Field-induced level crossings in spin clusters: Thermodynamics and magnetoelastic instability

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Quantum spin clusters with dominant antiferromagnetic Heisenberg exchange interactions typically exhibit a sequence of field-induced level crossings in the ground state as a function of magnetic field. For fields near a level crossing, the cluster can be approximated by a two-level Hamiltonian at low temperatures. Perturbations, such as magnetic anisotropy or spin-phonon coupling, sensitively affect the behavior at the level-crossing points. The general two-level Hamiltonian of the spin system is derived in first-order perturbation theory, and the thermodynamic functions magnetization, magnetic torque, and magnetic specific heat are calculated. Then, a magnetoelastic coupling is introduced and the effective two-level Hamiltonian for the spin-lattice system derived in the adiabatic approximation of the phonons. At the level crossings, the system becomes unconditionally unstable against lattice distortions due to the effects of magnetic anisotropy. The resultant magnetoelastic instabilities at the level crossings are discussed, as well as the magnetic behavior.

I. INTRODUCTION AND CONCLUSIONS

The issue of level crossings (LCs) in quantum spin clusters is of broad interest. The most elementary example is probably that of an effective spin $1/2$ with an avoided LC in a magnetic field, where the tunneling probability at constant field-sweep rate is described by the Landau-Zener-Stueckelberg model.[1] Experimental realizations are, for instance, the single-molecule magnets Mn_{12} or Fe_8.[2]

In antiferromagnetic (AFM) spin clusters, LCs also emerge from the interplay of Heisenberg exchange interactions in the cluster and the Zeeman term, which leads to a sequence of LCs in the ground state as a function of magnetic field.[3–9] More precisely, spin clusters are considered which are modeled by the microscopic spin Hamiltonian

$$\hat{H} = -\sum_{i \neq j}^{N} J_{ij}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + \mu_B g\hat{\mathbf{S}} \cdot \mathbf{B} + \hat{H}_1, \qquad (1)$$

consisting of the Heisenberg exchange term and the Zeeman term (N is the number of spin centers in the cluster and $\hat{\mathbf{S}} = \Sigma_i^N \hat{\mathbf{S}}_i$ is the total spin operator). The term $\hat{H}_1$ contains all remaining relevant terms, such as magnetic anisotropy (single-ion anisotropy, anisotropic exchange, dipole-dipole interactions, etc.) or couplings to the environment (phonons, intercluster magnetic couplings, nuclear spins, etc.), but should be small in the sense of a perturbation. Then, the eigenstates of $\hat{H}$ can be classified by the total spin quantum numbers S and M. The AFM Heisenberg interactions typically lead to an energy level scheme, where the energy of the lowest state for each value of $S > S_0$ increases according to $E(S_0) < E(S_0+1) < \cdots < E(S_{max})$ (S_0 is the ground-state spin and $S_{max} = \Sigma_i^N S_i$). As function of field, the Zeeman splitting produces a sequence of LCs, at which the ground state changes from $|S=S_0, M=-S_0\rangle$ to $|S=S_0+1, M=-S_0-1\rangle$, to $|S=S_0+2, M=-S_0-2\rangle$, and so on.[4] For magnetic fields close to the LC conditions, the system becomes almost degenerate, and is well described as a two-level system at low temperatures.

Studies on this type of LCs are interesting from several perspectives, and numerous experimental examples are known both in the area of molecular nanomagnets and inorganic magnetic compounds. For instance, the determination of the LC fields from field-dependent measurement of thermodynamic quantities, such as the magnetization or magnetic torque, directly yields the energies $E(S_0+1)-E(S_0)$, $E(S_0+2)-E(S_0)$, etc., of the next higher spin levels. This "thermodynamic" spectroscopy often enables a precise determination of the exchange coupling constants in the cluster.[3–9] In some molecular nanomagnets, such as the AFM wheels, the energy of the lowest spin levels increases quadratically with S according to $E(S) \propto S(S+1)$,[3,10–12] which reflects the quantized rotation of the Néel vector in these clusters.[13–16]

Interesting phenomena also emerge from the fact that near a LC, the system is rather susceptible to the perturbations represented by $\hat{H}_1$. Among the molecular nanomagnets, the AFM wheels[3,17] and related systems, such as the Mn-[3×3] grid or the modified wheels,[18–21] have become prototypical examples in this regard. The most important term in $\hat{H}_1$ usually is the single-ion anisotropy. In the wheels, however, because of their nominally high symmetry, the LCs would remain true LCs despite this perturbation,[22,23] but with small deviations from ideal cyclic symmetry, spin terms such as a Dzyaloshinsky-Moriya interaction may mix the two levels at a LC, thus leading to avoided LCs.[23,24] Indications of this have been reported for some ferric wheels.[23–25] In *a priori* less symmetric molecules, the symmetry restrictions are absent, and the single-ion anisotropy becomes efficient in mixing the spin levels at the LCs.[19,26–28] The result can be dramatic. For instance, the magnetic torque at low temperatures may display a pronounced oscillatory field dependence, i.e., show quantum magneto-oscillations. This phenomenon has been observed in the Mn-[3×3] grid[19] and in two modified wheels.[28] Since levels with different values of S are mixed, the total spin $\hat{\mathbf{S}}$ exhibits quantum fluctuations at the LCs, which could enable coherent oscillations of the total spin if dissipation is weak.[26] Moreover, the torque oscillations observed in Mn-[3×3] provided the experimental

demonstration of the so-called tower of states in a finite AFM square lattice.[16]

$\hat{H}_1$ also may include perturbations such as a coupling to the nuclear spins or the phonon system. In fact, the LCs in the molecular wheels were intensively studied by nuclear magnetic resonance (NMR).[23,29–32] Also, effects of the spin-phonon coupling were observed in the wheels $NaFe_6$ and Fe_{12} (Refs. 25 and 33) and other clusters,[34] where it resulted in magnetic butterfly hysteresis at the LCs due to a phonon-bottleneck effect. From a general perspective, at the LCs the clusters represent two-level systems with dissipation.[35] They open attractive experimental opportunities for exploring this model since, for instance, the strength of the mixing at the LCs and hence the influence of dissipation may be tuned by external parameters such as the orientation of the magnetic field.[19,27,28]

Other interesting examples are found in inorganic compounds, for instance, in materials characterized as weakly interaction dimers. Prototypical systems are $TlCuCl_3$ and $BaCuSi_2O_6$.[36,37] The dominant AFM interactions in the dimers lead to a $S=0$ dimer ground state and a higher lying $S=1$ level, which is split in a magnetic field resulting in a LC, exactly as described before. Weaker magnetic exchange interactions between the dimers, however, drastically modify the behavior of the system for fields close to the LC; they give rise to various field-induced magnetic long-range ordering phenomena, such as the Bose-Einstein condensation of triplets and dimensional reduction at quantum critical points.[38–40]

The (near) degeneracy of the levels at the LCs suggests also the possibility of spontaneous structural distortions of the cluster at the LC fields, driven by the interaction of the spin system with the phonons. In fact, in view of the resemblance of an AFM molecular wheel with a one-dimensional AFM quantum spin chain, a spin-Peierls type of effect seems to be obvious. However, general arguments imply that for finite spin clusters, which exhibit a gap in their excitation spectrum, the energies should vary quadratically with the distortion coordinate. Hence, a spontaneous structural instability would be conditional and not likely to occur in real materials. Furthermore, a recent theoretical study on AFM Heisenberg rings demonstrated that for $S_i > 1/2$, a spontaneous distortion would be of first order and so strong that it would disrupt the molecule.[41]

Recently, it has been shown, however, that the magnetic anisotropy terms in $\hat{H}_1$, in fact, give rise to an unconditional instability of the clusters against spontaneous distortions at the LCs.[42] The argument is based on a phenomenological model, which describes the spin system by a two-level Hamiltonian and treats the phonons in the adiabatic limit (the effective Hamiltonian of the coupled spin-phonon system will be called $\hat{H}_{SP}$). In the molecular wheel $CsFe_8$, phase transitions at the LC points were recently observed.[42] Since the crystal structure as well as other arguments disapproved the presence of sufficient magnetic interactions between the clusters, the findings were interpreted as magnetoelastic instabilities at the LCs. The experimental data, in fact, were consistent with the predictions of the phenomenological model $\hat{H}_{SP}$.

The primary goal of this work is to present a coherent derivation of $\hat{H}_{SP}$ and the field-induced magnetoelastic instabilities and to discuss the resultant magnetic behavior (extending a previous brief report[42]). As a preparatory step, the two-level Hamiltonian of the spin system is derived (Secs. II and III), and the thermodynamic magnetization, magnetic torque, and magnetic specific heat are calculated (Sec. IV). Then, the magnetoelastic coupling is introduced and the two-level Hamiltonian $\hat{H}_{SP}$ is established (Sec. V), and the magnetoelastic instabilities are discussed (Sec. VI). The subject of field-induced LCs has been investigated intensely in the last years by several authors. Accordingly, several pieces of the results were obtained before.

The results should be useful in several regards. The thermodynamic results provide insight into the different magnetic behaviors of, e.g., AFM wheels and the Mn-$[3 \times 3]$ grid (in the wheels, the sequence of LCs leads to staircaselike magnetization and torque curves; in the grid, it leads to oscillations in the torque). Furthermore, they provide a handy method to parametrize the experimental data and to extract from them the key parameters, such as the level-mixing strength. The presented model of the magnetoelastic instability has all the drawbacks and virtues of a phenomenological model. It cannot be expected to provide a full quantitative description of a specific material (e.g., of $CsFe_8$) or to answer specific microscopic details, such as which distortion mode is involved. However, it is the most simple model which describes the basic mechanism (it actually represents the mean-field model). As it is often with such models, they are very useful for a qualitative understanding of the phenomenon and a discussion of the observed behavior.

A connection between the weakly interacting dimer compounds and AFM molecular wheels is finally noted. The low-lying excitations in AFM wheels are well described by a dimer model, where the two spins correspond to the total spins on each AFM sublattice.[12,13,15] Hence, with magnetic interactions between the clusters, AFM wheels would perfectly mimic a weakly interacting dimer system and show the very same field-induced phenomena. In the AFM wheels, however, the magnetic intercluster interactions are usually negligible, which suggested the magnetoelastic origin of the observed field-induced phase transitions in $CsFe_8$.[42] In the weakly interacting dimer compounds, the observed field-induced phase transitions are undoubtedly of magnetic origin, but clear indications of magnetoelastic couplings have also been reported.[43–45] In particular, NMR experiments showed that the field-induced magnetic ordering in $TlCuCl_3$ is accompanied by a simultaneous lattice deformation.[43] These findings indicate that both intercluster magnetic interactions and magnetoelastic couplings are present, in general, in a specific material, and that it only depends on the relative strength whether the one or the other is considered as the driving force for the phase transitions at the LCs. Hence, as a conclusion, the phenomena of the field-induced magnetoelastic instabilities and field-induced magnetic ordering appear as the two extreme sides of one and the same medal—and it might be hard to distinguish them from each other in a specific material.

II. BASICS

In this section, some general results for an effective two-level Hamiltonian (TLH) are shortly reviewed. In matrix form, the TLH is written as

$$\hat{H}_{TL} = \begin{pmatrix} \varepsilon_1 & \Delta/2 \\ \Delta/2 & \varepsilon_2 \end{pmatrix}, \tag{2}$$

where ε_1 and ε_2 are the bare energies of the two involved levels and Δ describes a mixing between these levels. The approximation of the TLH works well if both the gap between the two levels and the temperature are much smaller than the gaps to the next higher-lying levels in the energy spectrum. The energies $E_\pm$ of the two eigenstates of the TLH are

$$E_\pm = \frac{1}{2}(\varepsilon_2 + \varepsilon_1) \pm \frac{1}{2}\sqrt{(\varepsilon_2 - \varepsilon_1)^2 + \Delta^2} \equiv E_1 \pm E_2, \tag{3}$$

where E_+ (E_-) denotes the energetically upper (lower) branch of the avoided LC. The partition function $Z = 2\exp(-\beta E_1)\cosh(\beta E_2)$ and the free energy $F = -k_B T\ln(Z)$ are functions of the temperature T, and further variables, which are abbreviated symbolically by x, i.e., $Z \equiv Z(T,x)$ and $F \equiv F(T,x)$. k_B is the Boltzmann constant and $\beta = 1/(k_B T)$. For some relevant derivatives, one obtains

$$\frac{\partial F(T,x)}{\partial x} = \frac{\partial E_1}{\partial x} - \tanh(\beta E_2)\frac{\partial E_2}{\partial x}$$

$$= \frac{\partial E_-}{\partial x} + [1 - \tanh(\beta E_2)]\frac{\partial E_2}{\partial x}, \tag{4a}$$

$$\frac{\partial^2 F(T,x)}{\partial T^2} = -k_B^2\beta^3[1 - \tanh^2(\beta E_2)](E_2)^2. \tag{4b}$$

A formulation of the expressions in terms of a factor $[1 - \tanh^n(\beta E_2)]$ (with integer n) is convenient for a discussion of the temperature dependence: For $T \to 0$, one finds $[1 - \tanh^n(\beta E_2)] \to 0$, and in the high-temperature limit $T \to \infty$, one finds $[1 - \tanh^n(\beta E_2)] \to 1$. E_2 is half of the energy gap between the two levels, $E_+ - E_- = 2E_2$.

III. TWO-LEVEL HAMILTONIAN

In this section, the effective TLH, which describes the behavior of a (rigid) spin cluster at a field-induced LC, is derived in first-order perturbation theory. The spin Hamiltonian $\hat{H}$ of the system is given by Eq. (1). The type of LCs considered in this work emerge from dominant Heisenberg interactions and the Zeeman term in the cluster, such that the effects of the term $\hat{H}_1$ can be treated perturbationally. For simplicity, it is further assumed that the cluster anisotropy is uniaxial. Then, the magnetic field is completely specified by its magnitude B and its angle φ with respect to the uniaxial z axis. No further restrictions are imposed on the treatment in this and the next section. It is noted that for most AFM wheels and $CsFe_8$ in particular, the anisotropy is very well characterized as uniaxial.[6–10,24,31,46–48]

The most important term in $\hat{H}_1$ is usually a single-ion anisotropy term,

$$\hat{H}_D = \sum_i \hat{\mathbf{S}}_i \cdot \mathbf{D}_i \cdot \hat{\mathbf{S}}_i, \tag{5}$$

but a Dzyaloshinsky-Moriya term,

$$\hat{H}_{DM} = \sum_{i \neq j} \mathbf{d}_{ij} \cdot (\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_j), \tag{6}$$

or a spin-phonon coupling term, etc., may also be included, depending on the situation under consideration. Since the single-ion anisotropy is of general importance, it is convenient to introduce a $\hat{H}_1'$ via $\hat{H}_1 = \hat{H}_D + \hat{H}_1'$. In the following and Sec. IV, $\hat{H}_1'$ is mostly disregarded, but it will become crucial in Secs. V and VI.

Since the main part of the microscopic Hamiltonian $\hat{H}$ is isotropic, the appropriate zero-order states are eigenstates of the total spin operator $\hat{\mathbf{S}}$ and classified by the quantum numbers S and M. The two states involved in the LCs have spin quantum numbers S differing by one unit and $M = -S$.[49] The wave functions may be written as $|\gamma, S, -S\rangle$ and $|\gamma', S+1, -S-1\rangle$, where γ denotes the additional quantum numbers. The obvious shorthand notation $|S\rangle$ and $|S+1\rangle$ will be used in the following. In first order, the TLH Eq. (2) is obtained with $\varepsilon_1 = \varepsilon_S$, $\varepsilon_2 = \varepsilon_{S+1}$, and

$$\varepsilon_S = \langle S|\hat{H}|S\rangle, \tag{7a}$$

$$\Delta/2 = \langle S|\hat{H}|S+1\rangle. \tag{7b}$$

It is important to note that the quantization axis for the magnetic quantum number M is along the direction of the magnetic field and not, for instance, along the uniaxial z axis.[6,27,50–52] For the calculation of the matrix elements, an operator such as $\hat{S}_{iz}^2$, which is expressed in a reference frame with the quantization axis along the z axis, thus has first to be rotated to a frame with the z' axis (the "new" z axis) along the magnetic field.

For the diagonal matrix elements, one directly calculates $\varepsilon_S = \Delta_S^0 - bS + \langle S|\hat{H}_1|S\rangle$,[6,50] where Δ_S^0 is the energy of the level $|S\rangle$ in zero magnetic field and without $\hat{H}_1$, and the abbreviation $b = g\mu_B B$ is introduced. The first-order approximation thus results in a linear field dependence of the bare levels near a LC. The nondiagonal matrix element reduces to $\Delta/2 = \langle S|\hat{H}_1|S+1\rangle$, since the Heisenberg and Zeman terms do not mix states with different S. As an important result, it follows that, in first order, Δ does not depend on the magnetic field, but only on the angle φ, i.e., $\Delta \equiv \Delta(\varphi)$.

Because of the importance of the single-ion anisotropy, the situation with $\hat{H}_1 = \hat{H}_D$ is discussed in some detail. The matrix elements of $\hat{H}_D$ were calculated previously.[6,7,24,27,50,53] For the diagonal elements, $\langle S|\hat{H}_D|S\rangle = D_S S(S-1/2)(\cos^2\varphi - 1/3)$ holds, where D_S is the zero-field-splitting parameter of the spin multiplet to which $|S\rangle$ belongs. One thus obtains

$$\varepsilon_S(b,\varphi) = \Delta_S(\varphi) - bS, \tag{8}$$

where $\Delta_S(\varphi)$ denotes the zero-field energy of the level $|S\rangle$ due to the combined effects of the Heisenberg interactions and the single-ion anisotropy $\hat{H}_D$. It is interesting to note that the dependence on the angle φ comes entirely from the zero-field gaps $\Delta_S(\varphi)$.

The magnetic field b_0, at which the LC occurs, is determined by the condition $\varepsilon_1(b_0)=\varepsilon_2(b_0)$, yielding $b_0(\varphi)=\Delta_2(\varphi)-\Delta_1(\varphi)$ or

$$b_0(\varphi) = a + b(\cos^2\varphi - 1/3), \tag{9}$$

with the constants $a=\Delta_2^0-\Delta_1^0$ and $b=D_{S+1}(S+1)(S+1/2)-D_S S(S-1/2)$.[6,49] The LC field b_0, in general, exhibits an angle dependence due to the anisotropic terms in $\hat{H}_1$. For $\hat{H}_D$, one finds the generic behavior $b_0(\varphi) \propto (\cos^2\varphi-1/3)+\text{const}$. This angle dependence of the LC fields has been observed in high-field torque experiments on several molecular AFM wheels and was used to experimentally determine the zero-field-splitting parameters D_S.[6–10]

Concerning the nondiagonal elements of $\hat{H}_D$, one finds

$$\langle S|\hat{H}_D|S+1\rangle = \cos\varphi\sin\varphi\sum_i D_i\langle S|\hat{T}_1^{(2)}(i)|S+1\rangle,$$

where D_i is the projection of the single-ion anisotropy $\mathbf{D}_i$ on the uniaxial axis, and $\hat{T}_1^{(2)}(i)$ the irreducible tensor operator (ITO) of rank 2 related to the ith spin center.[53–55] Accordingly, the angle dependence of the mixing parameter follows

$$\Delta(\varphi) \propto \cos\varphi\sin\varphi, \tag{10}$$

so that the level mixing induced by $\hat{H}_D$ is zero for parallel and perpendicular fields, $\varphi=0°$ and $90°$, respectively, and maximal for $\varphi=45°$.

The above first-order results are often a very good approximation. In systems, however, with a large magnetic anisotropy, such as the CsFe$_8$ wheel,[9,47] the effects of higher-order contributions become non-negligible and would have to be considered for a fully quantitative description. For instance, in second order, an additional quadratic field term $\propto b^2$ would arise, but even then, the first-order results are useful for qualitative or semiquantitative considerations.

The inclusion of further magnetic anisotropic terms via $\hat{H}_1'$ produces additional contributions to ε_1, ε_2, and Δ, i.e., adds the respective matrix elements of $\hat{H}_1'$ to Eqs. (8) and (10). One term of potential importance is the Dzyaloshinsky-Moriya interaction $\hat{H}_{DM}$.[24,42] For this term, the diagonal contributions are zero, so that ε_1 and ε_2 [as well as $b_0(\varphi)$] are not affected. For the nondiagonal element, one finds

$$\langle S|\hat{H}_{DM}|S+1\rangle = \sum_{i\neq j}(i\cos\varphi d_{ijx} + d_{ijy} - i\sin\varphi d_{ijz})$$
$$\times\langle S|\hat{T}_1^{(1)}(ij)|S+1\rangle,$$

where $\hat{T}_1^{(1)}(ij)$ is an ITO of rank 1.[50–52] The contribution of $\hat{H}_{DM}$ to the angle dependence of the mixing parameter Δ is thus quite complicated in general. For a planar uniaxial clus-
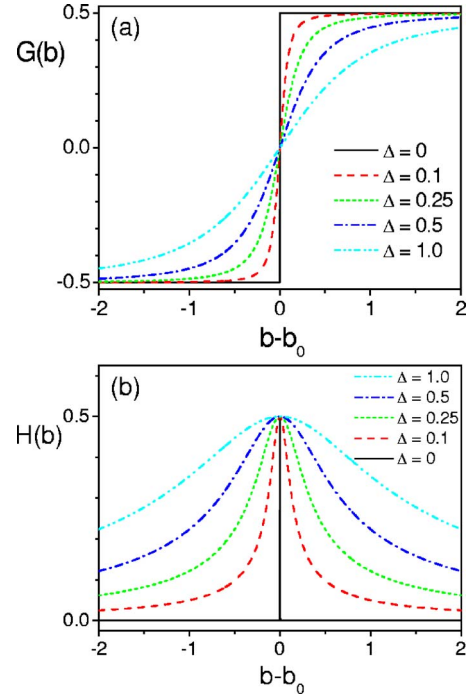

FIG. 1. (Color online) Field dependence of the functions (a) $G(b,\varphi)$ and (b) $H(b,\varphi)$ discussed in the text for various values of the level-mixing parameter Δ.

ter with sufficiently high symmetry, such as molecular wheels or grids, only d_{ijz} is nonzero and Δ will have a component which varies as $\sin\varphi$.[24]

IV. THERMODYNAMICS

The thermodynamic properties for magnetic fields close to a LC can be calculated analytically, keeping in mind Eq. (8) and $\Delta=\Delta(\varphi)$. Since a system with uniaxial magnetic anisotropy is considered, the free energy F is a function of temperature T, of the magnitude of the magnetic field B (or b), and of its orientation φ: $F\equiv F(T,b,\varphi)$. In this section, the magnetic specific heat, the magnetization, and the magnetic torque is calculated. For the calculation, it is noted that $\varepsilon_2-\varepsilon_1=b_0(\varphi)-b$. It is also convenient to introduce the two functions,

$$G(b,\varphi) = \frac{b-b_0(\varphi)}{2\sqrt{[b-b_0(\varphi)]^2+\Delta^2(\varphi)}}, \tag{11a}$$

$$H(b,\varphi) = \frac{\Delta(\varphi)}{2\sqrt{[b-b_0(\varphi)]^2+\Delta^2(\varphi)}}. \tag{11b}$$

As a function of field, $G(b,\varphi)$ describes a step from $-1/2$ to $1/2$ centered at the LC field b_0, which is broadened by the level mixing due to Δ, as shown in Fig. 1(a). The field derivative dG/db exhibits a peak at the LC with a height of $1/(2|\Delta|)$ and a full width at half maximum (FWHM) of $2\sqrt{2^{2/3}-1}|\Delta|=1.124|\Delta|$.[56] $H(b,\varphi)$ is essentially the square root of a Lorentz function and accordingly describes a peak at the LC field b_0 with a height of $\pm1/2$, depending on the
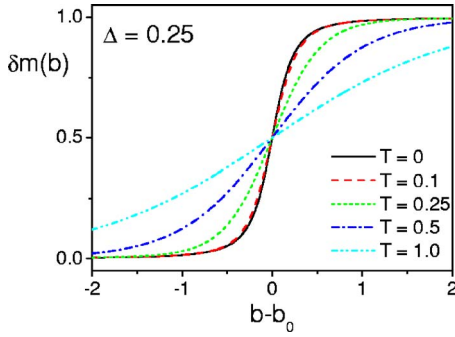
FIG. 2. (Color online) Field dependence of the magnetization change $\delta m(b,\varphi)$ for various temperatures. The level-mixing parameter was set to $\Delta=0.25$.

sign of Δ, and a FWHM of $2\sqrt{3}|\Delta|=3.464|\Delta|$ (Ref. 56) [see Fig. 1(b)]. Both G and H can be expressed in terms of the reduced variable $x=(b-b_0)/|\Delta|$: $G(x)=xH(x)$, $H(x)=(2\sqrt{x^2+1})^{-1}$, which makes the dependencies on b_0 and Δ transparent.

The magnetic specific heat is given by $c_M=-T\partial^2 F/\partial T^2$, which with Eq. (4b) yields

$$c_M(b,\varphi) = \frac{E_2^2}{k_B T^2 \cosh^2(\beta E_2)} = k_B\left(\frac{2E_2}{k_B T}\right)^2 \frac{\exp(\beta 2 E_2)}{[1+\exp(\beta 2 E_2)]^2}.$$
(12)

Since $2E_2$ is the energy gap between the two levels, the specific heat exhibits a Schottky anomaly as a function of temperature (with a maximum of height of $0.4392 k_B$ at $k_B T = 0.4168|2E_2|$) and a double-peak feature as a function of field, as was noted and discussed before by several authors, to whose works we hence refer.[23,52,40,57,58]

The magnetization is given by $m=-\partial F/\partial b$ (in units of $g\mu_B$) and calculated to

$$m(b,\varphi) = S + \frac{1}{2} + G(b,\varphi)\tanh(\beta E_2).$$
(13)

It is convenient to separate the magnetization as $m=m_\ll+\delta m$, where $m_\ll=S$ is the zero-temperature magnetization at fields well below the LC field, $b\ll b_0$. δm is the change in the magnetization upon passing the LC coming from fields below b_0,

$$\delta m(b,\varphi) = \frac{1}{2} + G(b,\varphi)\tanh(\beta E_2)$$

$$= \left[\frac{1}{2} + G(b,\varphi)\right] - [1-\tanh(\beta E_2)]G(b,\varphi).$$
(14)

As a function of field, the magnetization exhibits a step at the LC, where it changes from S to $S+1$ (or by one unit $g\mu_B$). Figure 2 shows $\delta m(b)$ at various temperatures for $\Delta=0.25$. The magnetization can be expressed in terms of the reduced variables $x=(b-b_0)/|\Delta|$ and $t=k_B T/|\Delta|$ $[\beta E_2 = \sqrt{x^2+1}/(2t)]$. In these units, the variation of the behavior with b_0 and Δ becomes most apparent.

At low temperatures, $k_B T \ll |\Delta|$, the magnetization change is given by $1/2+G$ and is independent of temperature. At high temperatures, $k_B T \gg |\Delta|$, it reduces to $1/2+\tanh[(b-b_0)/(2k_B T)]/2$ as for a true LC, i.e., the effects of level mixing become indiscernible in this temperature regime.

The magnetization step is broadened by the effects of temperature and nonzero level mixing Δ. The broadening may be analyzed by considering the width of the peak in the field derivative dm/db. At low temperatures, $k_B T \ll |\Delta|$, the peak is characterized by a temperature-independent FWHM of $1.124|\Delta|$, and at high temperatures, $k_B T \gg |\Delta|$, by a linearly increasing FWHM of $4\ln(\sqrt{2}+1)k_B T = 3.525 k_B T$.[7,24,56] With temperature, the shape of the peak changes also, so that a careful analysis of the shape of experimental dm/dB curves in principle provides additional information on the level mixing.

The magnetic torque is given by $\tau=\partial F/\partial\varphi$ (Ref. 59) and calculated to[60]

$$\tau(b,\varphi) = \frac{1}{2}\left(\frac{\partial\Delta_1}{\partial\varphi} + \frac{\partial\Delta_2}{\partial\varphi}\right)$$
$$+ \tanh(\beta E_2)\left[G(b,\varphi)\frac{\partial b_0}{\partial\varphi} + H(b,\varphi)\frac{\partial\Delta}{\partial\varphi}\right]. \quad (15)$$

This equation can be transformed into a more useful form by considering (i) $(\Delta_1+\Delta_2)/2=\Delta_1+b_0/2$ and Eq. (14) and by separating (ii) the torque into $\tau=\tau_\ll+\delta\tau$, where $\tau_\ll = \partial\Delta_1/\partial\varphi$ is the torque for fields well below the LC field and $\delta\tau$ the change in the torque upon passing the LC. One finds[60]

$$\delta\tau(b,\varphi) = \delta m(b,\varphi)\frac{\partial b_0}{\partial\varphi} + H(b,\varphi)\frac{\partial\Delta}{\partial\varphi}\tanh(\beta E_2)$$

$$= \delta m(b,\varphi)\frac{\partial b_0}{\partial\varphi} + H(b,\varphi)\frac{\partial\Delta}{\partial\varphi}$$

$$- [1-\tanh(\beta E_2)]H(b,\varphi)\frac{\partial\Delta}{\partial\varphi}. \quad (16)$$

Interestingly, the torque consists of two contributions, $\delta\tau=\delta\tau_1+\delta\tau_2$, where $\delta\tau_1$ refers to the first term on the right-hand-side of Eq. (16) and $\delta\tau_2$ to the remaining terms. The first contribution $\delta\tau_1$ is proportional to the magnetization change δm. It accordingly also produces a step as a function of field in the torque signal, which is broadened by a nonzero level mixing and temperature. The second contribution $\delta\tau_2$, as it is proportional to $H(b,\varphi)$, produces a peak in the torque signal centered at the LC field. The field dependence of $\delta\tau_2$ is depicted in Fig. 3 for different temperatures and several values of Δ. At low temperatures, $k_B T \ll |\Delta|$, the peak follows $H(b,\varphi)$ and is accordingly characterized by a temperature-independent height of $(1/2)\partial\Delta/\partial\varphi$ and FWHM of $3.646|\Delta|$.[56] With increasing temperature, the peak smears out to disappear at temperatures $k_B T \gg |\Delta|$. As with the magnetization, the torque is expressible in terms of the reduced variables x and t, clarifying the trends with Δ and T visible in Fig. 3. Several points shall be noted.

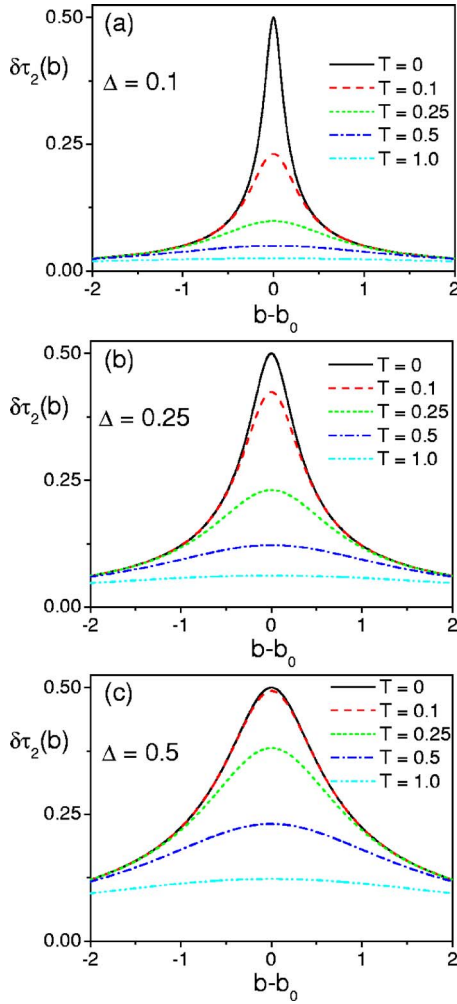(1) For the special case of zero level mixing ($\Delta=0$), most

FIG. 3. (Color online) Field dependence of the torque contribution $\delta\tau_2(b,\varphi)$ at several temperatures for the level-mixing parameters (a) $\Delta=0.1$, (b) $\Delta=0.25$, and (c) $\Delta=0.5$.

of the results have been obtained before, in particular, that both the field-dependent magnetization and torque curves exhibit steps at the LC field. In fact, from Eq. (16) one finds $\delta\tau(b,\varphi) \propto \delta m(b,\varphi)$, since $\delta\tau_2(b,\varphi)=0$ for $\Delta=0$. In reality, however, Δ will never be exactly zero, but as long as it is sufficiently small, the torque will be characterized by steps [small means $\partial\Delta/\partial\varphi \ll \partial b_0/\partial\varphi$, which is obeyed if $\Delta(\varphi)$ is either small in magnitude or almost constant as a function of angle]. Vice versa, whenever $\tau(b,\varphi)$ is observed to be mostly steplike, one can conclude that (i) Δ is very small and (ii) $\delta\tau(b,\varphi) \propto \delta m(b,\varphi)$. This situation has been observed, for instance, in many AFM wheels.[3,5–9,24,48]

(2) If level mixing, however, is significant, then the magnetization and torque curves in general will be very different, since then the peaklike contribution $\delta\tau_2(b,\varphi)$ significantly adds to the torque signal. A similar contribution is not present in the magnetization, and it is thus a unique feature of torque. This contribution is rooted in the fact that the mixing parameter Δ does not depend on the magnetic field but on the angle φ, and is hence directly probed by torque. If level mixing is actually very strong, i.e., $\partial\Delta/\partial\varphi \gg \partial b_0/\partial\varphi$, then the torque curve will be characterized by peaks at the

LCs. At nonzero temperature and/or strong level mixing, the peaks of several nearby LCs may superimpose to yield an oscillatory field dependence of the torque.[16] This situation has been observed for the Mn-[3×3] grid and the modified wheels Cr_7Ni and Cr_7Zn.[19,28]

(3) Interestingly, if one writes the ground-state wave function as

$$|0\rangle = c|S\rangle + s|S+1\rangle, \tag{17}$$

with $c^2+s^2=1$, one finds

$$s^2 = 1/2 + G(b,\varphi), \tag{18a}$$

$$cs = H(b,\varphi). \tag{18b}$$

Hence, at zero temperature, $\delta m(b,\varphi)$ and $\delta\tau_1(b,\varphi)$ directly reflect s^2, while $\delta\tau_2(b,\varphi)$ reflects the product cs.

(4) From the above points, it is clear that the peaks in the torque curves due to $\delta\tau_2(b,\varphi)$ are a direct signature of level mixing, as pointed out previously in Ref. 26. In this work, it has also been shown that the peaks in the torque are related to the enhancement of the quantum fluctuations of the total spin $\hat{\mathbf{S}}$ by a level mixing. In fact, a derivation has been given which yielded $\tau \propto 2B\Delta S_z$, where $(\Delta S_z)^2 = \langle\hat{S}_z^2\rangle - \langle\hat{S}_z\rangle^2$ denotes the quantum fluctuations in $\hat{S}_z$.[26] This relation cannot be correct, or complete, since for zero level mixing it would predict $\tau=0$, in contrast to the theoretically expected and experimentally observed steplike torque curves. In view of the above findings, however, $2B\Delta S_z$ can be associated with the contribution $\delta\tau_2$, as both are related to cs.

(5) The generic behavior of the angle dependence of the LC field is $b_0(\varphi) \propto (\cos^2\varphi - 1/3) + \text{const}$, so that $\partial b_0/\partial\varphi \propto \sin\varphi\cos\varphi$. Thus, the steplike part of the torque will follow $\delta\tau_1(b,\varphi) \propto \delta m(b)\sin\varphi\cos\varphi$, which is the expected angle dependence.

(6) In the above treatment, an isotropic g factor was assumed. The calculations for anisotropic g factors are simple but the results are lengthy. As a general trend, an anisotropic g factor produces an additional contribution to the torque (and only to the torque) which increases linearly with the magnetic field in first approximation.[61]

V. MAGNETOELASTIC HAMILTONIAN

Within the spin-Hamiltonian formalism, a magnetoelastic (ME) coupling is introduced by allowing the magnetic parameters (coupling constants, anisotropy parameters, g factors, etc.) to depend on the distortion coordinates $\mathbf{Q}_k = \mathbf{u}_k - \mathbf{u}_{k,0}$ of the atoms in the lattice.[41,62–67] $\mathbf{u}_{k,0}$ is the equilibrium and $\mathbf{u}_k$ the distorted position vector of the kth atom; $\mathbf{Q}_k$ are usually the normal coordinates. For the exchange coupling constants, for instance, hold $J_{ij}(\mathbf{Q}_1,\mathbf{Q}_2,\ldots) = J_{ij} + \delta J_{ij}(\mathbf{Q}_1,\mathbf{Q}_2,\ldots)$. Assuming small deviations, a Taylor expansion yields $\delta J_{ij}(\mathbf{Q}_1,\mathbf{Q}_2,\ldots) \approx \sum_k \alpha_{ij,k}\cdot\mathbf{u}_k$, with the ME coupling constants $\alpha_{ij,k} \equiv \partial J_{ij}/\partial\mathbf{u}_k$. In the following, it is assumed that only one distortion mode, and hence only one (scalar) distortion coordi-

nate Q, is relevant. For the exchange constant, one then finds $J_{ij}(Q)=J_{ij}+\delta J_{ij}(Q)$ with $\delta J_{ij}=\alpha_{ij}Q$. Similar relations hold for the other magnetic parameters $\mathbf{D}_i$, $\mathbf{d}_{ij}$, g, and so on.

Inserting the modulated magnetic parameters into the microscopic spin Hamiltonian produces additional, Q-dependent terms which will be denoted collectively as $\hat{H}_Q$. For the terms considered in this work, one finds

$$\hat{H}_Q = -\sum_{i\neq j}\delta J_{ij}\hat{\mathbf{S}}_i\cdot\hat{\mathbf{S}}_j + \sum_i \hat{\mathbf{S}}_i\cdot\delta\mathbf{D}_i\cdot\hat{\mathbf{S}}_i + \sum_{i\neq j}\delta\mathbf{d}_{ij}\cdot(\hat{\mathbf{S}}_i\times\hat{\mathbf{S}}_j)$$
$$+\cdots, \qquad (19)$$

The combined system of the magnetic molecule and the elastic lattice is then described by the spin-phonon Hamiltonian

$$\hat{H}_{sp\text{-}ph} = \hat{H} + \hat{T} + \frac{k}{2}Q^2, \qquad (20)$$

where $\hat{H}_Q$ is included in $\hat{H}$ via $\hat{H}_1$ or $\hat{H}_1'$. $\hat{T}$ is the kinetic energy of the phonons and k the elastic constant.

In this work, the phonons are treated as classical oscillators, which is justified if the lattice dynamics is much slower than the spin dynamics. This situation is known as the adiabatic limit and has been often used to infer the ground state in spin-phonon systems.[41,62,65] Under this conditions, the ground state is obtained for zero kinetic energy of the phonons (atoms at rest) and by minimizing the potential

$$V(Q) = E(Q) + \frac{k}{2}Q^2 \qquad (21)$$

of the total system, where $E(Q)$ is the ground-state energy of the magnetic part $\hat{H}$ (which now depends on Q due to the inclusion of $\hat{H}_Q$). One may approximate $E(Q)=-aQ^\kappa$, with some positive constants a and κ. A stable minimum is obtained for $\kappa<2$ at $Q_0=\sqrt[2-\kappa]{\kappa a/k}>0$. This situation corresponds to unconditional instability. For $\kappa=2$, conditional instability is realized, where $V(Q)<0$ is obtained for any $Q>0$ if $a>k/2$. For $\kappa>2$, the only solution is $Q_0=0$, i.e., no distortion is obtained.

Within the framework of the TLH approximation, $E(Q)\equiv E_-(Q)$ (E_- depends on Q via ε_1, ε_2, and Δ). Apparently, the ME coupling enters in two ways, namely, via the diagonal matrix elements $\langle S|\hat{H}_Q|S\rangle$ and via the nondiagonal matrix element $\langle S|\hat{H}_Q|S+1\rangle$. The first mechanism shall be called diagonal, the second nondiagonal ME coupling. These two coupling modes have to be carefully distinguished.

Before proceeding further, a point concerning the Heisenberg-exchange part shall be clarified. Within the context of the present work, it sets the largest energy scale. In several models treated in the literature, it is actually the only term in the spin Hamiltonian.[41,62,68–71] Two cases have to be distinguished, namely, those where the Heisenberg exchange results in (i) a degenerate or (ii) nondegenerate ground state. Case (i) is encountered, for instance, in spin triangles or tetrahedra.[68,71] The description bears some analogy to the Jahn-Teller effect (JTE), and the phenomenon hence has been denoted frequently as the spin JTE. Such situations have been analyzed theoretically several times in the

literature,[68–71] but to the best of our knowledge, no experimental evidence has been reported to date. Case (ii) is clearly distinct and is the one of interest in the present work. Here, an unconditional lattice instability is obtained in zero field for gapless spin systems, such as a spin-1/2 chain (spin-Peierls effect).[64] For gapped systems, such as the finite spin clusters considered here, a spontaneous instability typically does not occur. With appropriate magnetic fields, a degenerate ground state can be created via the LC mechanism, but for a purely isotropic model, a spontaneous instability nevertheless does not occur: The degeneracy at the LC points cannot be lifted by whatever distortion since the two involved levels are eigenstates of $\hat{\mathbf{S}}$ with different values of S. They hence cannot be mixed by the Heisenberg exchange. This already indicates the crucial role of a magnetic anisotropy in $\hat{H}_1$ for a spontaneous instability at a LC in case (ii) systems.

The analysis of the diagonal ME coupling requires the evaluation of $\langle S|\hat{H}_Q|S\rangle$. There is no general reason why $\langle S|\hat{H}_Q|S\rangle$ should be zero, but a nonzero value would lead to somewhat unphysical situations. The effect of a diagonal ME coupling would be a shift of the LC fields by a distortion, $b_0=b_0(Q)$. A change of b_0, however, corresponds to a change of the zero-field splitting [see Eq. (8)]. For the exchange coupling, e.g., this would imply a change of the average coupling strength, i.e., of the overall magnetic energy scale. This is not what one normally expects. For instance, for a ringlike model the generic distortion mode would be a dimerization, upon which the average $\Sigma_i J_{i,i+1}$ is not altered. Hence, $\Sigma_i \delta J_{i,i+1}=0$, implying a zero diagonal element. Similar arguments can be put forward for the other magnetic terms ($\hat{H}_{DM}$ gives zero anyhow). Thus, for typical physical models the diagonal ME coupling is zero in first order. Second-order terms, however, are always expected to be nonzero, and one accordingly concludes that

$$\langle S|\hat{H}_Q|S\rangle \propto Q^2, \qquad (22)$$

corresponding to conditional instability. These considerations are in agreement with the findings of Refs. 41 and 54. For a gapped quantum spin system, one expects the generic behavior $E(Q)\propto Q^2$.

The situation is different for the nondiagonal ME coupling $\langle S|\hat{H}_Q|S+1\rangle$. For the Heisenberg contribution in $\hat{H}_Q$, the matrix element is strictly zero, but for the anisotropic terms, it will be nonzero in general. This is demonstrated by the simplified example of a regular AFM spin ring, for which a Dzyaloshinsky-Moriya interaction emerges upon a dimerization, $d_{i,i+1,z}(Q)=(-1)^i\alpha Q$ $(d_{i,i+1,x}=d_{i,i+1,y}=0)$. Then, $\langle S|\hat{H}_Q|S+1\rangle\propto\Sigma_i(-1)^i\alpha Q\langle S|\hat{T}_1^{(1)}(i,i+1)|S+1\rangle\propto Q$, since $\langle S|\hat{T}_1^{(1)}(i,i+1)|S+1\rangle=(-1)^i\langle S|\hat{T}_1^{(1)}(1)|S+1\rangle$. The point is, in a qualitative language, that the diagonal elements essentially probe the *average* of the modulation (in our example $\Sigma_i\delta d_{i,i+1,z}=0$), while the nondiagonal matrix element is sensitive to the *span* of the modulation [in our example $\Sigma_i(-1)^i\delta d_{i,i+1,z}\neq 0$]. Hence, in general,

$$\langle S|\hat{H}_Q|S+1\rangle \propto Q + \text{const}, \tag{23}$$

which allows for unconditional instability.

The above considerations imply the following TLH to describe the ME effects at a LC,

$$\hat{H}_{SP} = \begin{pmatrix} \varepsilon_S(b,\varphi) & \Delta(\varphi,Q)/2 \\ \Delta(\varphi,Q)/2 & \varepsilon_{S+1}(b,\varphi) \end{pmatrix} + \frac{k}{2}Q^2,$$

$$\Delta(\varphi,Q) = \Delta(\varphi,0) + \alpha(\varphi)Q. \tag{24}$$

The essential elements of this model are that (i) the diagonal elements do not depend on the distortion Q, (ii) the nondiagonal elements do not depend on the magnetic field b, and (iii) $\Delta(Q)$ varies linearly with Q.

The model explicitly allows for the possibility of a nonzero nondiagonal matrix element even for the nondistorted molecule, i.e., for $\Delta(0) \neq 0$.[72] It is easy to show that the system exhibits an unconditional instability for any value of $\Delta(0)$. However, the most interesting situation arises for sufficiently small $\Delta(0)$ (what small means will be made precise later), and this case is also the one of relevance for $CsFe_8$.[73] The behavior for small $\Delta(0)$ is not essentially different from that for zero $\Delta(0)$, and in the following, $\Delta(0)=0$ is hence always assumed. The case of $\Delta(0) \neq 0$ will be considered at the end of the next section. The other approximations and limitations leading to $\hat{H}_{SP}$ have been carefully discussed in the above.

Formally, $\hat{H}_{SP}$ is equivalent to the standard TLH discussed in the JTE. Indeed, the problems are in many respects similar, and much of the insights and results developed for the JTE can be directly carried over to the current problem (key words to mention are cooperative JTE, pseudo-JTE, etc.).[74] The physical difference, however, is that the JTE is related to a degeneracy in the electronic system, while here it originates from a degeneracy in the spin system. The effect described by $\hat{H}_{SP}$ hence might be called a spin JTE. This notation is not quite satisfying, since the underlying mechanism is different from the spin JTE for Heisenberg spin systems with a degenerate spin ground state, which was mentioned before. The effect discussed here therefore is tentatively called field-induced spin JTE (FISJTE).

An interesting feature, as compared to the electronic and spin JTE, is the possibility to continuously tune through the instability via an applied magnetic field. At the LC, $\varepsilon_{S+1} - \varepsilon_S$ is zero, but can be adjusted to any value by moving away from the LC point, realizing a situation similar to the pseudo-JTE. In the next section, the behavior of the system as a function of magnetic field is considered in detail.

VI. FIELD-INDUCED MAGNETOELASTIC INSTABILITY

For the discussion of the field-induced ME instability, it is convenient to first describe the potential-energy surfaces (PES) produced by $\hat{H}_{SP}$. Two PES are obtained, $V(b,Q)_{\pm} = E_{\pm}(b,Q) + (k/2)Q^2$ (where of course $V_- \equiv V$). The dependence on Q is shown in Fig. 4(a) for several magnetic fields. At the LC, $b-b_0=0$, the PES are degenerate at $Q=0$ and
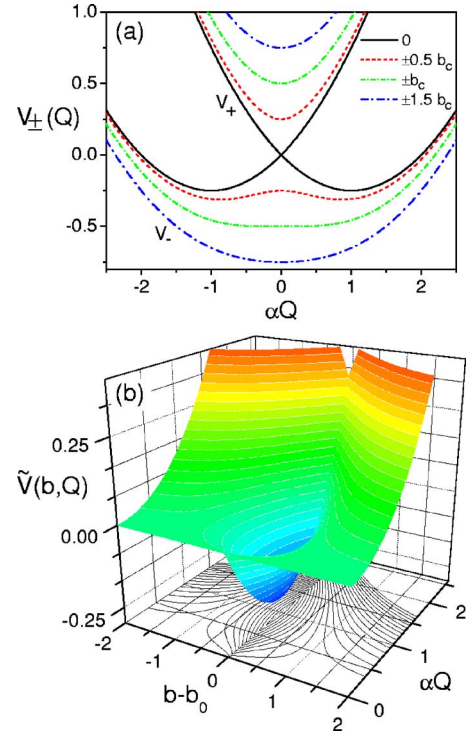

FIG. 4. (Color online) (a) Distortion dependence of the two PES $V_{\pm}(b,Q)$ for several fields $b-b_0$ and (b) field and distortion dependences of the potential $\tilde{V}(b,Q) = V_-(b,Q) - E_-(b,0)$ for positive values of Q ($b_c = \Delta_0^{max} = 1$, $k=1/2$).

exhibit two minima at $Q_0^{max} = \alpha/(2k)$. With increasing distance from the LC field, i.e., increasing $|b-b_0|$, a gap opens between the PES due to the Zeeman splitting, and the two minima accordingly shift to lower Q values. For fields below $b_0 - b_c$ or above $b_0 + b_c$, where $b_c = \alpha^2/(2k)$, the minima disappear completely (in the context of the electronic JTE, b_c is the JT energy).

The spontaneous distortion in the ground state is determined by the minima in the PES, $\partial V/\partial Q = 0$. It is more convenient, however, to discuss $\tilde{V}(Q) = V(Q) - E_-(Q=0)$, which directly measures the gain in potential energy due to a distortion. $\tilde{V}$ is determined to

$$\tilde{V}(b,Q) = -\frac{1}{2}\sqrt{(b-b_0)^2 + \Delta(Q)^2} + \frac{1}{2}|b-b_0| + \frac{k}{2}Q^2. \tag{25}$$

The field and distortion dependences of $\tilde{V}$ are shown in Fig. 4(b) for positive values of Q (and $k=1/2$). One clearly observes a field range around the LC where $\tilde{V}$ is negative for nonzero Q. At these fields, the system gains energy by distorting to a finite distortion Q, i.e., a spontaneous instability occurs.

From minimizing $V(Q)$ or $\tilde{V}(Q)$, the condition for the equilibrium distortion Q_0 or the equilibrium mixing $\Delta_0 \equiv \Delta(Q_0) = \alpha Q_0$, respectively, is obtained as
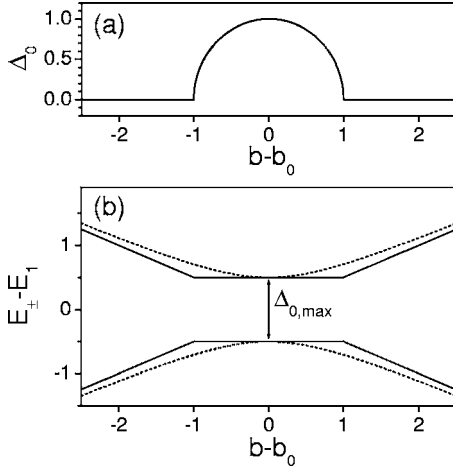
FIG. 5. Field dependence of (a) the equilibrium mixing parameter (or order parameter) Δ_0 and (b) the energies $E_\pm - E_1$ of the two levels ($b_c = \Delta_0^{max} = 1$, $k = 1/2$). The dashed lines in (b) show the energies of an ordinary avoided LC with a mixing parameter $\Delta = \Delta_0^{max}$.

$$(b - b_0)^2 + \Delta_0^2 = \left(\frac{\alpha^2}{2k}\right)^2. \tag{26}$$

This is of the form $x^2 + y^2 = r^2$; hence, the mixing Δ_0 (or Q_0, either one can be used as the order parameter) describes a semicircle with radius b_c as a function of the relative magnetic field $b - b_0$, as shown in Fig. 5(a). For fields below $b_0 - b_c$ and above $b_0 + b_c$, one finds $\Delta_0 = 0$ and the system is undistorted. For fields in the range $[b_0 - b_c, b_0 + b_c]$, however, Δ_0 becomes nonzero signaling the spontaneous instability. At exactly the LC, the mixing and the distortion are maximal, assuming the values Δ_0^{max} and Q_0^{max} [$\Delta_0^{max} = \alpha Q_0^{max} = b_c = \alpha^2/(2k)$].

Concerning the ground-state wave function $|0\rangle$ [Eq. (17)], the coefficient $s = \langle S+1|0\rangle$ is calculated to $s^2 = [1 + (b - b_0)/b_c]/2$ by inserting Eq. (26) into Eq. (18a). Thus, in the field range $[b_0 - b_c, b_0 + b_c]$, the parameter s^2 increases linearly from 0 to 1 as a function of field (and is 0 and 1, respectively, for fields outside this range).

With Eqs. (3) and (26), the energies of the two levels are calculated to $E_\pm = (\varepsilon_2 + \varepsilon_1 \pm \Delta_0^{max})/2$ for fields in $[b_0 - b_c, b_0 + b_c]$. Outside this field range, the energies exactly correspond to that of a true LC. The field dependence of $E_\pm - E_1$ is shown in Fig. 5(b). Thus, the distortion is such as to maintain a minimum gap of value Δ_0^{max} between the energy levels. For comparison, the energy diagram of a conventional avoided LC with a mixing Δ_0^{max} is also shown in order to emphasize the distinctly different behavior of the present model. In an avoided LC, the mixing is field independent. In the present model, in contrast, the mixing is zero for fields outside the range $[b_0 - b_c, b_0 + b_c]$ and nonzero within it due to the instability [see Fig. 5(a)] (it is recalled that the mixing is directly related to the spontaneous distortion via $\Delta_0 = \alpha Q_0$).

The model permits an analytical calculation of the thermodynamic functions at zero temperature (or sufficiently low
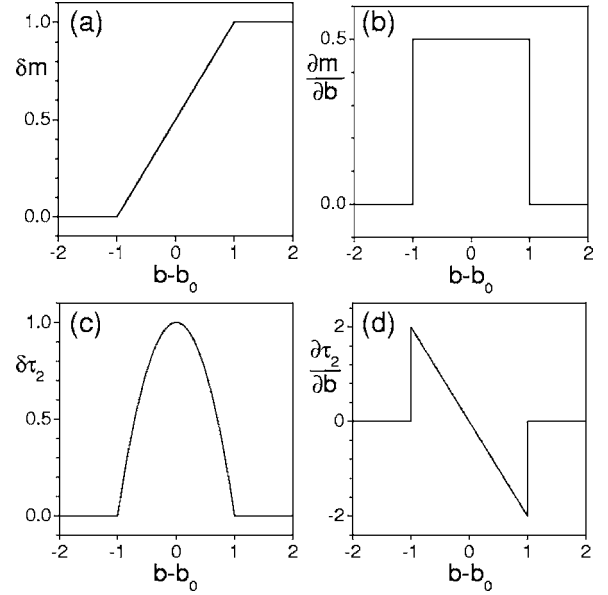

FIG. 6. Field dependence of (a) the magnetization change δm, (b) the field derivative of δm, (c) the torque contribution $\delta\tau_2$, and (d) the field derivative of the torque contribution $\delta\tau_2$ ($b_c = \Delta_0^{max} = 1$, $k = 1/2$).

temperatures, $k_B T \ll \Delta_0^{max}$). The specific heat is zero, since the energy levels never come closer than Δ_0^{max}. Concerning the calculation of the magnetization and torque, the two functions G and H [Eq. (4)] simplify to $G = (b - b_0)/(2b_c)$ and $H = \Delta_0/(2\Delta_0^{max})$ for fields in the range $[b_0 - b_c, b_0 + b_c]$. Outside this range they become $G = \pm 1/2$ and $H = 0$. Inserting this in Eqs. (14) and (16) (and considering $T \to 0$), one obtains[62]

$$\delta m(b, \varphi) = \frac{1}{2}\left(1 + \frac{b - b_0}{b_c}\right), \tag{27a}$$

$$\delta\tau(b, \varphi) = \frac{1}{2}\left(1 + \frac{b - b_0}{b_c}\right)\frac{\partial b_0}{\partial \varphi} + \frac{1}{2}\frac{\Delta_0}{\Delta_0^{max}}\frac{\partial \Delta_0}{\partial \varphi}. \tag{27b}$$

As a function of field, the magnetization change δm increases linearly from $\delta m = 0$ at $b = b_0 - b_c$ to $\delta m = 1$ at $b = b_0 + b_c$, as shown in Fig. 6(a). Figure 6(b) presents the field derivative of the magnetization, $\partial m / \partial b$.

As emphasized in Sec. IV, the torque consists of two contributions, $\delta\tau = \delta\tau_1 + \delta\tau_2$. The first contribution is simply proportional to the magnetization change, $\delta\tau_1 = \delta m(\partial b_0 / \partial \varphi)$ [see Eq. (16)], and hence also increases linearly in the field range $[b_0 - b_c, b_0 + b_c]$. The field dependence of the second contribution needs more consideration. As will be discussed in a moment, the term $\partial \Delta_0 / \partial \varphi$ should be interpreted as $(\partial \alpha / \partial \varphi)Q_0$. With respect to the field dependence, it is hence proportional to Δ_0. This yields $\delta\tau_2 \propto \Delta_0^2$. The field dependence of $\delta\tau_2$ and its field derivative are shown in Figs. 6(c) and 6(d), respectively. $\delta\tau_2$ displays a dome-shaped behavior in the field range $[b_0 - b_c, b_0 + b_c]$. Both types of torque curves, "linear slope" and "dome shaped," were observed in experiments on the AFM wheel $CsFe_8$.[42]

In general, since $\delta\tau = \delta\tau_1 + \delta\tau_2$, the torque is the sum of a linear slope and a dome-shaped contribution. The respective weights are governed by the factors $\partial b_0 / \partial\varphi$ and $(\partial\alpha / \partial\varphi) / \alpha$, or the ratio of them, respectively. The actually observed torque profiles hence will depend on the angle φ in general, as well as on the particular system under consideration. A careful investigation of the angle dependence of the torque profiles thus can provide information on the relevant ME coupling terms in $\hat{H}_Q$.

At this point, an apparent contradiction shall be addressed: In the field range $[b_0 - b_c, b_0 + b_c]$, the energies $E_\pm$ as well as the magnetization exhibit a linear slope, in conflict with the relation $m = -\partial E / \partial b$ valid at zero temperature. Also, the above procedure of just inserting Eq. (26) into the equations of Sec. IV seems questionable, since Δ_0 is implicitly field (and angle) dependent via Eq. (26). This violates the assumption $\partial\Delta / \partial b = 0$ in the derivations of Sec. IV. However, strictly spoken, the PES $V_\pm$ should be used in the calculations, and not $E_\pm$, since the combined system of spins and lattice vibrations is considered. This would add terms due to $\partial Q_0^2 / \partial b$ and $\partial Q_0^2 / \partial\varphi$ to the magnetization and torque. Such a more rigorous calculation, however, yields exactly the same results as with using the equations of Sec. IV and neglecting the implicit field and angle dependences of Δ_0. That is, for the thermodynamic functions, $\Delta_0 = \alpha Q_0$ can be used in the sense of $\partial Q_0 / \partial b = \partial Q_0 / \partial\varphi = 0$. The energy spectrum shown in Fig. 5(b) is not suited to derive the thermodynamics, but correctly reflects the gap as it would be observed in spectroscopic measurements.

The behavior for nonzero temperatures may be treated along the lines of, for instance, Ref. 69. With the two PES $V_\pm$, the free energy $F \equiv F(T, b, \varphi, Q)$ becomes

$$F = E_1 + \frac{k}{2}Q^2 - \frac{1}{\beta}\ln\left\{2\cosh\left[\frac{\beta}{2}\sqrt{(b-b_0)^2 + (\alpha Q)^2}\right]\right\}. \tag{28}$$

The equilibrium distortion Q_0 is determined by $\partial F / \partial Q = 0$. It is convenient to switch to the order parameter $\Delta = \alpha Q$ and to express the resulting condition in terms of the reduced variables $\bar{b} = (b - b_0)/b_c$, $\bar{\Delta}_0 = \Delta_0/\Delta_0^{max}$, and $\bar{T} = T/T_c^{max}$ (where $k_B T_c^{max} = b_c/2$; we recall $\Delta_0^{max} = b_c$). In these units, one obtains

$$\tanh(\bar{X}/\bar{T}) = \bar{X}, \tag{29a}$$

$$\bar{X} \equiv \sqrt{\bar{b}^2 + \bar{\Delta}_0^2}. \tag{29b}$$

This sort of transcendent equation often appears in mean-field theories, for instance, the Weiss molecular-field theory of ferromagnets.[75] This shows that the above theory actually establishes the mean-field theory of the FISJTE.

At the LC, where $\bar{b} = 0$ and hence $\bar{X} \propto \bar{\Delta}_0$, the graphical solution of Eq. (29) proceeds exactly as in textbooks on the Weiss ferromagnet.[75] The critical temperature, below which a spontaneous distortion occurs, is determined by $\tanh(\bar{X}/\bar{T}_c) \approx \bar{X}/\bar{T}_c = \bar{X}$, which yields $\bar{T}_c = 1$ or $k_B T_c = k_B T_c^{max} = b_c/2$, respectively. At the LC, T_c assumes its maximal
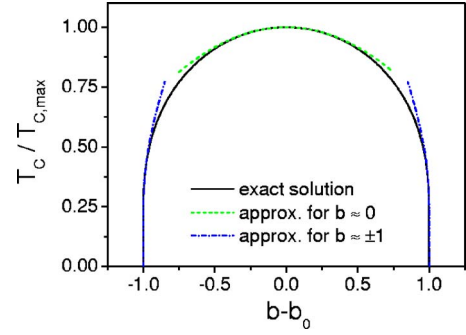

FIG. 7. (Color online) Field dependence of the reduced critical temperature $\bar{T}_c$ (solid line). The dashed (green online) and dash-dotted (blue online) lines represent the approximate solutions $\bar{b} \approx \sqrt{3(1-\bar{T}_c)}$ for $|\bar{b}| \ll 1$ and $\bar{T}_c \approx 2\ln[2/(1-|\bar{b}|)]^{-1}$ for $\bar{b} \to \pm 1$, respectively.

value, T_c^{max}. For fields below or above the LC, T_c is reduced, in accord with the finding that the distortion is largest at the LC point at zero temperature [see Fig. 5(a)].

The zero-temperature behavior is easily rederived. For $T = 0$, Eq. (29) reduces to the condition $\bar{b}^2 + \bar{\Delta}_0^2 = 1$, which is equivalent to Eq. (26).

The critical temperature for an arbitrary field is given by the solution of Eq. (29) for $\bar{\Delta}_0 = 0$, i.e., $\tanh(\bar{b}/\bar{T}_c) = \bar{b}$, which yields

$$\bar{T}_c(\bar{b}) = 2\bar{b}\ln\left(\frac{1+\bar{b}}{1-\bar{b}}\right)^{-1}. \tag{30}$$

The dependence of $\bar{T}_c$ on $\bar{b}$ (or b, respectively) is displayed in Fig. 7. Near the LC point, where $|\bar{b}| \ll 1$, one finds $\bar{b} \approx \sqrt{3(1-\bar{T}_c)}$, corresponding to a critical exponent of $1/2$ as expected for a mean-field theory. Near the upper or lower critical fields, $\bar{b} \to \pm 1$, the critical temperature $\bar{T}_c$ goes to zero according to $\bar{T}_c \approx 2\ln[2/(1-|\bar{b}|)]^{-1}$. The field dependencies of these approximations are also displayed in Fig. 7.

The analysis so far was based on the assumption of $\Delta(Q) = \alpha Q$ or $\Delta(0) = 0$, respectively. In real materials, however, $\Delta(Q) = \Delta(0) + \alpha Q$ could be more appropriate. For instance, in the AFM wheel $CsFe_8$, the molecular C_4 symmetry permits next-neighbor Dzyaloshinsky-Moriya interactions, which would result in $\Delta(0) \neq 0$ [for the specific example of $CsFe_8$, however, experiments indicate that $\Delta(0)$ is in fact rather small[73]]. The effect of a nonzero value of $\Delta(0)$ at zero temperature shall be shortly discussed.

The minimization of $V(Q)$ as in the above, but with $\Delta(Q) = \Delta(0) + \alpha Q$, reveals that the system is unconditionally instable for any magnetic field and not only in the range $[b_0 - bc, b_0 + b_c]$ as in the case of $\Delta(0) = 0$. This is expected since the unconditional instability is not related to $\Delta(0) = 0$, but to the presence of a nondiagonal ME coupling. An analytic solution is not possible for general values of $\Delta(0)$. Figure 8 hence displays the numerically calculated field dependencies of the order parameter Δ_0 for various values of the
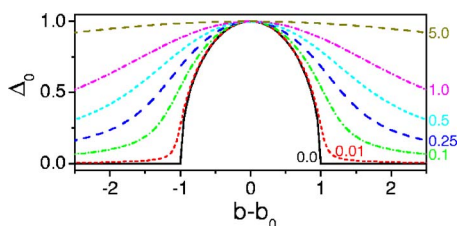
FIG. 8. (Color online) Field dependence of the order parameter Δ_0 for the indicated values of the ratio $\Delta(0)/\Delta_0^{max}$ ($b_c = \Delta_0^{max} = 1$, $k = 1/2$).

ratio $\Delta(0)/\Delta_0^{max}$. For $\Delta(0) = 0$, of course the previous result is reproduced. Although the system is unconditionally instable in the whole field range for any value $|\Delta(0)| > 0$, Fig. 8 reveals that for small $\Delta(0)$, i.e., $\Delta(0) \ll \Delta_0^{max}$, the distortion outside of the field range $[b_0 - bc, b_0 + b_c]$ is very small as compared to the maximum distortion $Q_0^{max} = \Delta_0^{max}/\alpha$. The behavior remains very similar to the one obtained for $\Delta(0) = 0$; only the onsets of the distortion at the fields $b_0 - b_c$ and $b_0 + b_c$ are less sharp. Hence, the magnetization and torque curves will look similar as in Fig. 6, but with the sharp features at $b_0 - b_c$ and $b_0 + b_c$ rounded by a small $\Delta(0)$.

For large values of $\Delta(0)$, $\Delta(0) \gg \Delta_0^{max}$, the situation changes. In this limit the minimization of $V(Q)$ yields for the

equilibrium distortion the simple result $Q_0 = (\alpha/k)H(b)$, where in the function $H(b)$ [Eq. (4b)], one has to insert $\Delta(0)$ for the level-mixing parameter Δ. In terms of the order parameter Δ_0, this corresponds to $\Delta_0 = 2\Delta_0^{max}H(b)$, which shows that Δ_0 will not exceed Δ_0^{max}, and in particular will remain much smaller than $\Delta(0)$. Physically—it is now more intuitive to think in terms of a small Δ_0^{max} or weak ME coupling, respectively—the coupling of the spin system to the lattice is so weak that a lattice distortion does not affect the energy of the system much. The distortion traces the (field-dependent) energy gap, as encoded in $H(b)$, but does not modify it significantly. The magnetization and torque curves thus essentially show the profiles found in Sec. IV for zero ME coupling, with a broadening parameter $\Delta = \Delta(0)$. Accordingly, for $\Delta(0) \gg \Delta_0^{max}$, a ME coupling will not lead to pronounced effects. This is reasonable; it just means that in order to raise the effects of the field-induced ME instability to an observable level, the system should exhibit a sufficiently strong coupling to the lattice and/or sufficiently soft vibration mode.

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[72] In this work, distortion refers to a distortion of the molecule's structure as compared to the structure without ME coupling. At zero field or far away from the LC, respectively, the molecule may be "distorted" in the sense that its structure exhibits devia-

tions from some idealized geometry, such as a perfect cyclic symmetry in the case of AFM wheels, but these distortions are not considered in this work as the result of a ME coupling. The presented model describes the (additional) field-induced distortions near a LC. It does not put any restrictions on the possible zero-field (i. e., nondistorted) structures of the molecule, besides that the molecule is magnetically uniaxial.

[73] A small value of $\Delta(0)$ in $CsFe_8$ is suggested by several experimental findings. From the field range of the field-induced phase, one can estimate Δ_0^{max} to be 2 K (Ref. 42). This represents quite a significant effect on the scale of the magnetic excitations in $CsFe_8$; the 2 K should be compared to the energy gap due to Heisenberg exchange and single-ion anisotropy of 6 K in zero field (Ref. 47). A Dzyaloshinsky-Moriya interaction of such a strength as to produce a splitting of 2 K is absolutely unrealistic; applying the findings and arguments of Ref. 24 to $CsFe_8$ could support a value of 0.1 K. Furthermore, a Dzyaloshinsky-Moriya interaction producing a 2 K effect is inconsistent with the inelastic neutron scattering (INS) experiments presented in Ref. 47 and the (unpublished) high-frequency, high-field single-crystal electron paramagnetic resonance (EPR) experiments mentioned in there. Finally, the fact that the experimentally observed anomalies in the torque signal are well reproduced by the model for small $\Delta(0)$ provides further strong evidence, in particular, as the effect of a Dzyaloshinsky-Moriya interaction varies as $\sin \varphi$ and is hence reduced by more than an order of magnitude for field orientations close to the z axis, where the anomalies in the torque signal, however, nevertheless are observed (Ref. 42).

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