# Octupolar ordering of $\Gamma_8$ ions in a magnetic field

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We study *f*-electron lattice models which are capable of supporting octupolar, as well as dipolar and quadrupolar, order. Analyzing the properties of the $\Gamma_8$ ground-state quartet, we find that (111)-type combinations of the $\Gamma_5$ octupoles $\mathcal{T}^{\beta}_{111}=\mathcal{T}^{\beta}_{x}+\mathcal{T}^{\beta}_{y}+\mathcal{T}^{\beta}_{z}$ are the best candidates for octupolar order parameters. Octupolar ordering induces $\Gamma_5$-type quadrupoles as secondary order parameter. Octupolar order is to some extent assisted, but in its basic nature unchanged, by allowing for the presence of quadrupolar interactions. In the absence of an external magnetic field, equivalent results hold for antiferro-octupolar ordering on the fcc lattice. In this sense, the choice of our model is motivated by the recent suggestion of octupolar ordering in $NpO_2$. The bulk of our paper is devoted to a study of the effect of an external magnetic field on ferro-octupolar ordering. We found that octupolar order survives up to a critical magnetic field if the field is lying in specific directions, while for general field directions, the underlying symmetry of the model is destroyed and therefore the phase transition suppressed even in weak fields. Field-induced multipoles and field-induced couplings between various order parameters are discussed on the basis of a group-theoretical analysis of the Helmholtz potential. We also studied the effect of octupolar ordering on the nonlinear magnetic susceptibility which satisfies Ehrenfest-type relations at continuous octupolar transitions.

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## I. INTRODUCTION

The nature of the 25-K phase transition of $NpO_2$ is a long-standing mystery. The developments up to 1999 are reviewed in Ref. 1. $NpO_2$ is a semiconductor with well-localized $5f^3$ shells, thus in principle relatively easy to understand in terms of crystal-field theory and superexchange interactions. However, it was concluded that the phase transition at 25 K cannot be modeled by any combination of dipolar and quadrupolar ordering phenomena. This leaves us with the possibility that the primary order parameter is one of the octupolar moments.[2] Recent experimental evidence is successfully interpreted by postulating that the primary order parameters are $\Gamma_5$ octupoles, and that the transition is accompanied by the induced order of $\Gamma_5$ quadrupoles.[3,4]

In comparison to well-studied quadrupolar phenomena, the physics of models supporting octupolar order is less explored.[5] Motivated by recent suggestions that certain actinide and rare-earth compounds undergo octupolar ordering transitions,[2,3,6] we study a lattice of *f* shells with $\Gamma_8$ quartet ground states, assuming symmetry-allowed octupole-octupole and quadrupole-quadrupole interactions. Our choice of model is motivated by certain features of $NpO_2$ (and to a lesser extent by $Ce_{1-x}La_xB_6$) physics, but we could not claim that we are offering a model for $NpO_2$. In particular, we consider only spatially uniform solutions though it is known that $NpO_2$ has antiferro-octupolar order following the four-sublattice triple-$\vec{q}$ pattern characteristic of the fcc lattice.[4] Nevertheless, our study of hypothetical ferro-octupolar ordering, in addition to having interest on its own, offers some insight into the physics of actual $NpO_2$. Some of the features of $NpO_2$ follow from the point group symmetry of the local Hilbert space, and from the mere fact of having symmetry breaking by $\Gamma_5$-type octupolar order; we are able to account for these. We are, however, missing the interesting consequences of antiferro-octupolar intersite interactions, and $\mathbf{Q}\neq(0,0,0)$ space-group symmetry. We plan to return to these questions in a sequel to our present work.

Analyzing the possible order parameters carried by the $\Gamma_8$ ground-state set, we find that the best choice of the local order parameter is the 111-type combination of $\Gamma_5$ octupoles. In contrast to the case of $CeB_6$ (which can also be modeled as an array of $\Gamma_8$ shells), the fourfold degeneracy is lifted in a single continuous transition. We find that the primary ordering of octupolar moments induces 111-type quadrupoles even in the absence of quadrupole-quadrupole interactions. However, allowing for a nonvanishing $\Gamma_5$-type quadrupole-quadrupole interaction assists the octupolar ordering. These features are common to our hypothetical ferro-octupolar ordering model, and the actual antiferro-octupolar ordering of $NpO_2$. This holds in the absence of external (magnetic or strain) fields. However, our main interest lies in the study of field effects.

The effect of external magnetic fields on ferro-octupolar transitions is analyzed in detail. Since octupolar ordering is a mechanism for the spontaneous breaking of time reversal invariance, and the application of a magnetic field removes this invariance, it might have been guessed that the ground-state degeneracy is completely lifted in a magnetic field, and consequently no octupolar symmetry breaking is possible. Such is indeed the case for fields applied in general (nonsymmetrical) directions: the phase transition is smeared out by arbitrarily weak fields. However, we found that for magnetic fields lying in certain planes, or pointing along specific directions, there is a remaining ground-state degeneracy which is removed by a continuous symmetry-breaking transition (or a sequence of two transitions). The critical temperature is gradually suppressed by increasing the field, eventually vanishing at a critical magnetic field. In simple

 

terms, the explanation is the following. Magnetic fields will, in general, induce octupolar moments as a higher-order polarization effect. However, for special field directions, the field is not able to induce at least one of the $\Gamma_5$ octupole moments. Then this moment can be generated by intersite interaction only, and it will become nonzero below a critical temperature.

We stress that this latter part of our work rests on the assumption of uniform order, and we have not attempted to apply similar considerations to the antiferro-octupolar phase. The essential difficulty is that an external magnetic field will, in general, turn the octupole moments from their original direction, and therefore the symmetrical zero-field triple-$\vec{q}$ structure is expected to undergo a complicated distortion which is difficult to analyze.

There is a great variety of multipolar moments induced by the concerted action of pre-existing uniform octupolar order and an external magnetic field. The existence of such polarization effects can be deduced from general symmetry analysis (Sec. IV, and particularly Secs. V A and V C); herein we follow and extend the approach of Refs. 7–9. Illustrative examples are provided by mean-field calculations.

### A. Short review of $NpO_2$

The experimental results on $NpO_2$ are known from Refs. 1–4. We quote only the findings which are pertinent to our model study.

Actinide dioxides have the $CaF_2$ crystal structure at room temperature. The sublattice of the metal ions is an fcc lattice. $Np^{4+}$ ions have the configuration $5f^3$, the corresponding Hund's rule ground-state set belongs to $J=9/2$. The tenfold degenerate free-ion manifold is split by the cubic crystal field, yielding a $|\Gamma_6\rangle$ doublet and the $|\Gamma_8^{(1)}\rangle$ and $|\Gamma_8^{(2)}\rangle$ quartets. Neutron spectroscopy has shown that the ground-state quartet $|\Gamma_8^{(2)}\rangle$ is well separated from the first excited state (the other quartet).[10]

$5f^3$ states have both non-Kramers and Kramers degeneracies; the latter might have been expected to be lifted by magnetic ordering. There is, in fact, an apparently continuous phase transition at $T_0=25$ K, which was first observed as a large λ anomaly in the heat capacity.[11] The linear susceptibility rises to a small cusp at $T_0$, and stays almost constant below.[12,2] The observations were, at first, ascribed to antiferromagnetic ordering. However, diffraction experiments failed to detect magnetic order,[13] and Mössbauer effect has put the upper bound of $0.01\mu_B$ on the ordered moment. Thus we can exclude dipolar ordering, and have to consider the possibilities of multipolar order.

A $\Gamma_8$ ground-state quartet can carry a variety of local order parameters: in addition to the $\Gamma_4$ dipoles, also $\Gamma_3$ and $\Gamma_5$ quadrupoles, and $\Gamma_2$-, $\Gamma_4$-, and $\Gamma_5$-type octupoles.[7] The nature of intersite interactions decides which of these will actually undergo an ordering transition. Though magnetic ordering is the commonly expected outcome, there is no rule to guarantee that dipolar ordering is the leading instability. In fact, for light rare earths (and also for light actinides) quadrupolar ordering often preempts, or precedes, dipolar order. However, the possibility that octupolar order comes first, is quite recent.[6]

The possibility of an explanation in terms of quadrupolar ordering has been examined with great care.[14,1,4] The ordering pattern has to conform to the observed fact that the $T<T_0$ phase preserves cubic symmetry, but this requirement can be satisfied by the triple-$\vec{q}$ order of $\Gamma_5$ quadrupoles.[3] Indeed, resonant x-ray scattering finds long-range order of the $\Gamma_5$ electric quadrupole moments. However, the unquestionable appearance of quadrupolar order cannot be the whole story. Quadrupolar ordering alone could not resolve the Kramers degeneracy,[15] and thus there should remain low-$T$ magnetic moments giving rise to a Curie susceptibility; this is contrary to observations. Furthermore, muon spin relaxation shows that local magnetic fields, with a pattern suggestive of magnetic octupoles, appear below $T_0$.[3]

Though there are cases (as in $CeB_6$) when the Kramers and non-Kramers degeneracies of the $\Gamma_8$ quartet are lifted in separate phase transitions, this is not the case for $NpO_2$: quadrupolar and octupolar moments appear simultaneously. This alone suffices to show that they must be coupled, i.e., the octupolar moments must also be of $\Gamma_5$ symmetry.[16] Still, the question may be posed whether the transition is primarily octupolar or quadrupolar. We confirm the proposal made in Refs. 3 and 4: the primary order parameter is the octupole moment, and its ordering induces quadrupolar moments of the same symmetry. $NpO_2$ has antiferro-octupolar order. However, systems with a uniform polarization of octupolar moments may, in principle, exist and their study is logically the first step in studying the nature of octupolar order, and its coupling to other kinds of order, and to external fields. Incidentally, we find that there is a phenomenological similarity between our findings and the observed behavior of $NpO_2$ (and also $Ce_{1-x}La_xB_6$), the reason being that for $\Gamma_8$ Hilbert spaces, the $\Gamma_5$ octupolar states are non-magnetic, and magnetic susceptibility arises only due to transitions between octupolar levels. The mechanism relies only on the existence of an octupolar effective field, and it is basically the same for ferro- and and antiferro-type alignments. Naturally, the details of polarization phenomena depend on the kind of octupolar long-range order, and we hope to return to the case of antiferro-octupolar order in a future work.

In the absence of an external magnetic field, the thermodynamics of ferro- and antiferro-octupolar ordering is quite similar, as is also the case for more straightforward kinds of ordering. Our $H=0$ self-consistency equation for the uniform polarization is the same as the one for either of the sublattice polarizations in the triple-$\vec{q}$ structure. Also the results for nonvanishing quadrupolar interactions are transferable since the coupled quadrupolar order is of the same $\Gamma_5$ symmetry, and therefore the four-sublattice structure remains the same. For either ferro-octupolar, or triple-$\vec{q}$ antiferro-octupolar order we find the following.

(i) Octupole-octupole coupling alone is sufficient to select a unique ground state.

(ii) The ground state carries also quadrupolar moment.

(iii) Allowing for an additional quadrupole-quadrupole interaction does not change the character of the low-$T$ phase until the quadrupole-quadrupole interaction exceeds a threshold value; beyond that, a purely quadrupolar transition is followed by octupolar ordering.

## II. OCTUPOLAR MOMENTS IN THE $\Gamma_8$ QUARTET STATE

Neutron-diffraction measurements indicate that the ground state is one of the two $\Gamma_8$ quartets. Since the same irrep occurs twice, symmetry alone cannot tell us the basis functions: their detailed form depends on the crystal-field potential. Exploiting the fact that the crystal-field splittings are large, we neglect the higher-lying levels, and describe the phase transition within the ground-state set. Since thus the sequence and separation of levels is of little consequence, we have arbitrarily chosen one of the quartets obtained by assuming a purely fourth-order potential $\mathcal{H}_{\rm cryst}=\mathcal{O}_4^0+5\mathcal{O}_4^4$ as the ground state. We believe that this assumption has no influence on the main features of our results.[17] The general form of the basis states is (numerical coefficients will be given in Appendix A):

$$\Gamma_8^1=\alpha|\tfrac{7}{2}\rangle+\beta|-\tfrac{1}{2}\rangle+\gamma|-\tfrac{9}{2}\rangle,$$

$$\Gamma_8^2=\gamma|\tfrac{9}{2}\rangle+\beta|\tfrac{1}{2}\rangle+\alpha|-\tfrac{7}{2}\rangle,$$

$$\Gamma_8^3=\delta|\tfrac{5}{2}\rangle+\epsilon|-\tfrac{3}{2}\rangle,$$

$$\Gamma_8^4=\epsilon|\tfrac{3}{2}\rangle+\delta|-\tfrac{5}{2}\rangle. \qquad (1)$$

It is apparent that the $\Gamma_8$ quartet is composed of two time-reversed pairs, thus it has twofold Kramers, and also twofold non-Kramers, degeneracy. The above choice of the basis emphasizes the presence of $J_z$ dipole and $\mathcal{O}_2^0=\frac{1}{2}[3J_z^2-J(J+1)]$ quadrupole moments, but of course it is not unique. In fact, the decomposition

$$\Gamma_8\otimes\Gamma_8=\Gamma_{1g}\oplus\Gamma_{4u}\oplus\Gamma_{3g}\oplus\Gamma_{5g}\oplus\Gamma_{2u}\oplus\Gamma_{4u}\oplus\Gamma_{5u} \qquad (2)$$

[where $g$ ($u$) indicates invariance (change of sign) under time reversal] shows that the subspace carries 15 different kinds of moments: three dipolar $\Gamma_4$, two quadrupolar $\Gamma_3$, three quadrupolar $\Gamma_5$, and seven kinds ($\Gamma_2$, $\Gamma_4$, and $\Gamma_5$) of octupolar moments.[7] Within subspace (1), we can rotate so as to get nonvanishing expectation values of any of the 15 potential order parameters. Or in other words, if there is an effective field $-\mathcal{R}\langle\mathcal{R}\rangle$ (where $\mathcal{R}$ may be any of the fifteen components), then the fourfold ground-state degeneracy will be at least partially lifted.

In general, intersite interactions affect all 15 moments. Lacking a microscopic mechanism of Np-Np interactions in $NpO_2$, we have to assume some form of the interaction, and argue from the consequences.

Restricting our attention to octupolar ordering, we have to choose between $\Gamma_2$, $\Gamma_4$, and $\Gamma_5$. The possibility of $\Gamma_2$ octupolar ordering was first suggested by Santini and Amoretti.[2] In a later work, this choice was discarded because there would be no coupling to quadrupoles.[3] We may also add that $\Gamma_2$ ordering would still leave us with a twofold degenerate ground state. We can also exclude the $\Gamma_4$ type octupolar moments, because symmetry allows their mixing with the magnetic dipoles, and dipole moments are excluded by experiments.

This leaves us with the possibility of the ordering of $\Gamma_5$-type octupole moments,[7]

$$\mathcal{T}_x^\beta=\tfrac{1}{3}(\overline{J_xJ_y^2}-\overline{J_z^2J_x}),$$

$$\mathcal{T}_y^\beta=\tfrac{1}{3}(\overline{J_yJ_z^2}-\overline{J_x^2J_y}),$$

$$\mathcal{T}_z^\beta=\tfrac{1}{3}(\overline{J_zJ_x^2}-\overline{J_y^2J_z}), \qquad (3)$$

where the bars on the angular momentum operators mean the symmetrized combinations of operators $\overline{J_zJ_x^2}=J_zJ_xJ_x+J_xJ_zJ_x+J_xJ_xJ_z$, etc. Acting as a field, either of $\mathcal{T}_x^\beta$, $\mathcal{T}_y^\beta$, or $\mathcal{T}_z^\beta$ splits the $\Gamma_8$ quartet into two doublets. The doublets carry magnetic moments. Thus assuming, say, $\mathcal{T}_x^\beta$-type ordering would still leave us with a residual degeneracy which should be lifted by a separate magnetic (dipolar) phase transition.

However, we may choose a different orthogonal set of $\Gamma_5$ octupole operators as order parameters. Figure 1(b) shows the spectrum of octupoles[18]

$$\mathcal{T}(\vartheta,\phi)=\sin\vartheta(\cos\phi\,\mathcal{T}_x^\beta+\sin\phi\,\mathcal{T}_y^\beta)+\cos\vartheta\,\mathcal{T}_z^\beta \qquad (4)$$

for $\phi=\pi/4$. It appears that the ground state is always a singlet except for the special points $\vartheta=0$ and $\vartheta=\pi$ (i.e., $\mathcal{T}_z^\beta$ which we discussed above). Furthermore, the overall width of the spectrum varies with $\vartheta$, reaching its maximum at $\vartheta=\arccos(1/\sqrt{3})$, or equivalent positions. Thus within the $\Gamma_8$ subspace, the three-dimensional pseudovector of $\Gamma_5$ octupoles is ''longest'' in the (111) direction, or in equivalent directions. At any $(\vartheta,\phi)$ the maximum of the absolute value of the eigenvalues is taken as the magnitude of the octupolar moment (note that the spectrum is symmetrical about 0). This is the quantity shown in Fig. 1(a). We see sixteen maxima. However, it is easy to check that the plot range for $(\vartheta,\phi)$ gives *two* points for every direction, therefore the number of maxima is only eight. The directions (111), $(\bar{1}11)$, $(1\bar{1}1)$, and $(11\bar{1})$ are equivalent by cubic symmetry, and for each direction, the octupole moment may be of either sign [Fig. 1(b)].

Thinking of the ordering as caused by an octupole-octupole interaction with cubic symmetry[19]

$$\mathcal{H}_{\rm oc}=-J_{\rm oc}\sum_{i,j}(\mathcal{T}_{i,x}^\beta\mathcal{T}_{j,x}^\beta+\mathcal{T}_{i,y}^\beta\mathcal{T}_{j,y}^\beta+\mathcal{T}_{i,z}^\beta\mathcal{T}_{j,z}^\beta) \qquad (5)$$

it is plausible that it will occur in one of the (111) directions. We may think of it as the cubic crystal field giving rise to an octupolar single-ion anisotropy with the (111) directions as easy axes. Thus our candidates for order parameters are

$$\mathcal{T}_{111}^\beta=\mathcal{T}_x^\beta+\mathcal{T}_y^\beta+\mathcal{T}_z^\beta,$$

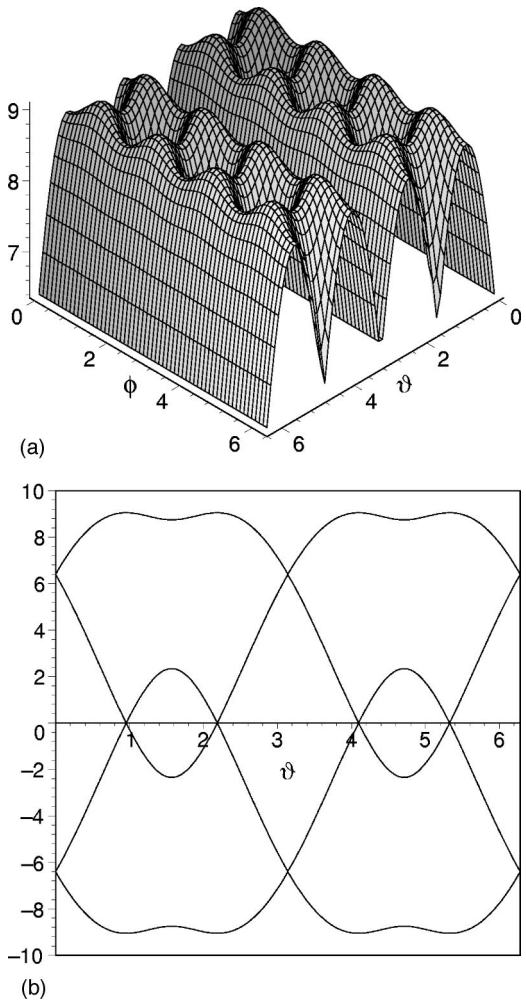


FIG. 1. (a) The direction dependence of the magnitude of the octupolar moment $\mathcal{T}(\vartheta,\phi)$ [see equation (4)]. (b) The spectrum of $\mathcal{T}(\vartheta,\phi)$ in the $[1\bar{1}0]$ plane ($\phi=\pi/4$).

$$\mathcal{T}^{\beta}_{111}=\mathcal{T}^{\beta}_{x}-\mathcal{T}^{\beta}_{y}-\mathcal{T}^{\beta}_{z},$$

$$\mathcal{T}^{\beta}_{11\bar{1}}=-\mathcal{T}^{\beta}_{x}+\mathcal{T}^{\beta}_{y}-\mathcal{T}^{\beta}_{z},$$

$$\mathcal{T}^{\beta}_{1\bar{1}1}=-\mathcal{T}^{\beta}_{x}-\mathcal{T}^{\beta}_{y}+\mathcal{T}^{\beta}_{z}. \tag{6}$$

The four minima seen in Fig. 1 belong to $\pm\mathcal{T}^{\beta}_{111}$ and $\pm\mathcal{T}^{\beta}_{11\bar{1}}$.[20] We have checked that the ground state of either of these operators carries a $\Gamma_5$-type quadrupolar moment, but *no magnetic dipole moment*.

We note that these single-ion properties would be useful for modeling $NpO_2$; however, the interionic interactions may still be chosen as either ferro-octupolar or antiferro-octupolar. Let us furthermore point it out that the four equivalent states (6) are ideally suited for constructing a four-sublattice ground state for nearest-neighbor antiferro-octupolar coupling on an fcc lattice. This would correspond to the experimentally motivated suggestion of triple-$\vec{q}$ order by Caciuffo *et al.*[4] The triple-$\vec{q}$ octupolar ordering can then induce the observed triple-$\vec{q}$ structure of the $\Gamma_5$ quadrupoles

$$\mathcal{O}_{111}=\mathcal{O}_{xy}+\mathcal{O}_{yz}+\mathcal{O}_{zx}, \tag{7}$$

etc., as a secondary order parameter. In the absence of a magnetic field, our mean-field results are formally valid for either the ferro- or antiferro-octupolar case, while as far as field effects are concerned, we stick definitely to the former case. We have to refrain from making detailed comments on $NpO_2$ until we completed work on the magnetic properties.

Denoting the ground state of $\mathcal{T}_{111}$ by $|\phi_0\rangle$, we quote the numerical values from Appendix B:

$$\langle\phi_0|\mathcal{T}^{\beta}_{111}|\phi_0\rangle=A=-15.683,$$

$$\langle\phi_0|\mathcal{O}_{111}|\phi_0\rangle=B=8.019,$$

$$\langle\phi_0|J_x|\phi_0\rangle=\langle\phi_0|J_y|\phi_0\rangle=\langle\phi_0|J_z|\phi_0\rangle=0, \tag{8}$$

and

$$\langle\phi_0|\mathcal{O}_{xy}|\phi_0\rangle=\langle\phi_0|\mathcal{O}_{yz}|\phi_0\rangle=\langle\phi_0|\mathcal{O}_{xz}|\phi_0\rangle. \tag{9}$$

One may be wondering whether the $\Gamma_5$ quadrupoles by themselves would like a different orientation than the one forced upon them by the octupoles. This is not the case: a calculation shows that the length of the pseudovector $(\mathcal{O}_{xy},\mathcal{O}_{yz},\mathcal{O}_{zx})$ is the same in all directions. There is no single-ion anisotropy for the $\Gamma_5$ quadrupoles; picking the (111) solution is exclusively the octupoles' doing.

## III. THE OCTUPOLAR-QUADRUPOLAR MODEL

We assume the presence of $\Gamma_5$-type quadrupolar and octupolar interactions

$$\mathcal{H}=\mathcal{H}_{\rm oc}+\mathcal{H}_{\rm quad}, \tag{10}$$

where $\mathcal{H}_{\rm oc}$ was given in Eq. (5) and analogously

$$\mathcal{H}_{\rm quad}=-J_{\rm quad}\sum_{i,j}\left(\mathcal{O}_{i,xy}\mathcal{O}_{j,xy}+\mathcal{O}_{i,yz}\mathcal{O}_{j,yz}+\mathcal{O}_{i,zx}\mathcal{O}_{j,zx}\right). \tag{11}$$

For the sake of simplicity, we assume $J_{\rm quad}/J_{\rm oc}\geqslant 0$.

For ferro-octupolar coupling ($J_{\rm oc}>0$), we may assume uniform (111) order. The mean-field single-site Hamiltonian is of the form

$$\mathcal{H}_{\rm MF}=-\mathcal{T}^{\beta}_{111}\langle\mathcal{T}^{\beta}_{111}\rangle-j\mathcal{O}_{111}\langle\mathcal{O}_{111}\rangle, \tag{12}$$

where we have chosen the octupolar effective field amplitude as the energy unit, and $j=J_{\rm quad}/J_{\rm oc}$. Henceforth we assume that all effects arising from lattice geometry, and the detailed form of the interactions, are included in $J_{\rm oc}$, $J_{\rm quad}$, and hence also in $j$.

We note that formally the same mean-field problem arises by assuming antiferro-octupolar interactions, and postulating four sublattices with local order parameters as defined in Eq. (6) and the analogous quadrupolar moments.

The temperature dependence of the order parameters $\mathcal{T}=\langle\mathcal{T}^{\beta}_{111}\rangle$ and $q=\langle\mathcal{O}_{111}\rangle$ is obtained by the numerical solution of the self-consistency equations derived from diagonal-

izing Eq. (12) in the basis (1). The overall behavior is similar to that found in dipolar-quadrupolar models used in the description of Pr compounds;[21,22] however, now octupoles play the role of dipoles.

The dimensionless free energy belonging to Eq. (12) is

$$\mathcal{F}=\tfrac{1}{2}\mathcal{T}^2+\tfrac{1}{2}jq^2-t\ln[2\exp(-Bjq/t)\cosh(A\mathcal{T}/t) + 2\exp(Bjq/t)], \tag{13}$$

where $A$ and $B$ were introduced in Eq. (8), and $t=k_BT/J_{oc}$ is the dimensionless temperature.

Octupolar order ($\mathcal{T}\neq 0$) induces quadrupolar moment even in the absence of a quadrupolar coupling, as we can see from setting $j=0$ in $\partial\mathcal{F}/\partial q=0$

$$q=B\frac{\exp(A\mathcal{T}/t)+\exp(-A\mathcal{T}/t)-2}{\exp(A\mathcal{T}/t)+\exp(-A\mathcal{T}/t)+2}. \tag{14}$$

The $T\to 0$ limit is expressed in Eq. (8). It states that by construction, the (111)-type octupolar eigenstates carry (111)-type quadrupolar moments. The same state of affairs prevails as long as $\mathcal{T}\neq 0$. In the "para" phase above the transition temperature, all moments vanish.

The continuous phase transitions of the model (10) can be described by the Landau expansion of the free energy (13),

$$\mathcal{F}\approx\mathcal{F}_0+\left(\tfrac{1}{2}-\frac{A^2}{4t}\right)\mathcal{T}^2+\left(\frac{j}{2}-\frac{B^2j^2}{2t}\right)q^2+\tfrac{1}{4}\frac{BjA^2}{t^2}q\mathcal{T}^2 + \frac{A^4}{96t^3}\mathcal{T}^4-\frac{BjA^4}{24t^4}q\mathcal{T}^4+\frac{B^4j^4}{12t^3}q^4-\frac{B^3j^3A^2}{12t^4}q^3\mathcal{T}^2+\cdots, \tag{15}$$

where $\mathcal{F}_0$ is the noncritical part of the free energy.

Critical temperatures are defined by the change of sign in the coefficient of either of the quadratic terms. Upon lowering the temperature, for small $j$, mixed octupolar-quadrupolar, while for large $j$, pure quadrupolar order sets in first. At intermediate $j$, there is a regime of first-order transitions (Fig. 2).

We consider first the weak-$j$ limit. The critical temperature is $t_{oc}=A^2/2$. At $t_{oc}$, octupolar moment appears as the primary order parameter, but there is also induced quadrupolar order. Minimizing $\mathcal{F}$ with respect to $q$, we get

$$q=\frac{BA^2\mathcal{T}^2}{4t(jB^2-t)}. \tag{16}$$

Thus terms of order $q^2$ and $q\mathcal{T}^2$ are effectively of $O(\mathcal{T}^4)$. Minimizing with respect to $\mathcal{T}$, the critical behavior of the octupolar and quadrupolar moment

$$\mathcal{T}\approx\sqrt{\frac{A^2}{2}-t}\sqrt{\frac{6(A^2-2B^2j)}{A^2-8B^2j}}, \tag{17}$$

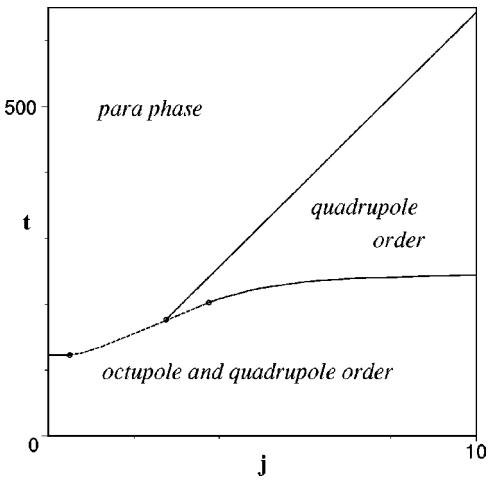


FIG. 2. The mean-field phase diagram of the zero-field quadrupolar-octupolar model (10) in the quadrupolar coupling-temperature plane ($j=J_{quad}/J_{oc}$ and $t=Tk_B/J_{oc}$). The dashed and continuous lines signify first- and second-order phase transitions, respectively. Observe the regime of first-order transitions bounded by two tricritical points (marked by black dots).

$$q\approx-\frac{6B}{A^2-8B^2j}\left(\frac{A^2}{2}-t\right) \tag{18}$$

is characteristic of the mean-field solution for primary and secondary order parameters.

The coefficient

$$\frac{A^4}{96t^3}\frac{4B^2j-t}{B^2J-t}$$

of the combined fourth-order $O(\mathcal{T}^4)$ term of $\mathcal{F}$ changes sign at $t=4B^2j$. Equating this with the critical temperature, we identify the coordinates of the lower tricritical point as $j_{tri,1}=A^2/8B^2=0.48$, and $t_{tri,1}\approx 123$. The critical temperature is constant for $j\leqslant j_{tri,1}$. For $j$ exceeding $j_{tri,1}$ the transition becomes first order. The nature of the coupled orders does not change, but they become more stabilized, and the common transition sets in at higher temperatures (Fig. 2). However, the ground-state moments remain independent of the coupling strengths: $q_{T\to 0}=B$ and $\mathcal{T}_{T\to 0}=A$. Representative temperature dependences of $\mathcal{T}$ and $q$ are shown in Fig. 3.

At large $j$, the first instability is associated with the change of sign of the coefficient of the $q^2$ term: pure quadrupolar order sets in at $t_{quad}=B^2j$. This critical line meets the boundary of first-order transitions at the critical end point $j_{end}\approx 2.75$, $t_{end}\approx 177$ (Fig. 2). For $j>j_{end}$ there are two phase transitions: the onset of pure quadrupolar order is followed by the emergence of mixed octupolar-quadrupolar order at $t_{oc}$. The lower phase transition is of first order up to the second tricritical point $j_{tri,2}\approx 3.75$, $t_{tri,2}\approx 185$. For $j<j_{tri,2}$, the onset of octupolar order is reflected in a discontinuity of $q$ [Fig. 3(c)]. For $j>j_{tri,2}$, both transitions are continuous.

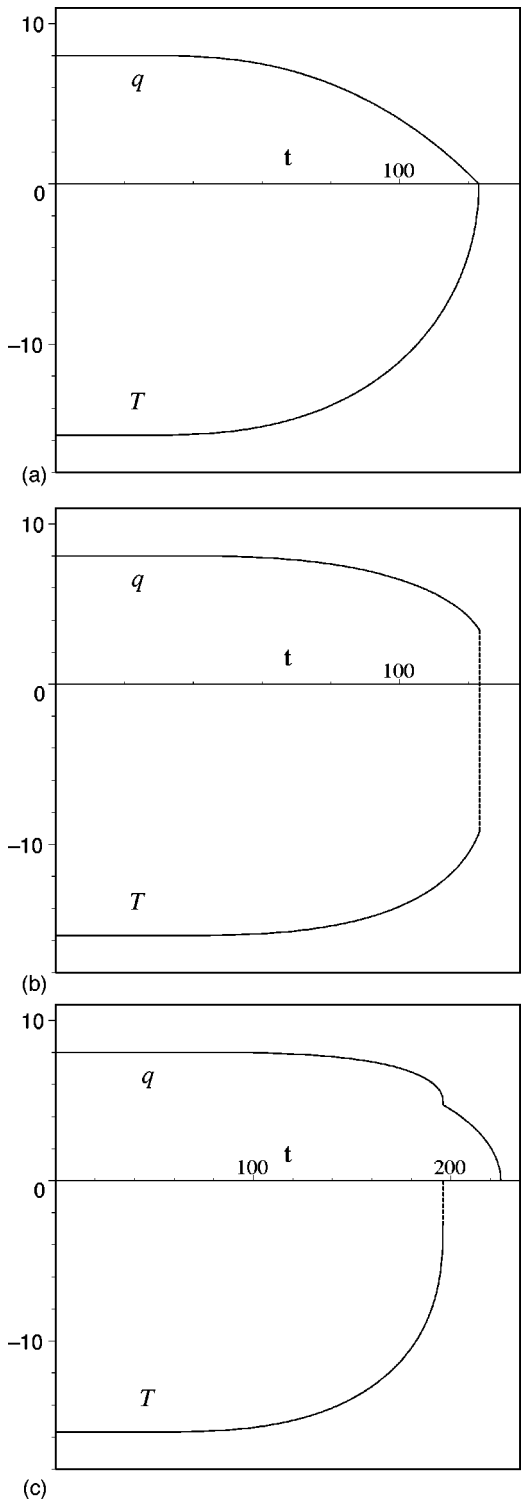


FIG. 3. Octupolar ($\mathcal{T}$) and quadrupolar ($q$) order parameters as a function of $t=k_BT/J_{oc}$ for $J_{quad}/J_{oc}=0$ (a), $J_{quad}/J_{oc}=0.75$ (b), and $J_{quad}/J_{oc}=3.5$ (c).

Deep inside the quadrupolar ordered phase, the development of the octupolar order is essentially unaffected by what the quadrupoles are doing, apart from a weak effect on the transition temperature $t_{oc}$ (note in Fig. 2 that $t_{oc}$ saturates to a constant). Though in this regime, we cannot use Landau expansion to determine $q$, we may assume that it is near its ground-state value $B$, and use a low-order expansion in $\mathcal{T}$ to obtain in the large-$j$ limit

$$\lim_{j\to\infty} t_{oc} = \lim_{j\to\infty} \frac{A^2 \exp(Bqj/t_{oc})}{\exp(Bqj/t_{oc})+\exp(-Bqj/t_{oc})} = A^2 \approx 246. \tag{19}$$

In familiar phase diagrams of dipolar-quadrupolar models, the mixed order would be completely suppressed at $J_{quad}/J_{dipole}\to\infty$ (see, e.g., Fig. 3 of Ref. 22). In contrast, we find the finite saturation value (19) as $J_{quad}/J_{oc}\to\infty$. The peculiarity of the situation depicted in Fig. 2 is the endurance of octupolar order even with infinitely strong quadrupolar coupling. The reason, as we understood earlier, is that in the $\Gamma_8$ subspace the $\Gamma_5$ quadrupoles are completely isotropic, thus they can accommodate a reorientation of the basis states without sacrificing any of their rigid order.

Even confining our attention to uniform states, the effects of an external magnetic field are variegated: It may gradually suppress octupolar ordering, without changing its character (111 direction); it may split the transition in two (001 direction); it may change the character of octupolar order but still facilitate a phase transition (11c direction); or it may completely forbid octupolar ordering (nonsymmetrical directions). We will understand this in detail in Secs. IV and V. A straightforward characterization of field effects in terms of the magnetization curve and its derivatives (the susceptibilities) is possible in the $\mathbf{H}\|(111)$ case only. This is the subject of the next subsection.

We emphasize that our entire analysis of magnetic-field effects is confined to spatially uniform states, and does not cover the cases of supercell ordering, such as the experimentally observable antiferro-octupolar order of $NpO_2$. The basic difficulty is that the intersublattice angles of various moments may get changed by the field; this effect will be treated in a subsequent work.

### A. Nonlinear susceptibility: the H‖(111) case

In certain symmetry directions such as (111), the magnetic field merely acts to suppress uniform octupolar ordering gradually [Fig. 4(a)]. It appears that the phase boundaries can be scaled onto a common curve by introducing the field-dependent transition temperature

$$\frac{T_{oc}(H)}{T_{oc}(H=0)} \approx 1 - a_H H^2 - b_H H^4 \ldots . \tag{20}$$

This bears some similarity to the field-induced suppression of antiferro-quadrupolar order in $PrFe_4P_{12}$.[22]

Our starting point is the mean-field-decoupled Hamiltonian

$$\mathcal{H} = \mathcal{H}_{oc} + \mathcal{H}_{quad} + \mathcal{H}_Z = \mathcal{H}_{oc} + \mathcal{H}_{quad} - \mathbf{H}\cdot\mathbf{J} = -\mathcal{T}T^{\beta}_{111} - jq\mathcal{O}_{111} - HJ_{111}, \tag{21}$$

where the notations follow Eq. (12), $J_{111}=(J_x+J_y+J_z)$, and in the Zeeman term $H$ is the reduced magnetic field.

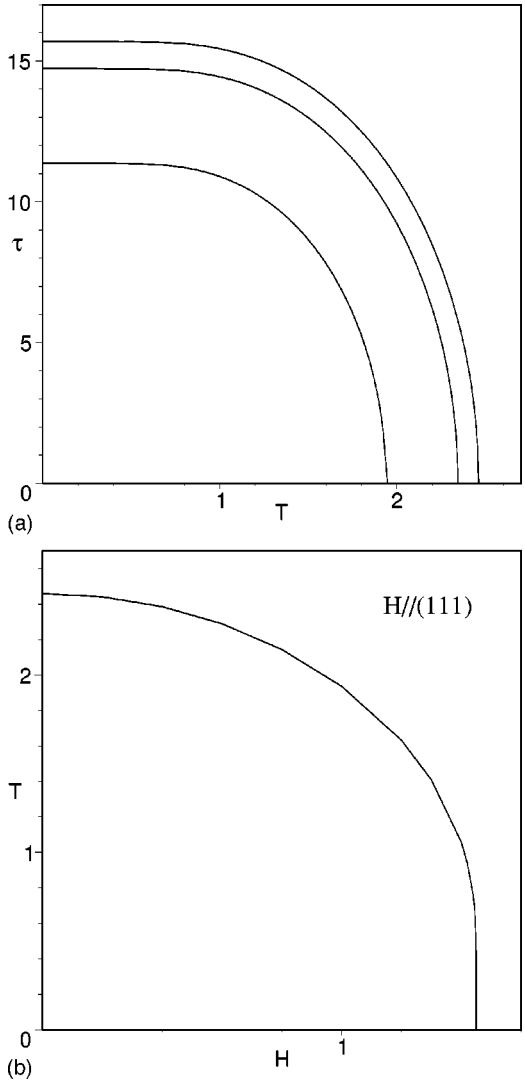


FIG. 4. (a) The $\langle \mathcal{T}^{\beta}_{111} \rangle = \mathcal{T}$ octupolar order parameter as a function of the temperature for $H=0$, 0.5, and 1.0 [$\mathbf{H} \| (111)$, $H$ in units of $g\mu_B$]. (b) the $T$-$H$ phase diagram of the $J_{oc}=0.02k_B$, $J_{quad}=0$ model for $H$ pointing in the (111) direction. The transition is continuous all along the phase boundary.

Multipolar phase transitions, even when nonmagnetic, tend to have a strong signature in the nonlinear magnetic response. The case of quadrupolar transitions has been extensively studied.[23] To obtain analogous results, we expand the free energy corresponding to Eq. (21),

$$\mathcal{F}(\mathcal{T},q,H) = \frac{1}{2}\mathcal{T}^2 + \frac{j}{2}q^2 - t \ln[2 \exp(-Bjq/t) \times \cosh(\sqrt{g_H^2 H^2 + A^2\mathcal{T}^2}/t) + 2 \exp(Bjq/t)\cosh(y_H H/t)]. \quad (22)$$

Here $g_H$ and $y_H$ are the two parameters of the Zeeman splitting scheme of the $\Gamma_8$ subspace (Appendix A). The overall shape of the phase boundary in the $t$-$H$ plane is obtained by expanding $\mathcal{F}(\mathcal{T},q,H)$ in powers of $\mathcal{T}$, and identifying the coefficient of the $\mathcal{T}^2$ term,

$$c_2(H,t) = \tfrac{1}{2} - \frac{A^2}{2g_H H} \frac{\sinh(g_H H/t)}{\cosh(g_H H/t) + \cosh(y_H H/t)}. \quad (23)$$

Solving $c_2(H,t)=0$ gives a line of continuous transitions in the $t$-$H$ plane [Fig. 4(b)].

It is interesting that the octupole ordered phase can be suppressed gradually by a magnetic field [Fig. 4(a)]. Dipole ordering and octupole ordering are two independent ways to break time-reversal invariance. However, octupolar moments are due to currents with zero total circulation, while dipole moments arise from nonzero integrated circulation. In a finite field $\mathbf{H} \| (111)$, the $5f^3$ ion must be able to sustain both kinds of currents simultaneously.

$\mathcal{F}(\mathcal{T},q,H)$ has to be expanded to $O(H^4)$ in order to derive both the susceptibility $\chi$, and the nonlinear magnetic susceptibility $\chi_3$. We do not give the detailed formulas here, but discuss the terms giving rise a quadratic shift of the transition temperature in Eq. (20),

$$\mathcal{F}(\mathcal{T},q,H) \approx \mathcal{F}(\mathcal{T},q,H=0) + \frac{g_H^2 - y_H^2}{4t^2} Bjq H^2 - \frac{g_H^2}{12t^4} H^2 A^2 Bjq \mathcal{T}^2 + \frac{g_H^2 + 3y_H^2}{48t^3} A^2 \mathcal{T}^2 H^2. \quad (24)$$

The first term in the second line describes field-induced $\Gamma_5$ quadrupoles. The general nature of octupoles would allow the presence of a $\mathcal{T}H$ term; it is the peculiarity of the (111) direction that it does not appear here. We have omitted field-induced terms of the noncritical part of the free energy; they have to be included when calculating the susceptibilities.

Further calculation is analogous to that given for the $H=0$ case. Minimizing with respect to $q$ gives for the secondary order parameter

$$q \approx -\frac{B}{4t(t - B^2 j)} [A^2\mathcal{T}^2 + (g_H^2 - y_H^2)H^2]. \quad (25)$$

Replacing this back into Eq. (24), we can determine the optimum value of the primary order parameter $\mathcal{T}$. Here we quote only the result for the quadratic shift of the transition temperature [cf. Eq. (20)]

$$a_H = \frac{1}{6A^4(A^2 - 2B^2 j)} [(A^2 - 8B^2 j) g_H^2 + 3A^2 y_H^2]. \quad (26)$$

One of the contributions to $a_H$ vanishes at the tricritical point ($j \to A^2/8B^2$), while the other remains finite.

Representative results for the linear susceptibility $\chi = -\partial^2 \mathcal{F}/\partial H^2$, and the third-order susceptibility $\chi_3 = -\partial^4 \mathcal{F}/\partial H^4$, are shown in Fig. 5. The octupolar transition appears as a cusp in $\chi$ [Fig. 5(a)]. The cusp can be also represented as the discontinuity of $\partial\chi/\partial T$ [Fig. 5(b)]. The

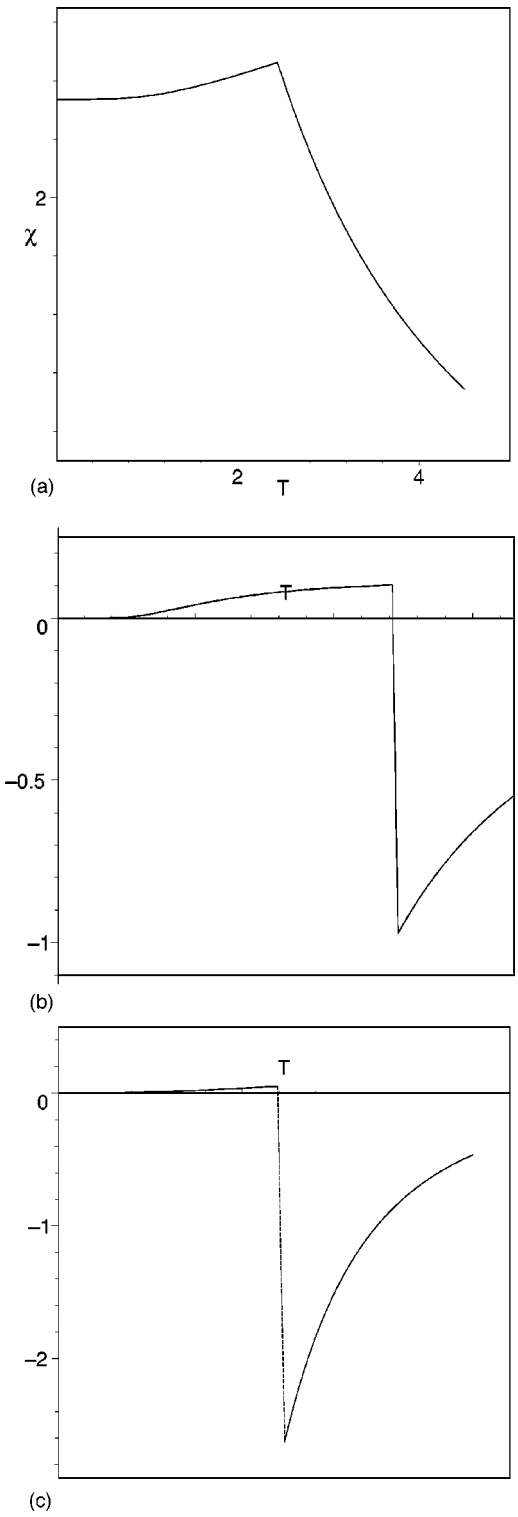


FIG. 5. Linear susceptibility (a), temperature derivative of linear susceptibility (b), and nonlinear susceptibility (c) as a function of temperature for magnetic field parallel to the (111) direction ($J_{oc}=0.02k_B$, $J_{quad}=0$).

nonlinear susceptibility has a discontinuity from positive to negative values [Fig. 5(c)]. These anomalies are related to each other, and the specific-heat discontinuity $\Delta C$, via the Ehrenfest-type equation[24]

$$\frac{a_H}{T}\Delta C+\frac{1}{12a_H}\Delta\chi_3=\Delta\left(\frac{\partial\chi}{\partial T}\right). \tag{27}$$

The derivation[25] of Eq. (27) relies only on the fulfillment of Eq. (20) to order $H^3$.[26] In particular, $b_H$ does not come into Eq. (27). The relationship (20) is often found for the critical temperature of transitions to nonferromagnetic phases such as antiferromagnets, spin-gapped phases, quadrupolar order, etc. Octupolar ordering belongs to this class of transitions.

Though the example shown in Fig. 5 was for $J_{quad}=0$, relationship (27) holds everywhere along the lines of continuous phase transitions shown in Fig. 2. As long as we are dealing with ordinary second-order transitions, Landau theory would be consistent with all the discontinuities appearing in Eq. (27) being finite. However, approaching a tricritical point $\Delta C\to\infty$, and Eq. (27) allows several scenarios. We note from Eq. (26) that generically $y_H\neq 0$, thus $a_H$ remains finite, and then the simplest expectation is that the divergence of $\Delta C$ is matched by that of $\Delta\partial\chi/\partial T$. Such is indeed the finding for our standard $\Gamma_8$ subspace specified in Appendix A. The same holds for $\Gamma_8$ subspaces derived from a combination of fourth-order and sixth-order crystal-field potentials. However, at one particular value of the ratio of the sixth-order and fourth-order terms, the Zeeman spectrum consists of a doublet and two singlets, i.e., the $y_H=0$ case is realized. For this special model[27] $a_H\to 0$ as one approaches the tricritical point, and the field dependence of the transition temperature is purely quartic (20). Here, a peculiar form of the Ehrenfest relation can be derived. $a_H\to 0$ cancels the mean-field divergence of $\Delta C$, and at the same time $\Delta\chi_3\to 0$. The discontinuity of $(\partial\chi/\partial T)$ is now balanced by that of the fifth-order nonlinear susceptibility

$$\frac{1}{120}\Delta\chi_5=b_H\Delta\left(\frac{\partial\chi}{\partial T}\right). \tag{28}$$

It should be interesting to find a situation where Eq. (28) is experimentally testable.[28]

## IV. SUPPRESSION OF FERRO-OCTUPOLAR ORDER BY A MAGNETIC FIELD

Next, we consider the effect of a finite magnetic field of arbitrary orientation on a system of interacting $\Gamma_5$ octupoles. Henceforth, our mean-field arguments will be based on a simplified version of Eq. (21),

$$\mathcal{H}=\mathcal{H}_{oc}+\mathcal{H}_Z=\mathcal{H}_{oc}-\mathbf{H}\cdot\mathbf{J}, \tag{29}$$

where $\mathcal{H}_{oc}$ is taken from Eq. (5), and $J_{quad}=0$. Here, as in Sec. V, we will confine our attention to uniform states. An essential extension of our argument would be needed to cover the case of $NpO_2$.

First, let us reconsider the case of a field $\mathbf{H}\|(111)$ (Fig. 4). The nature of the octupolar order parameter is not influenced by the field, only its saturation value and the transition temperature are scaled down. Conversely, since there is a $T=0$ phase transition at a critical field $H_{cr}$ [Fig. 6(a)], there must

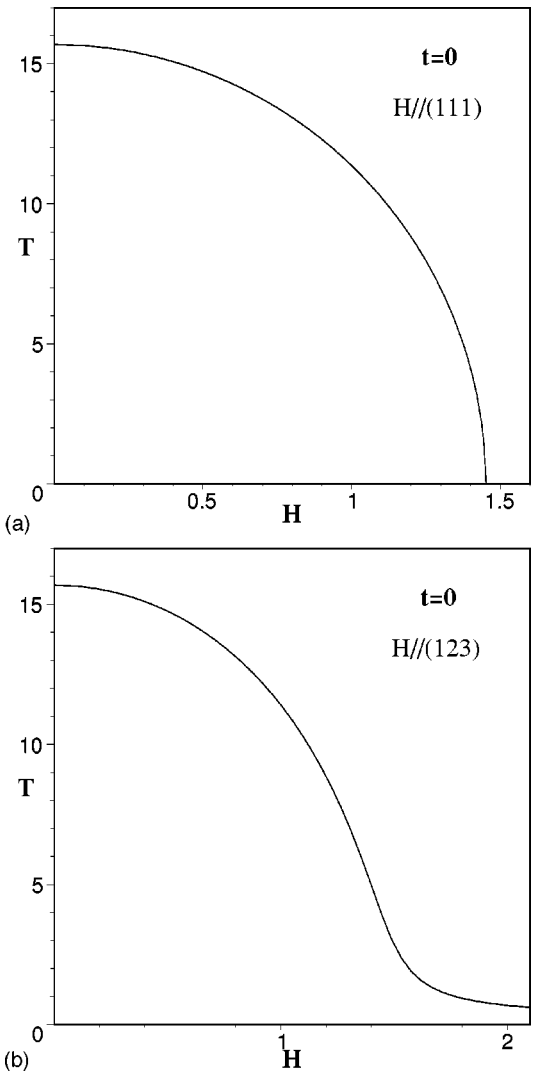


FIG. 6. (a) Field-induced ground-state transition from octupolar order to the disordered state for $\mathbf{H}\|(111)$. (b) Expectation value of the octupole moment in the ground state as a function of magnetic field for $\mathbf{H}\|(123)$. For fields pointing in nonsymmetric directions, there is no sharp phase transition.

exist (in mean-field theory) a finite-$T$ ordered phase at $H<H_{\mathrm{cr}}$ [Fig. 4(a)]. Generally, the nature of the field direction dependence of octupolar ordering can be studied by confining our attention to the ground state ($T=0$). First, we use mean-field theory; later, we give general symmetry arguments.

Let $E_0$ be the minimal eigenvalue of the mean-field Hamiltonian which contains both the external magnetic field, and the octupolar effective field

$$E_0(\langle \mathcal{T}_{\mathbf{H}} \rangle) = \langle \mathcal{H} \rangle = -\langle \Phi_0 | \mathcal{T}_{\mathbf{H}} | \Phi_0 \rangle \langle \mathcal{T}_{\mathbf{H}} \rangle - \mathbf{H} \cdot \langle \mathbf{J} \rangle, \quad (30)$$

where $|\Phi_0\rangle$ is the interacting ground state, and $\langle\ \rangle$ denotes expectation values taken with $|\Phi_0\rangle$. The energy unit is like in Eq. (21). We have to minimize

$$E(\langle \mathcal{T}_{\mathbf{H}} \rangle) = \tfrac{1}{2} \langle \mathcal{T}_{\mathbf{H}} \rangle^2 + E_0(\langle \mathcal{T}_{\mathbf{H}} \rangle) \quad (31)$$

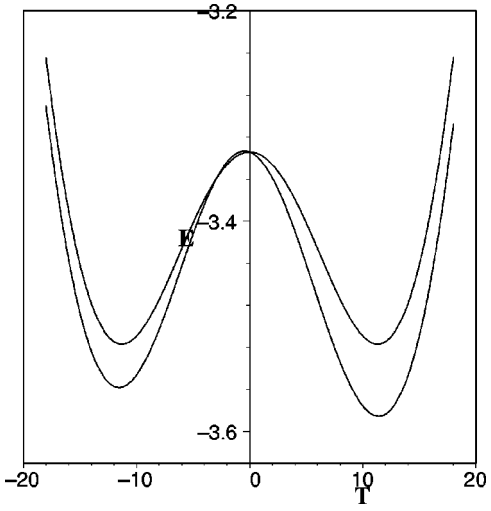


FIG. 7. The Landau-type ground-state energy expression has symmetric or asymmetric minima depending on whether the field is applied in a symmetry direction [$\mathbf{H}\|(111)$, upper curve] or nonsymmetry direction [$\mathbf{H}\|(123)$, lower curve].

with respect to $\langle \mathcal{T}_{\mathbf{H}} \rangle$. In general, $\mathcal{T}_{\mathbf{H}}$ is not pointing in the same direction in the $\Gamma_5$ space as the zero field $\mathcal{T}=\langle \mathcal{T}^{\beta}_{111} \rangle$, but neither is it collinear with $\mathbf{H}$; it has to be chosen in an optimization procedure, observing the symmetry lowering due to the magnetic field.

Figure 6 shows results obtained by minimizing $E(\mathcal{T})$ with respect to $\mathcal{T}=\langle \mathcal{T}^{\beta}_{111} \rangle$, our original choice of order parameter. For $\mathbf{H}\|(111)$, the field does not introduce any inequivalence of $x$, $y$, and $z$, thus the above choice of the order parameter is optimal, and the second-order transition seen in Fig. 6(a) is genuine.

Figure 6(b) shows the self-consistent solution for $\mathcal{T}$ for fields $\mathbf{H}\|(123)$. (123) is taken to represent general nonsymmetric directions. We find behavior characteristic of smeared-out phase transitions (the marked upward curvature at $H\sim 1.5$ shows where the phase transition might have been; clearly, intersite interactions are important for $H<1.5$, while their effect is negligible in the high-field tail).

The reason for the discrepancy between the $\mathbf{H}\|(111)$ and $\mathbf{H}\|(123)$ behaviors becomes clear from plotting the Landau-type ground-state energy density for different field directions (Fig. 7). For $\mathbf{H}\|(111)$, equivalent minima remain at the positions $\pm\mathcal{T}_0$, thus the system can pick one of these in a symmetry-breaking transition (upper curve). On the other hand, for $\mathbf{H}\|(123)$, the two minima are not equivalent, the ground state remains always on the right-hand side. There is no symmetry-breaking transition though the $T$ dependence may be nontrivial, showing the shadow of the phase transition which might have happened.

One might object that for $\mathbf{H}\|(123)$, $\mathcal{T}_x$, $\mathcal{T}_y$, and $\mathcal{T}_z$ are no longer equivalent, thus the optimal mean-field solution should be sought in the form

$$\mathcal{T}_{\mathbf{H}} = r_x \mathcal{T}_x + r_y \mathcal{T}_y + r_z \mathcal{T}_z . \quad (32)$$

This is true but we do not have to make the considerable effort of a three-parameter optimization. We will bring gen-

eral arguments to show that the solution would be like that in Fig. 6(b), whatever $\mathcal{T}_{\mathbf{H}}$ is chosen. It remains true that for general (nonsymmetric) field directions, the ground state of Eq. (29) is nondegenerate and therefore no symmetry breaking transition (in particular, no continuous octupolar ordering transition) is possible.

For some symmetry directions which are not equivalent to (111) [e.g., for (001)], the character of the solution is different from either of those shown in Fig. 6. We will discuss these later.

## V. SYMMETRY ANALYSIS OF FIELD-INDUCED MULTIPOLES

### A. The high-field limit

We learn from Fig. 6 that at sufficiently high fields the ground state is determined by the external field only: either because ordering has been suppressed, or because there was no transition to begin with. The following analysis of the field-induced multipoles does not rely on the mean-field approximation, but each of the cases will be illustrated by a mean-field calculation.

The octupole operators are third-order polynomials of $J_x$, $J_y$, and $J_z$. The $\Gamma_5$ octupoles can be expressed in terms of dipole and quadrupole operators[9]

$$\mathcal{T}_x^\beta=(\tfrac{1}{3}\mathcal{O}_2^0+\tfrac{1}{6}\mathcal{O}_2^2)J_x+\tfrac{2}{3}(\mathcal{O}_{zx}J_z-\mathcal{O}_{xy}J_y),$$

$$\mathcal{T}_y^\beta=(-\tfrac{1}{3}\mathcal{O}_2^0+\tfrac{1}{6}\mathcal{O}_2^2)J_y+\tfrac{2}{3}(\mathcal{O}_{xy}J_x-\mathcal{O}_{yz}J_z),$$

$$\mathcal{T}_z^\beta=-\tfrac{1}{3}\mathcal{O}_2^2J_z+\tfrac{2}{3}(\mathcal{O}_{yz}J_y-\mathcal{O}_{zx}J_x), \tag{33}$$

where the quadrupoles are well-known quadratic expressions

$$\mathcal{O}_2^0=\tfrac{1}{2}(2J_z^2-J_x^2-J_y^2),$$

$$\mathcal{O}_2^2=J_x^2-J_y^2,$$

$$\mathcal{O}_{xy}=\tfrac{1}{2}(J_xJ_y+J_yJ_x),$$

$$\mathcal{O}_{yz}=\tfrac{1}{2}(J_yJ_z+J_zJ_y),$$

$$\mathcal{O}_{zx}=\tfrac{1}{2}(J_zJ_x+J_xJ_z). \tag{34}$$

Equation (33) contains exact identities respecting the noncommutative nature of the operators. However, $\mathcal{T}_z^\beta$, etc., are themselves defined as symmetrized expressions (3), so it must be true that the order of the operators on the right-hand side cannot really matter. In fact, there is an arbitrariness in representation (33): it would be also true that

$$\mathcal{T}_z^\beta=-\tfrac{1}{3}\overline{\mathcal{O}_2^2J_z} \tag{35}$$

or

$$\mathcal{T}_z^\beta=\tfrac{2}{3}(\overline{\mathcal{O}_{yz}J_y}-\overline{\mathcal{O}_{zx}J_x}). \tag{36}$$

Similar relationships can be listed for the first two lines of Eq. (33). This suggests that relationships (33) can also be interpreted in terms of *c* numbers, i.e., classical polarization densities.[29] Such considerations are valid for either field-induced, or interaction-induced multipole densities. This enables us to use relationships like Eq. (33) in Landau expansions.

First, we discuss field-induced densities. The basic idea is that an external field induces $\langle\mathbf{J}\rangle=(\langle J_x\rangle,\langle J_y\rangle,\langle J_z\rangle)\|\mathbf{H}$, and this gives rise to induced quadrupoles $\langle\mathcal{O}_{xy}\rangle=\langle J_x\rangle\langle J_y\rangle$ as a second-order effect, and induced octupoles as a third-order effect, etc. If an octupole component is field induced, it can no longer play the role of the order parameter of a symmetry-breaking transition. The question is, can it happen that certain octupole moments are *not* induced by the field.

Equations (35) and (36) are still separate operator identities, but they must have the same classical meaning when $J_x$, etc., are treated as *c* numbers. Indeed from Eq. (36)

$$\mathcal{T}_z^\beta=\overline{\mathcal{O}_{yz}J_y}-\overline{\mathcal{O}_{zx}J_x}\to(\langle J_y\rangle\langle J_z\rangle)\langle J_y\rangle-(\langle J_z\rangle\langle J_x\rangle)\langle J_x\rangle$$
$$=(\langle J_y\rangle^2-\langle J_x\rangle^2)\langle J_z\rangle\propto(H_y^2-H_x^2)H_z, \tag{37}$$

which is the same that we would have obtained from Eq. (35). Similarly,

$$\mathcal{T}_x^\beta=\overline{\mathcal{O}_{zx}J_z}-\overline{\mathcal{O}_{xy}J_y}\to(\langle J_z\rangle\langle J_x\rangle)\langle J_z\rangle-(\langle J_x\rangle\langle J_y\rangle)\langle J_y\rangle$$
$$=(\langle J_z\rangle^2-\langle J_y\rangle^2)\langle J_x\rangle\propto(H_z^2-H_y^2)H_x, \tag{38}$$

and

$$\mathcal{T}_y^\beta=\overline{\mathcal{O}_{xy}J_x}-\overline{\mathcal{O}_{yz}J_z}\propto(H_x^2-H_z^2)H_y. \tag{39}$$

We can also argue in the following manner. Higher-order polarizations in a magnetic field give rise to the following general *H* dependence of the energy

$$\mathcal{E}(H)\sim\mathcal{E}(H=0)-\frac{\chi}{2}H^2-\frac{\chi_3}{12}H^4\cdots. \tag{40}$$

The lowest-order time-reversal invariant expression containing $\mathcal{T}$ is $\mathcal{T}H$, thus the coupling of octupolar moments to fields may appear in terms from $O(H^4)$ upwards. If it does, the minimal eigenvalue of the mean-field energy (30) will not be symmetrical under the sign change of octupole moments: $E_0(\mathcal{T})\neq E_0(-\mathcal{T})$. Nonequivalent minima like in Fig. 7 (lower curve) mean that there is no symmetry to break, a phase transition is not possible. However, for fields in the special directions discussed above, there is no field-induced $\Gamma_5$ octupole,[30] the $\pm\mathcal{T}$ minima of $E_0(\mathcal{T})$ remain equivalent (Fig. 7, upper curve) and spontaneous symmetry breaking remains possible. The eventual merging of the two minima is no longer a question of symmetry, but of field intensity; a sufficiently strong field will suppress octupolar (or any other) order, and produce a unique polarized state for any field direction [Fig. 6(b)].

In what follows, we calculate the induced $\Gamma_5$ octupoles using Eqs. (37)–(39) for several field directions, and discuss the possibility of symmetry-breaking transitions.

#### *1. Nonsymmetric directions*

First let us observe that a field pointing in a general direction will give nonzero values for $\mathcal{T}_x^\beta$, $\mathcal{T}_y^\beta$, and $\mathcal{T}_z^\beta$. Since the field induces all $\Gamma_5$ octupoles, there remains no degeneracy to be lifted, no symmetry-breaking transition is possible.[31] This corresponds to the situation in the lower panel of Fig. 6.

#### *2. $H\|(111)$*

Taking now $\mathbf{H}\|(111)$, we find $\mathcal{T}_x^\beta=\mathcal{T}_y^\beta=\mathcal{T}_z^\beta=0$, and so also $\mathcal{T}_{111}^\beta=0$. The field does not induce $\Gamma_5$ octupoles, and therefore a symmetry-breaking transition is possible. Furthermore, as we remarked earlier, the *x*, *y*, and *z* axes play equivalent roles, and therefore the choice of the order parameter $\mathcal{T}=\langle\mathcal{T}_{111}^\beta\rangle$ is correct. The situation corresponds to Fig. 6 (b).

#### *3. $H\|(001)$*

Next consider $\mathbf{H}\|(001)$. Also here we find $\mathcal{T}_x^\beta=\mathcal{T}_y^\beta=\mathcal{T}_z^\beta=0$ from Eqs. (37)–(39), and therefore the possibility of continuous phase transitions. However, it is intuitively clear that the *z* axis is inequivalent to *x* and *y*, and therefore the order parameter may be either $\mathcal{T}_z$, or some linear combination of $\mathcal{T}_x$ and $\mathcal{T}_y$. We have to perform a two-parameter minimization using the suitably modified form of Eq. (31)

$$E_0(\langle\mathcal{T}_z\rangle,\langle\mathcal{T}_\perp\rangle)=-J((\mathcal{T}_x+\mathcal{T}_y)\langle\mathcal{T}_\perp\rangle+\mathcal{T}_z\langle\mathcal{T}_z\rangle) \qquad (41)$$

with $\langle\mathcal{T}_x\rangle=\langle\mathcal{T}_y\rangle=\langle\mathcal{T}_\perp\rangle$. Like in Fig. 7, we expect that the ground-state energy functional has degenerate local minima: at low fields, we find a pair of these as a function of $\langle\mathcal{T}_z\rangle$, and another pair along the $\langle\mathcal{T}_x+\mathcal{T}_y\rangle$ direction (the latter choice is arbitrary in the sense that we could also have taken $\langle\mathcal{T}_x-\mathcal{T}_y\rangle$) [Fig. 8, (a)]. These two pairs of minima are not symmetry related, as is also shown by the fact that at intermediate fields, only the $\langle\mathcal{T}_x+\mathcal{T}_y\rangle\neq0$ minima survive [Fig. 8(b)]. At high fields, the ground state is nondegenerate with $\langle\mathcal{T}_x+\mathcal{T}_y\rangle=\langle\mathcal{T}_z\rangle=0$ [Fig. 8(c)].

The corresponding sequence of two second-order ground-state transitions is shown in Fig. 9(a). $\langle\mathcal{T}_x^\beta+\mathcal{T}_y^\beta\rangle>0$ (or alternatively, $\langle\mathcal{T}_x^\beta-\mathcal{T}_y^\beta\rangle>0$) order develops at higher critical field $H_{\rm cr}^>$, with $\langle\mathcal{T}_z^\beta\rangle=0$. Upon reducing the field to a lower critical value $H_{\rm cr}^<$, a second symmetry breaking occurs. In the low-field phase $H<H_{\rm cr}^<$, $\langle\mathcal{T}_x^\beta+\mathcal{T}_y^\beta\rangle\neq0$ and also $\langle\mathcal{T}_z^\beta\rangle\neq0$. $\langle\mathcal{T}_z^\beta\rangle\neq\langle\mathcal{T}_x^\beta+\mathcal{T}_y^\beta\rangle/2$ as long as $H>0$; the $\mathcal{T}_{111}$ order ($\langle\mathcal{T}_x^\beta\rangle=\langle\mathcal{T}_y^\beta\rangle=\langle\mathcal{T}_z^\beta\rangle$) appears continuously as $H\to0$.

#### *4. $H\|(11c)$*

$\mathbf{H}\|(11c)$ ($c\neq0$) induces $\langle\mathcal{T}_x^\beta-\mathcal{T}_y^\beta\rangle\neq0$, leaving $\langle\mathcal{T}_x^\beta+\mathcal{T}_y^\beta\rangle=0$ and $\langle\mathcal{T}_z^\beta\rangle=0$. There is a remaining octupolar degeneracy which is is lifted in a single continuous transition, where $\langle\mathcal{T}_z^\beta\rangle\neq0$ and $\langle\mathcal{T}_x^\beta+\mathcal{T}_y^\beta\rangle\neq0$ appear simultaneously [(Fig. 9(b)]. For $c=0$ [i.e., $\mathbf{H}\|(110)$], $\mathcal{T}_z^\beta$ and $\mathcal{T}_x^\beta+\mathcal{T}_y^\beta$ can order independently, like in the case of $\mathbf{H}\|(001)$.

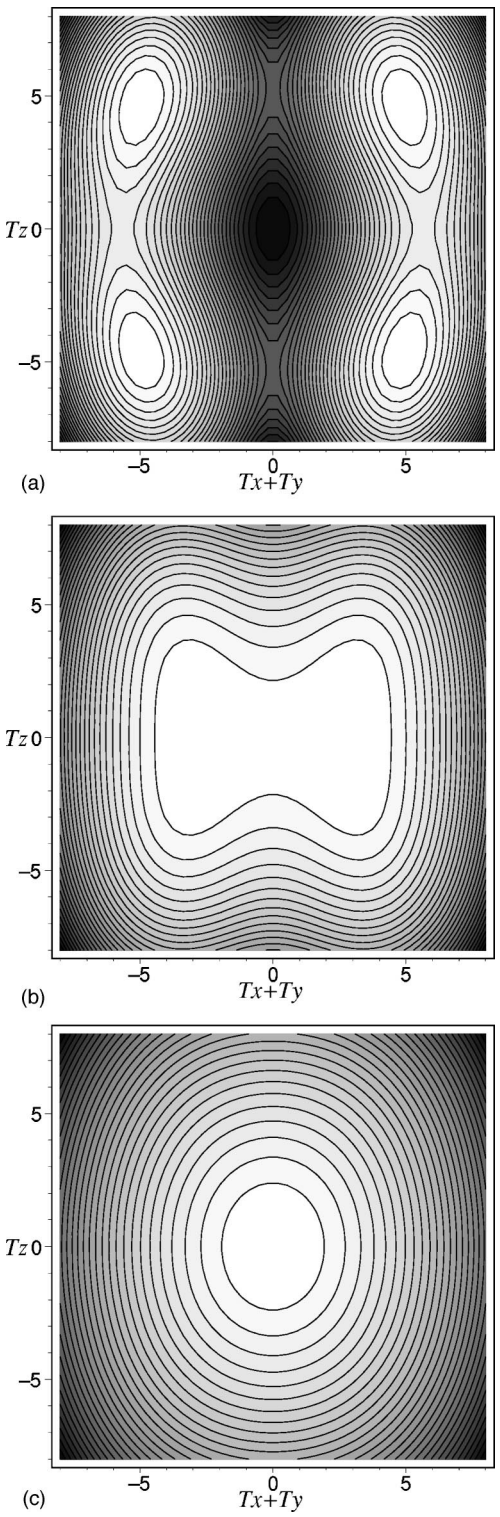


FIG. 8. The contour plot of the ground-state energy functional in the $\langle\mathcal{T}_x^\beta+\mathcal{T}_y^\beta\rangle$-$\langle\mathcal{T}_z\rangle$ plane for $\mathbf{H}=(0,0,H)$ magnetic fields $H=0.2$ (a), $H=0.42$ (b), and $H=0.8$ (c).

#### *5. Field direction dependence: Summary*

We have discussed field directions which do not subtend a too large angle with (111), thus it holds that the limit $H\to0$ picks the (111) ground state. For other field directions,

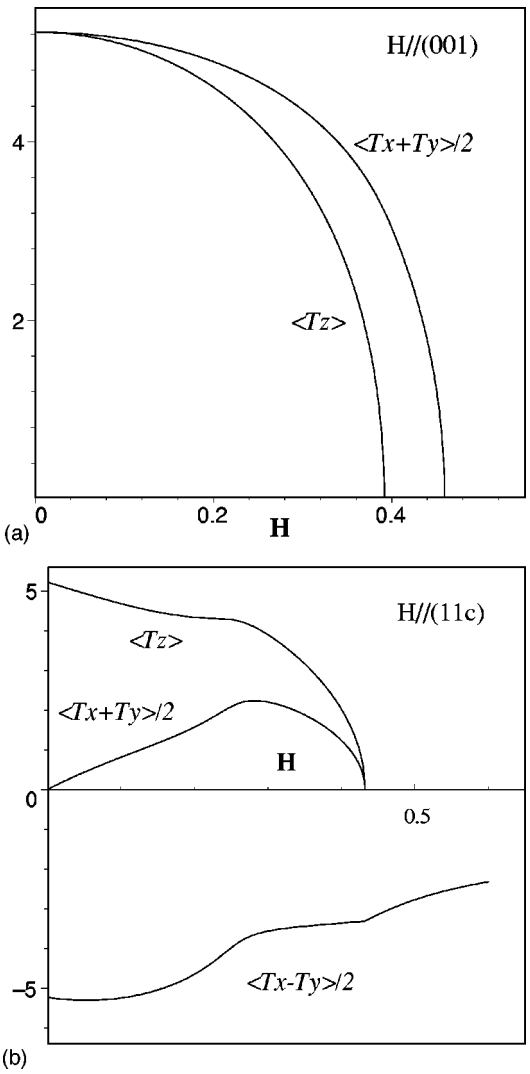


FIG. 9. (a) The field dependence of $\langle \mathcal{T}_x^\beta + \mathcal{T}_y^\beta \rangle/2$ and $\langle \mathcal{T}_z \rangle$ in a field $\mathbf{H} \| (001)$. (b) Octupolar components for $\mathbf{H} \| (11c)$, $c \neq 0$.

the limit $H \to 0$ may give one of the other ground states, e.g., $(1\bar{1}\bar{1})$ type order [see Eq. (6)].

The previously discussed special directions which allowed a symmetry-breaking transition, were all lying in the plane with normal vector $\vec{n}=(1,-1,0)$. Because of the cubic symmetry, the behavior is the same for magnetic fields lying in planes with normal vectors $\vec{n}=(1,1,0)$, $\vec{n}=(1,0,-1)$, $\vec{n}=(1,0,1)$, $\vec{n}=(0,1,-1)$, and $\vec{n}=(0,1,1)$, only the ordering phases change correspondingly. These six planes intersect along the directions $[111]$, $[\bar{1}11]$, $[1\bar{1}1]$, and $[11\bar{1}]$ (Fig. 10). Any direction outside these planes excludes the possibility of a continuous octupolar transition.

### B. Field-induced multipoles

We may also regard the problem of field-induced $\Gamma_5$ octupoles as a special case of field-induced multipoles in general.[7,8] It is best to begin with quadrupoles. When the magnetic field is zero, the $\Gamma_5$-type quadrupolar moments $\mathcal{O}_{xy}$, $\mathcal{O}_{zx}$, $\mathcal{O}_{yz}$ are equivalent by cubic symmetry. Switching

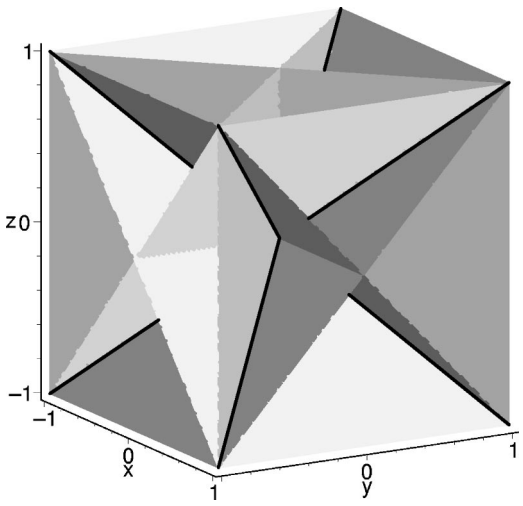


FIG. 10. Field directions lying in any of the planes shown allow a continuous octupolar ordering transition. Special rules hold for the lines of intersection, and other high-symmetry directions.

on an external magnetic field with general direction $\vec{H} \| \vec{n}$, where $\vec{n}=(\kappa,\lambda,\mu)$, the quadrupolar operator along the $\vec{n}$ direction can be given as

$$\begin{aligned} Q(\vec{n}) \approx & 3(\vec{n}\vec{J})^2 - J(J+1) = 3\kappa\lambda(J_xJ_y + J_yJ_x) + 3\kappa\mu(J_xJ_z \\ & + J_zJ_x) + 3\lambda\mu(J_xJ_y + J_yJ_x) + \kappa^2 J_x^2 + \lambda^2 J_y^2 + \mu^2 J_z^2 \\ & - J(J+1) = 3\kappa\lambda\mathcal{O}_{xy} + 3\kappa\mu\mathcal{O}_{zx} + 3\lambda\mu\mathcal{O}_{yz} \\ & + (\mu^2-\lambda^2)(J_z^2 - J_y^2) + (\kappa^2-\mu^2)(J_x^2 - J_z^2) \\ & + (\lambda^2-\kappa^2)(J_y^2 - J_x^2) + (\kappa^2+\lambda^2+\mu^2-1)J(J+1). \end{aligned} \tag{42}$$

This means that the $\mathcal{O}_{xy}$, $\mathcal{O}_{zx}$, and $\mathcal{O}_{yz}$ $\Gamma_5$-type quadrupolar operators are no longer equivalent, the quadrupolar moment is distorted along the external magnetic-field direction. Above, we obtained the components of the quadrupolar operator in the rotated new basis. The $\Gamma_5$ quadrupole moments $\mathcal{O}_{xy}$, $\mathcal{O}_{zx}$, $\mathcal{O}_{yz}$ are proportional to $\kappa\lambda \sim H_xH_y$, $\kappa\mu \sim H_xH_z$, $\lambda\mu \sim H_yH_z$. The next three quadrupolar terms, which are linear combinations of the two $\Gamma_3$ quadrupoles, are shown because they appear in the expressions of the $\mathcal{T}^\beta$ octupoles: $J_z^2 - J_y^2 \sim H_z^2 - H_y^2$, $J_x^2 - J_z^2 \sim H_x^2 - H_z^2$, $J_y^2 - J_x^2 \sim H_y^2 - H_x^2$. The last term is an invariant number.

### C. Ordering in an external magnetic field

Now we consider arbitrary field intensities. At sufficiently low fields, symmetry-breaking transitions are possible. However, the magnetic field lowers the symmetry of the system in a peculiar way, and gives rise to couplings between order parameters which would be independent in the absence of a field. The nature of these couplings depends sensitively on field direction.

Our previous discussion was about the ground-state energy $E_0(y,\mathbf{H})$, where $\mathbf{H}$ is the external magnetic field, and $y$

stands for all other variables. The magnetic moment, or in our case **J**, is obtained as $\mathbf{J}=-(\partial E_0/\partial \mathbf{H})_y$.

In what follows, we prefer to use the Helmholtz free energy $\mathcal{G}$ which is related to $E_0$ by the Legendre transformation $\mathcal{G}=E_0+\mathbf{J}\cdot\mathbf{H}$. The magnetic field will be expressed as

$$\mathbf{H}=\frac{\partial \mathcal{G}}{\partial \mathbf{J}}. \tag{43}$$

The generalized Helmholtz free energy can be expanded in terms of the components of the symmetry-allowed multipoles[7]

$$\begin{aligned}\mathcal{G}&=\mathcal{G}(J_x,J_y,J_z;\mathcal{O}_2^2,\mathcal{O}_2^0,\mathcal{O}_{xy},\mathcal{O}_{yz},\mathcal{O}_{zx};\\ &\quad \mathcal{T}_{xyz},\mathcal{T}_x^\alpha,\mathcal{T}_y^\alpha,\mathcal{T}_z^\alpha,\mathcal{T}_x^\beta,\mathcal{T}_y^\beta,\mathcal{T}_z^\beta)\\ &=\sum_{i,j,\ldots}\mathcal{I}(\Gamma_i\otimes\Gamma_j\ldots).\end{aligned} \tag{44}$$

We have to go over the list of all possible product representations spanned by the order-parameter components, and identify the bases for the identity representation $\Gamma_1$; these are the invariants $\mathcal{I}(\Gamma_i\otimes\Gamma_j\ldots)$ (assuming that they are also time-reversal invariant).

It is obvious that the present argument is valid only for phases with uniform order. $\mathbf{q}\neq 0$ Fourier components of the multipole densities should be included in a Landau theory of modulated states, such as the antiferro-octupolar phase observed in $NpO_2$.

Returning to Eq. (44), to construct a Landau theory, we would need all the invariants up to some specified order, but to derive **H**, it is enough to consider those which contain the components of **J**. Their general form is $\mathcal{I}(\Gamma_4\otimes\Gamma_j\ldots)=\mathbf{J}\cdot\mathbf{V}$, where the components of **V** give the basis of $\Gamma_{4u}$ ($g$ and $u$ refer to parity under time reversal).

We arrange the invariants according to the number of factors in the underlying product representation. For the present purposes, we will call this number the order of the invariant.[32] The second order invariants containing **J** are $\mathbf{J}\cdot\mathbf{J}$ and $\mathbf{J}\cdot\vec{\mathcal{T}}^\alpha$. Third order invariants arise from $\Gamma_4\otimes\Gamma_5\otimes\Gamma_5$, $\Gamma_4\otimes\Gamma_3\otimes\Gamma_5$, $\Gamma_4\otimes\Gamma_2\otimes\Gamma_5$, and $\Gamma_4\otimes\Gamma_4\otimes\Gamma_5$. To take the simplest example, consider $\Gamma_4\otimes\Gamma_2\otimes\Gamma_5$, for which

$$\mathcal{I}(\Gamma_4\otimes\Gamma_2\otimes\Gamma_5)=J_x\mathcal{O}_{yz}\mathcal{T}_{xyz}+J_y\mathcal{O}_{zx}\mathcal{T}_{xyz}+J_z\mathcal{O}_{xy}\mathcal{T}_{xyz}, \tag{45}$$

and the corresponding term of **V** is

$$\mathbf{V}(\Gamma_2\otimes\Gamma_5)=(O_{yz}\mathcal{T}_{xyz},\mathcal{O}_{zx}\mathcal{T}_{xyz},\mathcal{O}_{xy}\mathcal{T}_{xyz}). \tag{46}$$

Taking, e.g., the $z$ component, we find that the magnetic field couples to $\mathcal{O}_{xy}\mathcal{T}_{xyz}$. One possible interpretation is that, in the presence of $\mathbf{H}\|(001)$, $\mathcal{O}_{xy}$-type quadrupolar moment induces the octupole $\mathcal{T}_{xyz}$.[7] Alternatively, $\mathcal{T}_{xyz}$-type octupole order would induce $\mathcal{O}_{xy}$ quadrupoles.

In our further discussion of third-order invariants, we confine our attention to those which have a bearing on the question of $\Gamma_5$ octupolar order, i.e., one of the factors is $\Gamma_{5u}$. As for $\Gamma_4\otimes\Gamma_4\otimes\Gamma_5$ invariants, since one of the $\Gamma_4$ has to give **J**, i.e., it is $\Gamma_{4u}$, the remaining $\Gamma_4$ must be $\Gamma_{4g}$. The lowest-order $\Gamma_{4g}$ multipole is a hexadecapole. However, within our $\Gamma_8$ subspace, hexadecapoles cannot be independent of the first 15 multipoles, thus the formally third-order expression would have to be rewritten as a fourth-order invariant. We generally neglect terms of fourth order, and seek to draw conclusions from the genuinely third-order terms. These belong to $\Gamma_{4u}\otimes\Gamma_{5u}\otimes\Gamma_{5g}$ which gives

$$\begin{aligned}\mathcal{I}(\Gamma_{4u}\otimes\Gamma_{5u}\otimes\Gamma_{5g})&=J_x(-\mathcal{O}_{xy}\mathcal{T}_y^\beta+\mathcal{O}_{zx}\mathcal{T}_z^\beta)+J_y(-\mathcal{O}_{yz}\mathcal{T}_z^\beta\\ &\quad+\mathcal{O}_{xy}\mathcal{T}_x^\beta)+J_z(-\mathcal{O}_{zx}\mathcal{T}_x^\beta+\mathcal{O}_{yz}\mathcal{T}_y^\beta),\end{aligned} \tag{47}$$

and to $\Gamma_{4u}\otimes\Gamma_{5u}\otimes\Gamma_{3g}$ which gives

$$\begin{aligned}\mathcal{I}(\Gamma_{4u}\otimes\Gamma_{5u}\otimes\Gamma_{3g})&=-\tfrac{1}{2}J_x(\mathcal{O}_2^0+\mathcal{O}_2^2)\mathcal{T}_x^\beta+\tfrac{1}{2}J_y(\mathcal{O}_2^0-\mathcal{O}_2^2)\mathcal{T}_y^\beta\\ &\quad+J_z\mathcal{O}_2^2\mathcal{T}_z^\beta.\end{aligned} \tag{48}$$

The invariants (47) and (48) appear with the independent coefficients $w_1$ and $w_2$ in $\mathcal{G}$. For the $z$ component of the field we give first a fuller expression derived from a number of low-order invariants,

$$\begin{aligned}H_z&=u_1J_z+u_2\mathcal{T}_z^\alpha+v_1J_z\mathcal{O}_2^0+v_2\mathcal{O}_{xy}\mathcal{T}_{xyz}\\ &\quad+w_1(-\mathcal{O}_{zx}\mathcal{T}_x^\beta+\mathcal{O}_{yz}\mathcal{T}_y^\beta)+w_2\mathcal{O}_2^2\mathcal{T}_z^\beta+\cdots.\end{aligned} \tag{49}$$

Terms in the first line are needed to recover the results by Ref. 7. However, we are now only interested in the interplay of $\Gamma_5$ octupoles and fields, therefore we omit from Eq. (49) terms not containing $\mathcal{T}_i^\beta$,

$$H_z=w_1(-\mathcal{O}_{zx}\mathcal{T}_x^\beta+\mathcal{O}_{yz}\mathcal{T}_y^\beta)+w_2\mathcal{O}_2^2\mathcal{T}_z^\beta. \tag{50}$$

If quadrupolar interactions induce any of the quadrupolar moments appearing in the above equation, the field will induce $\Gamma_5$ octupoles, thus explicitly breaks the symmetry of the problem. However, in the absence of such interactions, we can turn to the high-field expressions (37)–(39) which give none of these quadrupoles. Therefore, symmetry breaking by octupolar ordering is a possibility.

For fields of other orientation, we need also the following relationships:

$$H_x=w_1(-\mathcal{O}_{xy}\mathcal{T}_y^\beta+\mathcal{O}_{zx}\mathcal{T}_z^\beta)-\frac{w_2}{2}(\mathcal{O}_2^0+\mathcal{O}_2^2)\mathcal{T}_x^\beta \tag{51}$$

and

$$H_y=w_1(-\mathcal{O}_{yz}\mathcal{T}_z^\beta+\mathcal{O}_{xy}\mathcal{T}_x^\beta)+\frac{w_2}{2}(\mathcal{O}_2^0-\mathcal{O}_2^2)\mathcal{T}_y^\beta. \tag{52}$$

For a field in the (111) direction,

$$\begin{aligned}H_{111}&=w_1[(\mathcal{O}_{xy}-\mathcal{O}_{zx})\mathcal{T}_x^\beta+(\mathcal{O}_{yz}-\mathcal{O}_{xy})\mathcal{T}_y^\beta+(\mathcal{O}_{zx}-\mathcal{O}_{yz})\mathcal{T}_z^\beta]\\ &\quad+w_2[-\tfrac{1}{2}(\mathcal{O}_2^0+\mathcal{O}_2^2)\mathcal{T}_x^\beta+\tfrac{1}{2}(\mathcal{O}_2^0-\mathcal{O}_2^2)\mathcal{T}_y^\beta+\mathcal{O}_2^2\mathcal{T}_z^\beta].\end{aligned} \tag{53}$$

Neither of the quadrupolar coefficients seen above are field induced. Therefore, if there is no quadrupolar interaction to

introduce some of them as order parameters, $\mathbf{H}\|(111)$ fields will allow the same kind of $\Gamma_5$ octupolar ordering as in the absence of a field (remember, though, that the amplitude of the order will be gradually suppressed by the field).

In a (110) field

$$H_{110}=-\frac{w_2}{2}\mathcal{O}_2^0(\mathcal{T}_x^\beta-\mathcal{T}_y^\beta)-\frac{w_2}{2}\mathcal{O}_2^2(\mathcal{T}_x^\beta+\mathcal{T}_y^\beta)+w_1(\mathcal{O}_{zx}-\mathcal{O}_{yz})\mathcal{T}_z^\beta. \quad (54)$$

The point to note from Eqs. (37)–(39) is that though $(\mathcal{O}_{zx}-\mathcal{O}_{yz})$ and $\mathcal{O}_2^2$ are not induced by the field, $\mathcal{O}_2^0$ is, and therefore the octupolar component $(\mathcal{T}_x^\beta-\mathcal{T}_y^\beta)$ is also field induced. The remaining octupolar degeneracy arises from the fact that $(\mathcal{T}_x^\beta+\mathcal{T}_y^\beta)$ and $\mathcal{T}_z^\beta$ do not couple to the field. Since these are associated with different terms in expansion (44), $(\mathcal{T}_x^\beta+\mathcal{T}_y^\beta)$ and $\mathcal{T}_z^\beta$ may order independently.

Finally, we comment upon the case $\mathbf{H}\|(11c)$ ,

$$H_{11c}=w_1[(\mathcal{O}_{xy}-c\mathcal{O}_{zx})\mathcal{T}_x^\beta+(c\mathcal{O}_{yz}-\mathcal{O}_{xy})\mathcal{T}_y^\beta+(\mathcal{O}_{zx}-\mathcal{O}_{yz})\mathcal{T}_z^\beta]+w_2[-\tfrac{1}{2}(\mathcal{O}_2^0+\mathcal{O}_2^2)\mathcal{T}_x^\beta+\tfrac{1}{2}(\mathcal{O}_2^0-\mathcal{O}_2^2)\mathcal{T}_y^\beta+c\mathcal{O}_2^2\mathcal{T}_z^\beta]. \quad (55)$$

Again only $(\mathcal{T}_x^\beta-\mathcal{T}_y^\beta)$ is field induced. However, once octupole-octupole interaction gives rise to $\mathcal{T}_z^\beta$ order, it induces $\mathcal{O}_2^2$, which in turn induces $(\mathcal{T}_x^\beta+\mathcal{T}_y^\beta)$, thus there is a single phase transition [Fig. 9(b)].

## VI. CONCLUSION

The $\Gamma_8$ subspace supports a variety of competing order parameters. The fourfold ground-state degeneracy can be lifted either in two steps (removing Kramers and non-Kramers degeneracies separately), or in a single phase transition. The latter possibility is realized by the ordering of $\Gamma_5$ octupoles. We have found that the crystal field gives rise to a peculiar single-ion octupolar anisotropy which makes the choice of $\mathcal{T}_{111}^\beta=\mathcal{T}_x^\beta+\mathcal{T}_y^\beta+\mathcal{T}_z^\beta$ octupoles preferable as order parameter. Though it breaks time-reversal invariance, octupolar ordering is non-magnetic in the sense of yielding vanishing dipole moments. On the other hand, the ordering of $\Gamma_5$ octupoles induces $\Gamma_5$ quadrupoles as secondary-order parameter; this feature allows the simultaneous lifting of Kramers and non-Kramers degeneracies.

Our discussion is mainly about a hypothetical $\Gamma_5$-type ferro-octupolar ordering in a lattice of $\Gamma_8$ shells. The mean-field results presented in Fig. 2 and Fig. 3 are equally valid for ferro-octupolar, and the triple-$\vec{k}$ antiferro-octupolar, ordering patterns, but our main interest is in magnetic-field effects, and our arguments for the case of nonzero magnetic field are restricted to uniform phases.

Magnetic octupoles are not time-reversal invariant, thus we might have expected that spontaneous symmetry breaking due to uniform octupolar ordering is necessarily suppressed by magnetic fields. Indeed, for fields of a general orientation, we find that the degeneracy of different octupolar ground states is immediately lifted, and the para-octupolar state prevails at all temperatures. However, the analysis of field-induced multipoles shows that for field directions lying in certain planes, the field does not induce all the $\mathcal{T}^\beta$-type octupolar moments, and therefore sharp octupolar transitions remain possible up to a certain critical field. The size of the critical field, and the nature of the transition to the high-field dipolar state, depend on the details of field orientation within the symmetry-specified planes.

## ACKNOWLEDGMENTS

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## APPENDIX A: NUMERICAL COEFFICIENTS OF CUBIC CRYSTAL-FIELD LEVELS IN THE $\Gamma_8$ BASIS

$$\alpha=\frac{\frac{26}{3}+\frac{1}{6}\sqrt{206}\sqrt{14}}{\left[1+\left(\frac{26}{3}+\frac{1}{6}\sqrt{206}\sqrt{14}\right)^2+\left(-\frac{5}{6}\sqrt{14}-\frac{1}{6}\sqrt{206}\right)^2\right]^{1/2}}=0.9530,$$

$$\beta=\frac{-\frac{5}{6}\sqrt{14}-\frac{1}{6}\sqrt{206}}{\left[1+\left(\frac{26}{3}+\frac{1}{6}\sqrt{206}\sqrt{14}\right)^2+\left(-\frac{5}{6}\sqrt{14}-\frac{1}{6}\sqrt{206}\right)^2\right]^{1/2}}=-0.2980,$$

$$\gamma=\frac{1}{\left[1+\left(\frac{26}{3}+\frac{1}{6}\sqrt{206}\sqrt{14}\right)^2+\left(-\frac{5}{6}\sqrt{14}-\frac{1}{6}\sqrt{206}\right)^2\right]^{1/2}}=0.054\,09,$$

$$\delta=\frac{-\frac{1}{15}\sqrt{14}\sqrt{6}-\frac{1}{30}\sqrt{6}\sqrt{206}}{\left[1+\left(-\frac{1}{15}\sqrt{14}\sqrt{6}-\frac{1}{30}\sqrt{6}\sqrt{206}\right)^2\right]^{1/2}}=-0.8721,$$

$$\epsilon = \frac{1}{\left[1+\left(-\frac{1}{15}\sqrt{14}\sqrt{6}-\frac{1}{30}\sqrt{6}\sqrt{206}\right)^2\right]^{1/2}} = 0.4891.$$

The Zeeman splitting parameters appearing in Sec. III A are

$$g_H = \frac{3}{206}(129\,471+618\sqrt{206}\sqrt{14})^{1/2} = 5.736,$$

$$y_H = \frac{1}{618}(1\,078\,719-6798\sqrt{206}\sqrt{14})^{1/2} = 1.3665.$$

## APPENDIX B: MULTIPOLE MOMENTS IN THE GROUND STATE OF $\mathcal{T}_{111}$

$$A = \langle\phi_0|\mathcal{T}_{111}|\phi_0\rangle = \langle\phi_0|\mathcal{T}_{\bar{1}11}|\phi_0\rangle = \langle\phi_0|\mathcal{T}_{1\bar{1}1}|\phi_0\rangle$$
$$= \langle\phi_0|\mathcal{T}_{11\bar{1}}|\phi_0\rangle = -\frac{15}{103}(22660-206\sqrt{206}\sqrt{14})^{1/2} =$$
$$-15.683,$$

$$B/3 = \langle\phi_0|\mathcal{O}_{xy}|\phi_0\rangle = \langle\phi_0|\mathcal{O}_{yz}|\phi_0\rangle = \langle\phi_0|\mathcal{O}_{xz}|\phi_0\rangle = 2.673,$$

$$m = \langle\phi_0|J_x|\phi_0\rangle = \langle\phi_0|J_y|\phi_0\rangle = \langle\phi_0|J_z|\phi_0\rangle = 0.$$


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[6] The possibility of pure octupolar order was suggested for phase IV of $Ce_xLa_{1-x}B_6$ [H. Kusunose and Y. Kuramoto, J. Phys. Soc. Jpn. **70**, 1751 (2001)]. Some of the features (susceptibility cusp and apparent lack of dipole order) make $Ce_xLa_{1-x}B_6$ similar to $NpO_2$, but due to its metallic character, its physics is bound to be more complicated than that of the insulator $NpO_2$. We note, however, that the zero-field mean-field theory developed by Kusunose and Kuramoto is, to some extent, parallel with ours. However, they did not consider the effect of a magnetic field, which is the main point of interest for us. A very recent work (K. Kubo and Y. Kuramoto, cond-mat/0304689) discusses the effects of octupole ordering on elastic behavior.

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[15] We note that the octupolar scenario is not universally accepted. Relying on quadrupolar order alone, one may invoke singlet formation of $5f^3$ cores with ligand electrons [See A.V. Nikolaev and K.H. Michel, cond-mat/0212521; Similar ideas were advanced earlier by A. Zolnierek, G. Solt, and P. Erdös, J. Phys. Chem. Solids **42**, 773 (1981).

[16] Though as far as the subgroup of proper rotations is concerned, the symmetry of $\Gamma_5$ quadrupoles and $\Gamma_5$ octupoles is the same, they have different parity under time reversal. Their coupling is made possible by the invariant arising from $\Gamma_5 u \otimes \Gamma_5 u \otimes \Gamma_5 g$ (see Sec. V C).

[17] In other words, we do not aim at describing those features which would uniquely follow from adopting some specific ratio of the fourth-order and sixth-order terms of the crystal-field potential. It is known that finetuning the parameters can give rise to exceptional behavior [ G. Solt and P. Erdös, J. Magn. Magn. Mater. **15-18**, 57 (1980)]. A fit to the measured $\Gamma_8^{(2)}$-$\Gamma_8^{(1)}$ excitation energy of 49 meV is achieved in Ref. 2.

[18] This would be the spectrum of the mean-field Hamiltonian $\mathcal{T}(\vartheta,\phi)\langle\mathcal{T}(\vartheta,\phi)\rangle$ if we set $\langle\mathcal{T}(\vartheta,\phi)\rangle = 1$.

[19] Individual interaction terms depend on the orientation of the pair, but sum (5) as a whole respects cubic symmetry.

[20] While for general orientation, the spectrum of $\mathcal{T}$ consists of four singlets, the 111 directions are special by possessing the level scheme singlet-doublet-singlet. We exploit only the fact that the ground state is a singlet.

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[26] It means that Eq. (27) is, though often applicable, still system specific, and not literally an Ehrenfest relation. True Ehrenfest relations Ref. 24 are thermodynamic identities, once the assumption about finite discontinuities is made.

[27] A closely related observation was made by Solt and Erdös (Refs. 14 and 17). In their model, a ground state which appears nonmagnetic if the field is applied in a certain direction, can be selected by quadrupolar interaction.

[28] In our present model, the vanishing of $a_H$ at the tricritical point is not generic; however, in some other multipolar models it is. A detailed discussion of various possibilities admitted by relation (27) will be published elsewhere.

[29] A classical description of multipolar ordering was developed (with application to TmTe) by R. Shiina, H. Shiba, and O. Sakai, J. Phys. Soc. Jpn. **68**, 2105 (1999).

[30] Though octupoles of other symmetries may be induced by the same fields.

[31] There is a general resemblance to the well-known fact that the ferromagnetic Ising model does not have a sharp phase transition in an external magnetic field, basically because the field picks a preferred spin direction, and thus there remains no symmetry to break. More precisely, this rules out a continuous transition only. Suitably constructed models may have a sharp first-order transition. Similarly, our high-field analysis cannot exclude first-order octupolar transitions. However, we found no evidence for these.

[32] This *ad hoc* meaning is different from identifying the order as the power of $J$ when the familiar expansions are inserted. For instance, we call both $\mathbf{J}\cdot\mathbf{J}$ and $\tilde{\mathcal{T}}^{\alpha}\cdot\tilde{\mathcal{T}}^{\alpha}$ second-order invariant, though the latter is a sixth-order polynomial in $J_x$, $J_y$, $J_z$.