel axis z). $\hat{\mathbf{S}}_i$ is the spin operator of the ith ion with spin $s = 5/2$. Recent theoretical studies on isotropic AFM spin rings ($\hat{H}_A = 0$) yielded a magnetoelastic (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 degeneracy at the field-induced LCs. However, as will be

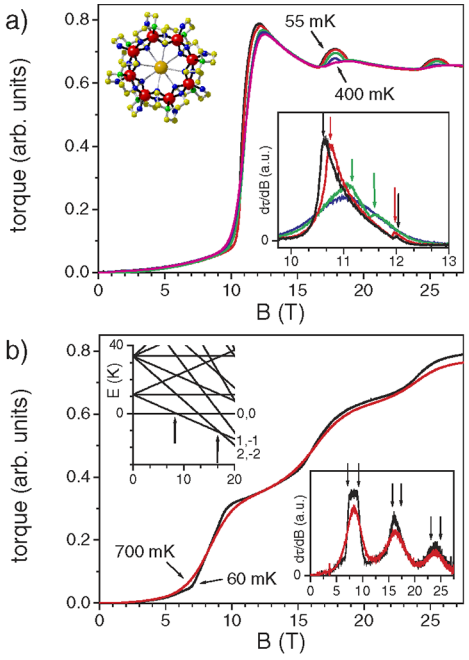

FIG. 1 (color online). (a) Torque vs field, $\tau(B)$, for a single crystal of **2** at 55, 100, 200, 300, and 400 mK (black, red, blue, green, magenta) ($\varphi = -3.3°$). The right inset shows $d\tau/dB$ at the first LC, arrows indicate the onset of anomalies. The left inset shows the structure of $CsFe_8$. (b) $\tau(B)$ for a single crystal of **1** at 60 and 700 mK (black, red) ($\varphi = 93.6°$). 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).

shown below, the situation changes markedly in the presence of a magnetic anisotropy, as in $CsFe_8$. 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 $CsFe_8$.

Single crystals of $CsFe_8$ were prepared as in Ref. [6], but crystallized either from a mixture of $CHCl_3$ and CH_2Cl_2 by pentane vapor diffusion yielding $CsFe_8 \cdot 5CHCl_3 \cdot 0.5H_2O$ (**1**) [14], or from ethanol by diethylether vapor diffusion yielding $CsFe_8 \cdot 8C_2H_5OH$ (**2**) [11]. **1**(**2**) crystallizes in the space group $P21/n(P4/n)$ and the molecules exhibit approximate (crystallographic) C_4 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 $CsFe_8$ 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 $d\tau/dB$ vs B shows Gaussian-like peaks with widths Γ). For $CsFe_8$, 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 $CsFe_8$ a very different behavior is observed at low temperatures. For fields close to the uniaxial axis, $\varphi \approx 0°$, a dome-shaped contribution to the torque, centered at the LC fields, appears. This is apparent in Fig. 1(a) for the LCs at 18 and 25.5 T, but also the first LC at 11 T shows the anomaly, as seen in $d\tau/dB$ [inset of Fig. 1(a)]. Anomalies were also observed for close to perpendicular fields, $\varphi \approx 90°$, Fig. 1(b). Here the torque exhibits a linear field dependence at the first LC at 7.7 T, but also at the LCs at 16.5 and 24 T anomalous behavior is evident, see the inset of Fig. 1(b).

Figure 2(a) presents $d\tau/dB$ near the first LC for $\varphi \approx 90°$ 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 T_c, of about 0.65 K for the shown sample, a plateau corresponding to a linear field dependence in $\tau(B)$ emerges. The temperature dependencies of the lower and upper critical fields, as defined by the kinks in $d\tau/dB$, are plotted in Fig. 2(b) (the difference will be denoted as ΔB_0). The figure also displays the maximum and half-maximum field values of the Gaussian-like curves for $T > T_c$.

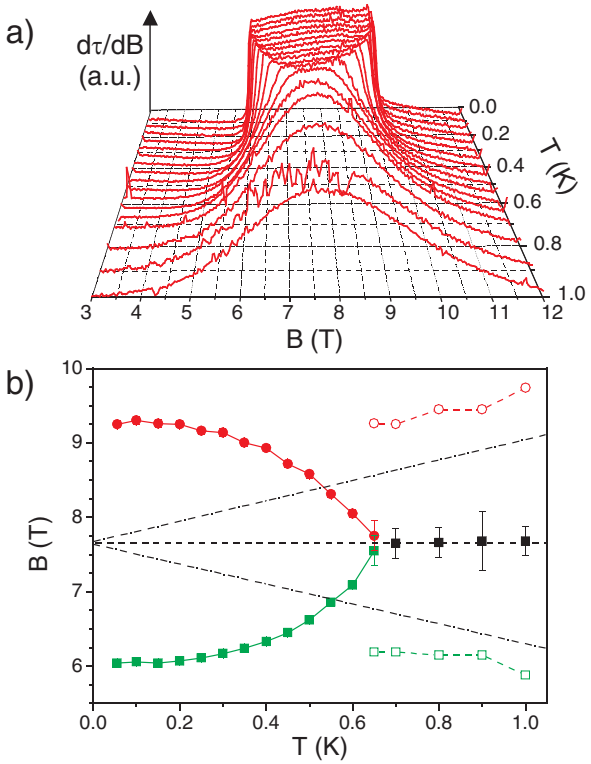

FIG. 2 (color online). (a) $d\tau/dB$ at the first LC for a single crystal of **1** for several temperatures from 55 mK to 1 K ($\varphi \approx 93°$). (b) B-T phase diagram as derived from the data shown in panel (a) (lines are guides to the eyes). The solid symbols indicate the critical fields, the open symbols the half-maximum fields for $T > T_c$. The dashed line indicates the field of the $S = 0 \rightarrow S = 1$ LC. The dash-dotted lines indicate the half-maximum fields as expected for thermal broadening.

All investigated crystals showed the anomalies at the LCs, with a variation in T_c (0.35 to 0.65 K) and ΔB_0 (1.5 to 3 T). Smaller ΔB_0 corresponded to smaller T_c and vice versa. One origin for the variation seems to be a dependence of T_c and ΔB_0 on the field orientation. Within experimental resolution, a hysteresis was not detected.

The above torque data clearly demonstrates a phase transition at the LCs in $CsFe_8$. The similarity of the torque curves in Fig. 1(b) with magnetization curves observed for systems exhibiting field-induced magnetic order [15] suggests to assign the anomalies in $CsFe_8$ 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 $[NaFe_6\{N(CH_2CH_2O_3\}_6]Cl \cdot 6CHCl_3$ down to 0.3 K, $[Fe_6\{N(CH_2CH_2O_3\}_6] \cdot 6MeOH$ down to 0.2 K, and $[NaFe_6(OCH_3)12(C_{17}H_{15}O_4)_6]ClO_4$ down to

40 mK [16–18]. Intermolecular interactions on the order of several 100 mK are not apparent in $CsFe_8$.

In view of the degeneracy at the LCs a ME effect might be suggested. For isotropic AFM spin rings such an effect is unrealistic, at least for spins $>1/2$ [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 Δ 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. [19], the low-T magnetic behavior near a LC is well described by the two-level Hamiltonian

$$\hat{H}_{S,S+1} = \begin{pmatrix} \epsilon_S & \Delta/2 \\ \Delta/2 & \epsilon_{S+1} \end{pmatrix}, \tag{2}$$

where S and $S+1$ index the two levels $|S, -S\rangle$ and $|S+1, -S-1\rangle$ involved in the LC. Here, a rotated axis system with the quantization axis parallel to the field $\mathbf{B}$ is used, and $|S, M\rangle$ refers to the labels of the total spin operator in the rotated frame, $\hat{\mathbf{S}}'^2$ and $\hat{S}'_z$. $\epsilon_S(B, \varphi)$ 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 $\hat{H}_A$ [7,20]. 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 $\Delta/2 = \langle S, -S|\hat{H}'_A|S+1, -S-1\rangle$ and is thus independent of the magnetic field ($\hat{H}'_A$ is $\hat{H}_A$ expressed in the rotated reference frame).

The symmetry of a nondistorted ring (C_8 symmetry of the spin Hamiltonian) prohibits a mixing of the levels, hence $\Delta = 0$ [21,22]. A structural distortion induces a modulation of the exchange and anisotropy constants, which affects both Δ_S and Δ [the ME coupling due to Δ_S (Δ) will be called diagonal (nondiagonal)]. Δ_S is not affected in first order by these modulations as it is only sensitive to the average of the exchange and anisotropy constants [11]. Thus, Δ_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. [12,13], and leads to similar conclusions. For the nondiagonal ME coupling, however, since it is sensitive to the amplitude of the modulations, one finds $\Delta \propto x$ [we write $\Delta(x) = \alpha x$ with the ME coupling constant α]. The gain in magnetic energy is now linear in the distortion resulting in an unconditional ME instability [23]. In this model, the microscopic details of the nondiagonal ME coupling are lumped into the parameter α. Questions concerning, e.g., the relevant distortion mode thus remain unanswered.

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

$$V(x) = -\frac{1}{2}\sqrt{(b-b_0)^2 + \Delta(x)^2} + \frac{1}{2}|b-b_0| + \frac{1}{2}kx^2, \tag{3}$$

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. [13]), the equilibrium distortion x_0 is given by the minimum of $V(x)$, yielding the condition

$$(b-b_0)^2 + \Delta_0^2 = \left(\frac{\alpha^2}{2k}\right)^2 \tag{4}$$

with $\Delta_0 = \Delta(x_0)$. Accordingly, as a function of magnetic field, the order parameter Δ_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 $b_0 \pm b_c$, with $b_c = \alpha^2/(2k)$.

The model permits an analytical calculation of the torque profiles at low temperature. Inserting Eq. (4) into Eq. (4) of Ref. [19], 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 $b \le b_0 - b_c$ to $\partial b_0/\partial\varphi$ at $b \ge b_0 + b_c$ [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 $\varphi \approx 0°$, Fig. 1(a), and the slopelike contribution of $\delta\tau_1$ resembles that for $\varphi \approx 90°$, Fig. 1(b).

In general, the torque signal in the critical region is a combination of a slopelike and a dome-shaped curve, with angle dependent relative weights. The dependence of the

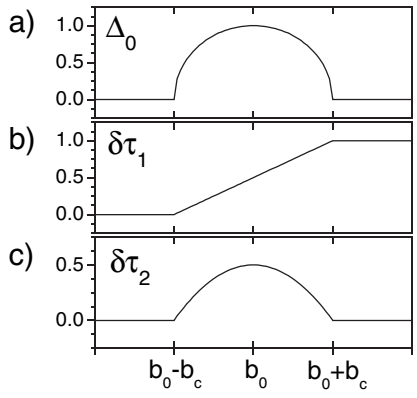

FIG. 3. Field dependence of (a) the order parameter Δ_0, (b) the torque contribution $\delta\tau_1$, and (c) the torque contribution $\delta\tau_2$ around a LC at b_0 [the plots were normalized to $\alpha^2/(2k)$, $\partial b_0/\partial\varphi$, and $-\partial\Delta_0/\partial\varphi$, respectively].

LC field on φ turns out to be $b_0(\varphi) \propto 3\cos^2\varphi - 1$ [7,11], so that the contribution of the slopelike 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 Δ_0. An anisotropy term $\hat{H}_D = \sum D_i[\hat{S}_{iz}^2 - S_i(S_i + 1)/3]$, for instance, gives rise to $\Delta \propto \sin(\varphi)\cos(\varphi)$. A Dzyaloshinsky-Moriya (DM) interaction $\hat{H}_{\mathrm{DM}} = \sum \mathbf{d}_i(\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_{i+1})$, on the other hand, which is likely to arise in the course of a structural distortion because of the lowered symmetry of the ring [25], varies as $\sin(\varphi)$, so that $\partial\Delta_0/\partial\varphi$ is important at small angles but negligible near 90°. This could explain a dominance of the dome-shaped contribution for parallel fields, and of the slopelike 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 $\mu = 14$), a b_c 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 $1/2(\partial^2 V/\partial x^2)x_0^2 \approx 1/2k_BT_c$, i.e., $k_BT_c \approx b_c/2$. 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 often BCS type of relations between order parameter and T_c are found [13]. Also, strain effects between the molecules in the crystal might result in cooperativity which would help to stabilize the distorted phase [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 AFM 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, magnetoelastic instabilities were discussed. Indeed, by introducing a generic model, it has been shown that a nondiagonal magnetoelastic coupling due to a magnetic anisotropy induces structural instabilities at the LCs. The predicted torque curves allowed the explanation of 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 experimental 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 needed for any microscopic model to be developed.

For a number of ferric wheels, evidence for gaps at the LCs have been reported [7,16,18,25]. 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 $CsFe_8$ 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.

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