Antiferro Quadrupole Orders in Non-Kramers Doublet Systems

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We investigate antiferro quadrupole orders in systems with non-Kramers doublet ground state with total angular momentum \( J = 4 \) in \( T_d \) point group symmetry. We demonstrate that a pure \( O^2_2 \) antiferro quadrupole order is impossible in general crystalline-electric field potential and should be accompanied by ferro \( O^0_3 \) quadrupole moment. The temperature and magnetic-field phase diagram is obtained by mean-field approximation of intersite quadrupole interactions and the excitation spectrum is analyzed by “spin”-wave approximations. Gapless excitations emerge at the border of antiferro \( O^2_2 \) quadrupole phases under magnetic field. Quadrupole susceptibilities in the antiferro quadrupole ordered state exhibit unusual singularity and especially the uniform quadrupole susceptibility diverges in addition to the staggered ones. These unusual singularities are also realized at the critical field along [111] direction. We also discuss recent experimental results in \( \text{Pr}T_2X_{20}(T=\text{Ir, Rh, Ti, V, and } X=\text{Zn, Al}) \).

1. Introduction

Orbital order appears in varieties of systems in condensed matter physics such as in \( d \)- and \( f \)-electron strongly correlated systems with orbital degrees of freedom\textsuperscript{1,2}. Quadrupole orders are typical and most intensively studied cases. Such orbital orders can be in principle described by similar theoretical approaches as in spin systems. As is evident from the nature of orbital degrees of freedom, interactions have spatial anisotropies depending on what kinds of orbital is considered and the symmetry is in general not fully isotropic in the orbital space. These differ from the typical case of spin systems, where the spin anisotropy is zero or not so strong unless the spin-orbit interaction is very strong. Each orbital order possesses a unique property and exploring such uniqueness is an important issue of the condensed matter theories and experiments.

Recently, \( Pr \)-based compounds \( \text{Pr}T_2X_{20} \) \((T=\text{Ir,Rh,Ti,V, and } X=\text{Zn,Al})\), so-called 1-2-20 compounds, have attracted great attention\textsuperscript{13-15}. In these compounds, each \( Pr \) ion has \((4f)^2\) electron configuration. Its ground state under the crystalline electric field (CEF) is a non-Kramers doublet\textsuperscript{13}, and this doublet couples with conduction electrons. This is a typical situation that the two-channel Kondo effects take place. Thus, it is expected that these compounds show exotic properties due to the two-channel Kondo effects\textsuperscript{6}.

Nevertheless, the doublet is not completely screened and all the compounds exhibit an orbital order below \( \sim 1 \) K. Surprisingly, some of them show even superconductivity at very low temperature in the ordered phase\textsuperscript{3,5,7,8}.

Since the first-excited CEF multiplet is located at \( \sim 30 \) \( K_3^3\)\textsuperscript{3-5,15,14} and the phase transition occurs at \( \sim 1 \) K, it is likely that the phase transition in the 1-2-20 compounds is about the degrees of freedom in the ground-state multiplet, \textit{i.e.}, an ordering of the non-Kramers doublets. The ground-state non-Kramers doublet is denoted as \( \Gamma_3 \) according to the standard notation of irreducible representations (irreps) of \( T_d \) group\textsuperscript{15}. Within the \( \Gamma_3 \) doublet states, two quadrupole operators and one octupole operator have finite matrix elements. The former belong to \( \Gamma_3 \) irrep, while the latter \( \Gamma_2 \). Thus, the (local) order parameter of the orbital order is either \( \Gamma_3 \) quadrupole or otherwise \( \Gamma_2 \) octupole. There has been no direct evidence for which type of order is realized, but results of the neutron scattering\textsuperscript{14} and the ultrasound experiments\textsuperscript{10,11} suggest a quadrupole order and no evidence for octupole or magnetic dipole order has been observed so far.

Quadrupole orders were intensively discussed for \( f \)-electron system \( \text{CeB}_6\textsuperscript{2,16,17} \) and another example \( \text{TmTe}\textsuperscript{18,19} \). The CEF ground state of Ce (Tm) ion is the \( \Gamma_5 \) quartet in \( O_h \) symmetry, where it has a \( 4f^2 \)\textsuperscript{13} electron configuration in contrast to the case of \( Pr \) 1-2-20 compounds. Despite this difference, they also exhibit a quadrupole order. On the basis of a localized model, the results by mean-field approximations are qualitatively consistent with the experimental ones\textsuperscript{16,19}. Several other systems also have a non-Kramers \( \Gamma_3 \) doublet ground state, and \( \text{PrPb}_3\textsuperscript{20} \), \( \text{PrInAg}_2\textsuperscript{21} \) and \( \text{PrMg}_3\textsuperscript{22} \) are examples. In the previous studies, experimental group tried fitting their experimental data by a mean-field approximation of the CEF model, for example, in \( \text{PrRh}_2\text{Zn}_{20}\textsuperscript{5} \), \( \text{PrPb}_3\textsuperscript{23} \) and \( \text{PrIr}_2\text{Zn}_{20}\textsuperscript{24} \). In this paper, we extend their analysis and provide detailed theoretical account of \( \Gamma_3 \) quadrupole ordering. We have also discovered unusual properties related to this order and unveiled their origin.

The main purpose of this paper is to provide a basic understanding of the \( \Gamma_3 \) quadrupole order and the

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nature of its transition, rather than to make quantitative comparisons with experimental data. Various points need careful analysis. These include (i) constraints on quadrupole ordered states by general arguments, (ii) excitation spectra in ordered states, and (iii) unusual criticality even within mean-field approximation. To this end, we employ the simplest model for inter-site interaction relevant to the quadrupole order and ignore all other interactions that might be present in the real systems.

In this paper, we will carry out a detailed theoretical analysis on the $\Gamma_3$ quadrupole order in a diamond-lattice model with a minimal quadrupole-quadrupole interaction on the basis of the CEF level scheme relevant to PrIr$_2$Zn$_{20}$ as an example. The model shows quadrupole anisotropy and this is general for the $\Gamma_3$ degrees of freedom in cubic symmetry. We will discuss it in detail, and determine and examine the mean-field phase diagram in Sect. 2. We will then in Sect. 3 study excitation spectra based on spin-wave type approximations and clarify unusual critical behaviors found in this system. In Sect. 4, we will discuss some experimental results of the 1-2-20 compounds. We will also study possible couplings of quadrupoles with other degrees of freedom including other multipole moments and phonons. Section 5 is a summary of the present paper.

2. A Basic Model and Mean-field Approximation

In this section, we will first discuss the effect of single-ion anisotropy and its effect on quadrupole orders. Then, we will analytically analyze the mean-field ground state for zero magnetic field. In the final part of this section, we will show numerical results and discuss the temperature vs. magnetic-field phase diagram.

2.1 Crystalline-electric-field Hamiltonian

We start with investigating a CEF model. Each Pr ion has total angular moment $J = 4$ and feels the CEF with the local $T_d$ point group symmetry. The CEF states are represented by the irreps of the $T_d$ group. The nine states in the $J = 4$ multiplet are split by the CEF as shown by

$$H_{CEF} = \sum_i \{ \epsilon_2 |Q(i)|^2 - \epsilon_3 \left[ Q_0^2(i) - 3Q_x(i)Q_y(i) \right] \}.$$  \hspace{1cm} (1)

Here, $\epsilon_{2,3}$ are constants and $Q(i)$ is the quadrupolar operator at the site $i$ which is represented by the Stevens operators as $Q(i) = (Q_z(i), Q_x(i), Q_y(i)) = (O_0^2(i), O_2^0(i), \sqrt{3}O_2^0(i))/8$. In terms of dipole operators $J_x,y,z(i)$ for the $J = 4$ manifold, $O_0^2(i) = 2J_z^2(i) - J_x^2(i) - J_y^2(i)$ and $O_2^0(i) = J_x^2(i) - J_y^2(i)$. The bar denotes a cyclic permutation of three operators: $\overline{ABC} \equiv AB^2 + BAB + B^2A$. With this normalization, the operator $Q(i)$ within the $\Gamma_3$ subspace is represented by the two Pauli matrices $Q \sim (\tau_x, -\tau_y)$ with the basis states listed in Appendix A. The relation between Eq. (1) and the conventional form of the CEF Hamiltonian (B-1) is summarized in Appendix B. The advantage in using Eq. (1) is that one can easily understand the single-ion anisotropy in the quadrupole sector.

2.2 Single-site anisotropy and quadrupole ordering

The CEF Hamiltonian (1) readily indicates that the anisotropic $\epsilon_3$ term affects the quadrupole order parameters $Q_x$ and $Q_y$ differently. This is related to the existence of $Z_3$ symmetry in $Q$ space. We can rewrite the $\epsilon_3$ term in Eq. (1) as

$$Q_z^3 - 3Q_x^2Q_y^2 = \frac{4}{3} \sum_{l=0}^2 Q_l^3,$$  \hspace{1cm} (2)

where we have omitted the site index $i$ and $Q_l = n_l \cdot Q$ with $n_l = (\cos 2l\pi/3, \sin 2l\pi/3)$. Any symmetry operations in cubic groups are reduced to permutations of $(lmn)$ in the $Q_l$ space with $0 \leq l, m, n \leq 2$. There exists an essential difference between $Q_x$ and $Q_y$. The inversion $Q_x \rightarrow -Q_x$ corresponds to the exchange of $Q_1$ and $Q_2$ and this is a symmetry operation of $H_{CEF}$. However, the inversion $Q_z \rightarrow -Q_z$ is not a symmetry operation. This is evident from the fact that the $\epsilon_3$ term contains odd numbers of $Q_z$.

To understand this point more intuitively, we map the $\epsilon_3$ term to a classical one. This leads

$$Q^3_z - 3Q_x^2Q_y^2 \rightarrow Q^3 \cos 3\theta,$$  \hspace{1cm} (3)

where we have introduced the polar coordinates $Q = Q[\cos \theta, \sin \theta]$. Thus, it is apparent that $\theta$ and $-\theta$ are equivalent in energy, while $\theta$ and $\pi - \theta$ is inequivalent as shown in Fig. 1.

This anisotropy in $Q$-space imposes an important constraint on the symmetry of quadrupole ordering. We will study this ordering in detail in Sect. 2.3, but now briefly discuss the constraint due to the anisotropy. The most important point is the impossibility of a pure antiferro $Q_x$ ($O_2^0$) order, $\langle Q_x(i) \rangle = (0, \pm Q)$ unless the Hamiltonian is finely tuned. This state is unstable because of the $\epsilon_3$ term. The single-ion anisotropy $H_{CEF}$ favors the three directions in the $Q$ space: $\theta = 2l\pi/3 (l = 0, 1, 2)$ for $\epsilon_3 > 0$ and $\theta = (2l + 1)\pi/3$ for $\epsilon_3 < 0$. Thus, a uniform $\langle Q_z \rangle$ is induced, and its sign is determined by the sign of the anisotropy energy $\epsilon_3$. When $\epsilon_3 > 0$, $\langle Q_z \rangle < 0$, while $\langle Q_z \rangle > 0$ when $\epsilon_3 < 0$. In contrast to the antiferro $Q_x$ order, a pure antiferro or ferri $Q_z$ ($O_2^0$) order is possible: $\langle Q_x(i) \rangle = (Q, 0), (-Q', 0)$. Note, however, that, when $\epsilon_3 < 0$, the ground state of $H_{CEF}$ is not $\Gamma_3$. Although this argument is based on the classical mapping (3), the result is valid for the quantum Hamiltonian as will be discussed in Sect. 2.4, where we will see similar anisotropic term appears in the free energy and in the ground-state energy.

The difference between $Q_x$ and $Q_z$ orderings discussed above becomes clearer if one notices the real symmetry in the $Q$ space. As the energy landscape in Fig. 1 shows, the
Q order parameter space has the trigonal symmetry $Z_3$, not the continuous O(2) symmetry. Any quadrupole ordering is actually the breaking of this $Z_3$ symmetry. The three-fold symmetry ($Z_3$) represents the equivalence of the three $(x, y, z)$ principle axes of quadrupole moments in real space.

To understand this, it is instructive to show the types of quadrupole order parameter in the two-dimensional Q space. Figure 2 illustrates shapes of quadrupole moments in the Q space. Namely $\theta = 0, 2\pi/3,$ and $4\pi/3$ correspond to quadrupole moments with $(3z^2-r^2), (3x^2-r^2),$ and $(3y^2-r^2)$, respectively, with $\theta + \pi$ corresponding to those with opposite sign and $r^2 = x^2 + y^2 + z^2$. Similarly, those for $(x^2-y^2), (y^2-z^2)$ and $(z^2-x^2)$ are at $\theta = \pi/2, 7\pi/6,$ and $11\pi/6,$ respectively with opposite sign for $\theta + \pi$.

2.3 A model for the Pr 1-2-20 compounds

The model we discuss throughout this paper includes only degrees of freedom of localized f-electrons with quadrupole-quadrupole exchange interaction under zero or finite magnetic field. Although quite simplified, this is a natural model to qualitatively describe essential aspects of the Pr-based 1-2-20 compounds. The transition temperature of the unidentified order in these systems is below 1 K, while the lowest CEF level above the $\Gamma_3$ ground state has the excitation energy of $\sim 30$ K.$^{3-5,13,14}$ This indicates that the doublet ground states play a dominant role in this transition. In the $\Gamma_3$ doublet, quadrupole and octupole moments are the only active operators. Therefore, their orderings are the most natural candidate of the transition. For example, a quadrupole order is suggested by anomaly observed in ultrasound experiments, and they also show that the inter-site quadrupole-quadrupole interaction is antiferro for PrIr$_2$Zn$_{20}$,$^{10}$ and PrRh$_2$Zn$_{20}$. For PrTi$_2$Al$_{20}$, the quadrupole interaction is ferro,$^{28}$ and this is also consistent with the neutron scattering experiments.$^{14}$ These strongly suggest that the transition is an ordering of these quadrupoles, and thus, we investigate this case in detail in this paper.

Concerning inter-site interactions, there also exist some magnetic exchange interactions, which excite the $\Gamma_3$ ground state to $\Gamma_1$ and $\Gamma_5$ levels. They may modify, for example, the details of the temperature-magnetic field phase diagram, but the essential part of all the properties in this transition is described by our minimal model. In this paper, we concentrate on analyzing the simplest model with quadrupole exchange interactions defined as

$$H = H_{CEF} + \lambda \sum_{(i,j)} Q(i) \cdot Q(j) - \mu \sum_i H \cdot J(i).$$

Here, we consider this Hamiltonian on the diamond lattice of Pr sites. $J(i) = (J_x(i), J_y(i), J_z(i))$ represents the magnetic dipole operator at the site $i$. When the magnetic field $H$ is applied, it couples with $J$. Here, the coupling constant is the “magnetic moment” (more precisely,
gyromagnetic constant) \( \mu \), and \( \mu = g \mu_B \) with \( g = 4/5 \) for \( J = 4 \) multiplet and \( \mu_B \) being the Bohr magneton. The quadrupole-quadrupole interaction \( \lambda \) is set to \( \lambda > 0 \), i.e., antiferro, and the summation is over nearest-neighbor pairs. Although a ferro quadrupole order is suggested in PrIr2Al20, we do not discuss the case for \( \lambda < 0 \) in detail in this paper. Some comments on ferro quadrupole orders will be given in Sect. 4.1.

For \( \varepsilon_2 \) and \( \varepsilon_3 \) in \( H_{CEF} \), we choose the representative values for the 1-2-20 compounds similar to those determined by inelastic neutron scattering experiments for \( \text{PrIr}_2\text{Zn}_{20} \). \( \varepsilon_2 = 9.709 \) K and \( \varepsilon_3 = 4.088 \) K. This leads CEF level scheme shown in Fig. 3: \( E_3 = 0 \) K, \( E_4 = 27.31 \) K, \( E_1 = 65.54 \) K, \( E_5 = 73.31 \) K. The CEF level scheme with fixed \( \varepsilon_3 = 4.088 \) K is plotted as a function of \( \varepsilon_2 \) in Fig. 3, where we show the part where the ground state is \( \Gamma_3 \) doublet.

It should be noted that conduction electrons in the 1-2-20 compounds is not taken into account in Eq. (4). We do not discuss the Kondo physics or other properties originating from coupling with conduction electrons.[6,7] One may regard our localized model as a renormalized system that minimizes Eq. (C-7) given by Eq. (C-7), where we show the part where the ground state is \( \Gamma_3 \) doublet.

It would be helpful to present one of our main results before explaining details of analysis. It is the mean-field phase diagram in the parameter space of temperature \( T \) and magnetic field \( H \). Figure 4 shows the results for \( H \) along three high-symmetry directions. In the followings, we will discuss the nature of each phase in details.

2.4 Analysis of ground state for zero magnetic field

In this subsection, we investigate the ground state for \( H = 0 \) by a mean-field approximation. For \( H = 0 \), relevant Hilbert space at one site is reduced to three states, \( \Gamma_3 \) doublet and \( \Gamma_1 \) singlet. The other states are decoupled since there are no quadrupole matrix elements between \( \Gamma_1, \Gamma_3 \) states and \( \Gamma_4, \Gamma_5 \) states, and thus, we can safely neglect them.

As shown in Appendix C, the ground-state energy is given by Eq. (C-7). We want to search for small \( z \lambda/E_1 \) a solution that minimizes Eq. (C-7). Here, \( z \) is the number of the nearest-neighbor sites (\( z = 4 \) for the diamond lattice). In the limit of \( E_1 \to \infty \), the moment modulus \(|\langle \text{Q} \rangle|\) approaches 1 on \( A \) and \( B \) sites, and the anisotropy energy vanishes. Therefore, in this limit, any antiferro quadrupole order \( \langle \text{Q}^B \rangle = -\langle \text{Q}^A \rangle \) with \(|\langle \text{Q}^{A,B} \rangle| = 1 \) is the ground state irrespective of the direction of \( \langle \text{Q}^{A,B} \rangle \). Here, we refer to this order as “antiferro,” but note that the ordering wave vector is \( \text{q} = 0 \). This is because the unit cell of the diamond lattice contains both \( A \) and \( B \) sublattices. This degeneracy is lifted in the order of \( (z \lambda/E_1)^3 \) as we will show below. When \( z \lambda/E_1 \) is finite but small, \(|\langle \text{Q}^{A,B} \rangle| = 1 + \delta \varphi^{A,B} \), \( \theta_A = \theta + \delta \theta \) and \( \theta_B = \theta + \pi - \delta \theta \). \( \delta \theta \) represents the deformation of the antiparallel alignment of \( \langle \text{Q}^A \rangle \) and \( \langle \text{Q}^B \rangle \), which will turn out to be important. To explicitly show the anisotropic term in the energy, we minimize this energy with respect to \( \delta \varphi^{A,B} \) and \( \delta \theta \) for a given value of \( \theta \). In the leading order, the optimized values of the parameters are

\[
\delta \varphi^{A,B} = \frac{35}{2} \left( \cos^2 \frac{3 \theta}{2} / \sin^2 \frac{3 \theta}{2} \right) (z \lambda/E_1),
\]

\[
\delta \theta = -\frac{105}{16} \sin 3 \theta (z \lambda/E_1).
\]

Higher order corrections in Eqs. (5) and (6) affect the ground-state energy \( C(\text{7}) \) in the order \( (z \lambda/E_1)^3 \), and thus can be safely neglected. Using Eqs. (5) and (6), we obtain

\[
\frac{E_{\text{mf}}^{\text{gs}}}{E_1} = -\left( \frac{z \lambda}{E_1} \right) - \frac{35}{4} \left( \frac{z \lambda}{E_1} \right)^2
\]

\[
+ \frac{35}{256} \left( 29 + 35 \cos \theta \right) \left( \frac{z \lambda}{E_1} \right)^3 + \cdots.
\]

From Eq. (7), one can see that \( \partial E_{\text{mf}}^{\text{gs}}/\partial \theta = 0 \) at \( \theta = n \pi/6 \) with \( n \) being integers and these values of \( \theta \) correspond to the order parameters depicted in Figs. 2(a) and (b). For sufficiently small \( z \lambda/E_1 \), odd \( n \) solutions [Fig. 2(b)] have a lower energy than even \( n \) solutions, and thus the ground state is six-fold degenerate with \(|\langle \text{Q}^A \rangle| = |\langle \text{Q}^B \rangle|\). The primary order parameter is antiferro quadrupole of \( Q_z(O^2_z) \) type, and as discussed in Sect. 2.2, this is generally accompanied by ferro quadrupole of \( Q_z(O^2_z) \). This is similar to the case of parasite ferromagnetism in antiferromagnets with Dzyaloshinskii-Moriya interaction. The amplitude of the parasite \( Q_z \) moment is determined by the deformation angle, \( \delta \theta \) between \( \langle \text{Q}^A \rangle \) and \( \langle \text{Q}^B \rangle \). It is small and of the order \( z \lambda/E_1 \), whereas the amplitude of primary order parameter is \( |Q_x| \approx 1 \).

The six-fold degeneracy of the ground state is due to \( Z_3 \otimes Z_2 \) symmetry of the lattice. \( Z_3 \) symmetry is about the equivalence of the three principle axes \( (x, y, z) \). \( Z_2 \) is the symmetry between the two sublattices. The emergence of the secondary order in the \( Q_z \) component is consistent with the analysis based on the single-site CEF anisotropy discussed in Sect. 2.2.

When the intersite coupling \( \lambda \) increases, the quadrupole order in the ground state changes from the \( Q_z \) antiferro order to the \( Q_x \) antiferro order through a first-order transition. One can see this behavior in the fact that the \( \cos \theta \) term in the variational energy (7) has a negative coefficient in the order \( (z \lambda/E_1)^4 \), i.e., the sign is opposite to that in the leading order \( (z \lambda/E_1)^3 \). To examine the change in \( \langle \text{Q}^{A,B} \rangle \) quantitatively, we have numerically solved the mean-field equations and found that the transition occurs at \( z \lambda/E_1 \approx 0.0375 \).

2.5 Non-linear Zeeman term for quadrupole moments

Let us briefly discuss effects of magnetic fields on \( \Gamma_3 \) degrees of freedom. For small magnetic field, its coupling
to the quadrupole is calculated by the second-order perturbation in $H$, in which the intermediate virtual states are excited magnetic $\Gamma_4$ and $\Gamma_5$ states, and is given as

$$H_Q = -\alpha \left[ (2H_x^2 - H_y^2 - H_z^2)Q_z + \sqrt{3}(H_x^2 - H_y^2)Q_x \right], \quad (8)$$

$$\alpha = \mu^2 \left( \frac{7}{3E_4} - \frac{1}{E_5} \right), \quad (9)$$

where $\alpha > 0$ for our choice of the CEF level scheme. This coupling leads to the effects of applied magnetic field on quadrupole orders.

Related to the cubic crystal symmetry or equivalently $Z_3$ symmetry in the $Q$-space for $H = 0$, there exist three equivalent ordered states, and they form a multi-domain structure. These three states correspond to the angle $\theta = \pi/2$, $7\pi/6$, and $11\pi/6$. Magnetic field $H$ favors some of the three domains and disfavor the others, depending on the field direction, and thus controls the domain structure. When $H \parallel [110]$, the domain of $\theta = \pi/2$ is favored. This domain corresponds to $\sim (x^2 - y^2)$ state. In a similar way, for $H \parallel [001]$ two domains $\theta = 7\pi/6 : (y^2 - z^2)$ and $11\pi/6 : (z^2 - x^2)$ are selected, since the magnetic field favors positive $Q_z$. For $[111]$ direction, the quadratic terms in (8) vanishes and the leading effect is the coupling to octupole, $\sim H_xH_yH_zT_{xyz}$. Thus, $T_{xyz}$ octupole moment is induced for $H \parallel [111]$ direction, where the degeneracy of the three domains of $Q_x$-type antiferro quadrupole states is not lifted.

Note that the above discussions do not include the contribution of induced magnetic multipoles that originate from the hybridization between $\Gamma_3$ and the excited states. When the magnetic field is weak, the induced magnetic parts do not play important roles in selecting domains and the direct effects in the $\Gamma_3$ sector dominates.

### 2.6 Temperature-magnetic field phase diagram

In this subsection, we will discuss the $T$-$H$ phase diagram shown in Fig. 4 in details and generalize the analysis in the previous subsection. To this end, we study the full model (4). The phase diagram shows several ordered phases under magnetic field and we will examine the nature of these phases.

Figure 4 shows $T$-$H$ phase diagrams determined by the mean-field analysis and $H$ is parallel to each of the three high-symmetry directions. The intersite coupling constant $\lambda$ is set to $\lambda = 0.03$ K with $z = 4$ neighbors. This leads to the transition temperature $T_c \simeq 0.122$ K at $H = 0$ and the critical magnetic field along $H \parallel [001]$: $H_c(001) \simeq 2.46$ T, $H_c(110) \simeq 1.46H_c(001)$, and $H_c(111) \simeq 2.13H_c(001)$ at $T = 0$, which roughly correspond to the experimental data. Anisotropy in the critical field strength is mainly determined by the non-linear Zeeman effect (8). The critical field is largest for $H \parallel [001]$, then next for $H \parallel [110]$, and smallest for $H \parallel [111]$. For $[111]$ direction, the effect (8) vanishes and as discussed before the critical field is determined by the octupole-field coupling as far as the magnetic field is not so strong.

First, let us investigate the case of $H \parallel [001]$. The phase diagram shows three ordered phases I, II, and III as shown in Fig. 4. The phase-I is a basically antiferro quadrupole state with $Q_z$ type order with small $Q_x$ ferro quadrupole components, and this is discussed in the previous subsection. For finite $|H|$, there are two stable domains characterized by $(y^2 - z^2)$ and $(z^2 - x^2)$ type sym-
pears a second-order transition at $|H| = H_c(001)$ from the canted phase-III to the polarized phase IV. In the phase-IV, the order parameter points to $Q_z$ direction on both of $A$ and $B$ sites. The phase-IV is smoothly connected to paramagnetic state above $T_c$.

Secondly, let us consider the case of $H \parallel [110]$. In this case, there is only one ordered phase, and the stable domain is also unique. This phase has an antiferro order of $(x^2 - y^2)$-type quadrupole component accompanied with ferro $Q_z < 0$. This is illustrated in Fig. 6 (a), and this coincides to one of the stable domains in the phase-I when $H \parallel [100]$ or [010]. With increasing field, the $Q_z$ components increase and finally the quadrupole moments align along $-Q_z$ direction at $|H| = H_c(110)$ through a second-order transition.

Thirdly, for $H \parallel [111]$, there is also only one ordered phase but three domains are all stable. One domain exhibits negative $Q_z$ as illustrated in Fig. 6 (c), while the other two have positive net $Q_z$ as illustrated in Figs. 6 (d) and (e). Increasing $|H|$ suppresses $Q_z$ for all the three, and, as discussed in the previous subsection, induces $T_{xyz}$ octupole moment. The transition to the high-field phase at $|H| = H_c(111)$ is also second order. In the high-field phase, no quadrupole moment exists, while there remains an induced $T_{xyz}$ octupole moments as shown in Fig. 6 (f).

2.7 Physical quantities

In this subsection, we show the details of magnetic field dependence of multipoles $Q$, $J_z$, and $T_{xyz}$. Figure 7 shows these quantities at $T = 0$ and for three directions of the magnetic field. The results for $H \parallel [001]$ are shown in Fig. 7 (a), where the domain of $(y^2 - z^2)$-type is chosen for the phase-I. For $H \parallel [110]$, the stable domain is unique, i.e., $(x^2 - y^2)$-type, and Fig. 7(b) shows multipole moments along $H \parallel [110]$. The results for $H \parallel [111]$ are shown in Fig. 7(c), and the $(x^2 - y^2)$-type domain is chosen for the ordered phase. Since we have already discussed the variations of $Q$ in Sect. 2.6, we here discuss a physical origin of induced magnetic moments $J_z$.

To discuss what kinds of multipoles are induced in the presence of both magnetic field and the order parameter $Q$, a group theoretical argument is very useful. In Appendix D, a list is shown for the reduction of several products of two irreps. This helps understanding the coupling of $J_z$ to $H$ and $Q_z$, and it is sufficient to notice that $Q$ transforms as $\Gamma_3$ representation, while $J_z$ and $H$ as $\Gamma_4$. The lowest-order local coupling that includes the three quantities is

$$Q_z - \frac{\sqrt{3}Q_z}{2} J_z H_x + \frac{Q_z + \sqrt{3}Q_z}{2} J_y H_y - Q_z J_z H_z.$$  \hspace{1cm} (10)

This indicates that antiferromagnetic $J_z$ component is induced by the antiferro $Q_z$ order for $H \parallel [001]$ as shown in Fig. 7(a), while antiferromagnetic $J_z - J_y$ component is induced for $H \parallel [110]$ [Fig. 7(b)] and $[111]$ [Fig. 7(c)] by the antiferro $Q_z$ order. Note also that Eq. (10) holds for any $\Gamma_4$ operators by replacing $J_z$ by them.

Fig. 6. (Color online) Schematic pictures of the quadrupole orders for $H \parallel [110]$ and [111]. (a) antiferro quadrupole state for [110] direction. (b) high-field state for [110] direction. (c),(d),(e) three domains in antiferro quadrupole state for [111] direction. (f) high-field state for [111] direction. In (f), the third axis represents octupole $T_{xyz}$. A list of the irreps and their products is shown in Appendix D.
Similarly, one can construct a coupling between a magnetic $\Gamma_5$ operators, e.g., $T^3$ octupole moment, and $H$ and $Q$.

$$\frac{\sqrt{3}Q_z}{2} T^3_x H_x + \frac{-\sqrt{3}Q_z}{2} T^3_y H_y - Q_x T^3_z H_z. \tag{11}$$

Although we do not show the results for $\Gamma_5$ operators, $T^3$ octupole moments are induced as discussed by Shiina et al.\textsuperscript{16}

Now, let us discuss changes in the ground-state wavefunction $|0\rangle_{A,B}$ with $H$. With varying the strength of magnetic field, we numerically obtained the mean-field ground state on the $A$- and $B$-sublattices, $|0\rangle_{A,B} = \sum_i\sum_n a_{A,B}(\Gamma_i,n)|\Gamma_i,n\rangle_{A,B}$. $w_{A,B}(\Gamma_i,n) = |a_{A,B}(\Gamma_i,n)|^2$ is the occupation of the basis state $n$ in the $\Gamma_i$ multiplet for the paramagnetic state at $H = 0$ in the ground state, and of course $\sum_{\Gamma_i} w_{A,B}(\Gamma_i,n) = 1$.

Figures 8(a)-(e) show the occupation $w_A(\Gamma_i,n)$ of the five multiplets as a function of magnetic field strength for three field directions. The states not shown in each panel have occupation negligibly small or exactly zero. The occupation at the $B$-sublattice is the same, $w_B(\Gamma_i,n) = w_A(\Gamma_i,n)$ except for the case of $H \parallel [001]$, for which $w_B(\Gamma_i,n)$ is shown in Fig. 8(f).

For $H \parallel [001]$, two stable domains in the phase-I have the same occupations $w$'s. In the phase-II the wavefunction at the $A$-sublattice is almost pure $\Gamma_{3u}$ as in the high-field phase, since this is a collinear order. At the $B$-sublattice, $\langle Q_z \rangle \sim -1$ and $\langle Q_x \rangle = 0$, and therefore, the wavefunction is almost a pure $\Gamma_{3u}$ state. In the phase-III, both $\Gamma_{3u}$ and $\Gamma_{3v}$ states have large occupation at each sublattice and their hybridization yields a canted configuration of $Q$. With increasing field strength, one of the two states dominates, and correspondingly the ferro $Q_z$ component increases.

Let us check the amplitude of the secondary component and confirm that $\langle Q_x \rangle \neq 0$ at $H = 0$. Figure 9(a) shows the magnetic-field dependence of ferro $Q_z$ component near $H = 0$ for $H \parallel [001]$. As one can clearly see, the ferro component is indeed finite even at $H = 0$ and the limiting value at $H = 0$ agrees with that obtained by perturbative expressions (5) and (6).

Temperature dependence of $Q_z$ near $T_c$ exhibits an evidence that the ferro $Q_z$ moment is a secondary order parameter, and induced by $Q_x$ antiferro moment. Figure 9(b) shows the temperature dependence of $Q$ near $T_c$. The primary order parameter $Q_x$ shows a typical mean-field criticality, $|Q_x| \propto \sqrt{T_c - T}$, but as for the ferro $Q_z$ component, the temperature dependence is linear, $Q_z \propto -(T_c - T) \propto -Q_x^2$. This fact is consistent with our early analysis based on the third-order anisotropic term in $H_{CEF}$. As shown in Appendix E, the local Landau free energy has a third-order term. Combining this with the second-order term, the $Q_z$ part of the Landau free energy is given as

$$F_{Q_z} \sim \frac{1}{2\chi} Q_z^2 + \frac{\kappa_3}{\chi} Q_x^2 Q_z, \tag{12}$$

where the expression of $\chi$ and $\kappa_3$ are shown in Appendix E. It is important that $Q_x^2$ have a static value in the ordered phase below $T_c$, and therefore, $h_{Q_z} = -\frac{\kappa_3}{\chi} Q_x^2$ behaves as a uniform conjugate field of $Q_z$. The induced moment is then

$$Q_z = \chi h_{Q_z} = -\frac{\kappa_3}{\chi} Q_x^2, \tag{13}$$

This is consistent with the results in Fig. 9(b). This also explains why the induced $Q_z$ moment is ferro $Q_z$ and not antiferro $Q_z$. 

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Fig. 7. (Color online) Order parameters vs. magnetic field for (a) $H \parallel [001]$, (b) $H \parallel [110]$, and (c) $H \parallel [111]$. 
3. Excitations and Responses

In this section, we will investigate “spin” wave excitations for $T = 0$ and static quadrupole susceptibilities in detail.

3.1 “Spin” wave approximation at zero temperature

In this subsection, we will briefly explain the method of “spin” wave approximation for a general exchange type Hamiltonian. This analysis is equivalent to the equation of motion method with decoupling at $T = 0$, and useful for analyzing excitation spectra. Note, however, that because of the nature of the approximation, the method is valid at low temperatures.

3.1.1 Formulation

We represent the fluctuation beyond the mean-field approximation by using a set of bosons $\{a_{il}\}$ and $\{b_{il}\}$ and their conjugates. Here, $a_{il}^\dagger |0\rangle_A (l = 1, \cdots, 8)$ represents the $l$th mean-field excited state at the site $j$ in the $A$-sublattice, while $b_{il}^\dagger |0\rangle_B$ for $B$-sublattice, and $|0\rangle_{A,B}$ represents the mean-field ground state at each site. The fluctuation term in our model is

$$H_2 \equiv \lambda \sum_{(i,j)\mu=z,x} \left[ Q_{\mu}^A(i) - \langle Q_{\mu}^A \rangle \right] \left[ Q_{\mu}^B(j) - \langle Q_{\mu}^B \rangle \right]. \quad (14)$$

and in more general cases it is represented as

$$H_2 = \sum_{m,(i,j)} \lambda_m \left[ \langle O_{m}^{A}(i) - \langle O_{m}^{A} \rangle \rangle \left[ \langle O_{m}^{B}(j) - \langle O_{m}^{B} \rangle \rangle \right] \right]. \quad (15)$$

In terms of the introduced boson operators, this reads as

$$H_2 = \sum_{m,(i,j)} \lambda_m \left[ \langle O_{m}^{A}(i) \rangle a_{il}^{\dagger} + \text{h.c.} \right] \left[ \langle O_{m}^{B}(j) - \langle O_{m}^{B} \rangle \rangle b_{jl}^{\dagger} + \text{h.c.} \right]. \quad (16)$$

Here, $O_{m}^{A,B}$ is a general operator at $A(B)$-sublattice appearing in the Hamiltonian labeled by $m$ and $\langle O_{m}^{A,B} \rangle_l$ is the matrix element of $O_{m}^{A,B}$ between the ground state and the $l$th excited state for the $A(B)$-sublattice.

Note that the linear term in the bosons vanishes due to the mean-field condition. Combining on-site excitation energy $E_{l}^{A(B)}$ for the $l$th excited state at the $A(B)$-sublattice, we obtain a Hamiltonian for the bosons,

$$H_b = \sum_{l} \left( E_{l}^{A} a_{il}^{\dagger} a_{il} + E_{l}^{B} b_{il}^{\dagger} b_{il} \right)$$

$$+ \sum_{m,(i,j)} \lambda_m \left[ \langle O_{m}^{A}(i) \rangle a_{il}^{\dagger} + \text{h.c.} \right] \left[ \langle O_{m}^{B}(j) - \langle O_{m}^{B} \rangle \rangle b_{jl}^{\dagger} + \text{h.c.} \right] . \quad (17)$$

This Hamiltonian is bilinear in the boson operators and therefore we can diagonalize this by the Bogoliubov transformation to obtain its eigenenergies $\omega_m (n = 1, \cdots, 16 \text{ in our case})$ with $\mathbf{q}$ being the wavevector.
3.1.2 Excitation spectrum at zero temperature

Using the boson Hamiltonian introduced above, we now calculate the evolution of excitation energy spectrum with the variation of magnetic-field strength. Diagonalization of $H_0$ is similar to random-phase approximation. However, in contrast to the standard spin-wave theory for magnets, all the local degrees of freedom are taken into account. The inter-site correlations are taken into account only through the channels included in the microscopic Hamiltonian, and they are $\mathbf{Q}$ operators in our case.

Figure 10 shows the lowest excitation gap as a function of magnetic field for the three directions, where $H_c(001)$ is the critical field between the phase-III and the phase-IV for $\mathbf{H} \parallel [001]$. The excitations have an energy minimum at $\mathbf{q} = \mathbf{0}$ for all the parameter regimes. For each $\mathbf{H}$ direction, the excitation becomes gapless at the critical points between the ordered state and the high-field polarized state. This is very similar to the case in transverse-field Ising systems. For $\mathbf{H} \parallel [001]$, there is an additional gapless point at $|\mathbf{H}| = H_c^{(1)}$ between the phase-I and the phase-II. At the first-order transition point $|\mathbf{H}| = H_c^{(2)}$ between the phase-II and the phase-III, the magnetic field dependence of the gap exhibits a small jump (not visible in the scale in Fig. 10). One can see kinks near $H/H_c(001) \sim 0.8$ for $\mathbf{H} \parallel [001]$ and $H/H_c(001) \sim 1.2$ for $\mathbf{H} \parallel [110]$. These are not due to any phase transitions but due to level crossing between different excited states.

Let us note that the scaling of the gap near the critical fields. For $\mathbf{H} \parallel [001]$ and [110], the gap varies as $\propto |\delta H|^{1/2}$, where $\delta H$ is the deviation from the critical field $H_c$ for each magnetic-field direction: $\delta H \equiv H - H_c$.

Interestingly, the gap for $\mathbf{H} \parallel [111]$ varies as $|\delta H|^{3/2}$ for $H < H_c(111)$ and as $|\delta H|$ for $H > H_c(111)$. This leads to unusual divergence in susceptibilities near the critical point for $\mathbf{H} \parallel [111]$. We will discuss this in more detail in Sects. 3.2.1 and 3.2.2.

![Fig. 10. (Color online) Spin wave excitation gap at $\mathbf{q} = \mathbf{0}$ for $\mathbf{H} \parallel [001]$ (solid line), for $\mathbf{H} \parallel [110]$ (dashed line), and for $\mathbf{H} \parallel [111]$ (dotted line). Beware that the scale of both axes is different depending on field direction. Inset: Zoom up of the low field regime for $\mathbf{H} \parallel [001]$.](image)

![Fig. 11. (Color online) Excitation spectra for $\mathbf{H} \parallel [001]$. Full-red (dotted-blue) lines represent “in” (“out”) mode. See the text for the definition of the modes.](image)

![Fig. 12. (Color online) Excitation spectra at critical fields: $|\mathbf{H}| = H_c(001), H_c(111), H_c(110)$ and $H_c^{(1)}$ for $\mathbf{H} \parallel [001]$.](image)
orders are considered in this paper.

First, we discuss the nature of these two lowest-energy modes. They are rotation of $Q^A_B$ in the two-dimensional $Q$-space from the ground-state configuration in each phase. There are basically two types of rotations. One is an in-phase rotation of $Q^A$ and $Q^B$; that is, the two quadrupole moments rotate in the same direction. The other is an out-phase rotation; the two rotate in an opposite direction. We label them by “in” and “out” in Fig. 11. Note that in the phase-III a level crossing occurs between these two excitations as shown in Fig. 10. This means that “in” and “out” are interchanged for the higher field part of the phase-III. Figure 11 (c) shows the spectra in the lower field part.

To understand the nature of each of these modes, it is easiest to study the high-field phase-IV. In the high-field phase, the lowest-energy excitation is the “out” mode and thus has a finite matrix element of staggered $Q_z$ with the ground state. Since the system starts to exhibit the $Q_z$ antiferro quadrupole order as the magnetic field decreases, this is natural and it is this softening that leads to the phase transition. For other phases, similar arguments are also possible.

Secondly, we note that the flat band in the excitation spectrum along X-W direction has the same energy as the lowest excited level of an isolated single site calculated by the mean-field theory. This is because the form factor of the diamond lattice structure vanishes there. One can see that the two modes in Fig. 11 are degenerate along X-W except for (b). This is related to the symmetry between $A$- and B-sublattices for $|H| = 0$ and $H_c^{(2)} < |H|$, while there is no such symmetry for $0 < |H| < H_c^{(2)}$, since $|Q^A| \neq |Q^B|$.

Finally, we show the excitation spectra at the critical fields in Fig. 12. At or near the continuous transition for $H \parallel [001]$ and $[110]$, the energy dispersion is $|q|$-linear around the $\Gamma$ point, which also indicates that the system becomes critical. At the critical field for $H \parallel [111]$, however, the dispersion is $|q|^2$ and this is due to the absence of induced quadrupole moment in this field direction. This is qualitatively understood by considering an effective pseudospin-1/2 XY model with a field perpendicular to the XY plane. This corresponds to the fact that the inter-site interactions are only about the quadrupoles, while the magnetic field couples with the octupole when $H \parallel [111]$. Within the spin-wave approximation, anomalous terms $a_i^\dagger b_j^\dagger$ and $a_i b_j$ vanish and only hopping terms $a_i^\dagger b_j$ and $b_j a_i$ remain in Eq. (17). This is the same for spin waves in isotropic ferromagnets and there the dispersion is $|q|^2$.

### 3.2 Quadrupole susceptibilities

In this subsection, we study the quadrupole susceptibilities. We first show the numerical results of the quadrupole susceptibilities as a function of magnetic field for three symmetric directions in Sect. 3.2.1. As we will show, unusual critical behaviors appear for $H \parallel [111]$, and to clarify them, we analyze the nature of the unusual criticality in Sect. 3.2.2.

#### 3.2.1 Numerical results

Let us first define two components of the susceptibilities with respect to the sublattice indices. Because of $A$ and $B$ sublattices, the quadrupole susceptibility is a $2 \times 2$ matrix, and we consider two parity-conserving responses that are also diagonal in $Q$-space. Just for notational convenience, we denote them in terms of $\chi^\pm$ in Eq. (F-7) as $\chi^Q_{\mu} = (\chi^\pm)_{\mu\mu}$, where $\mu = z$ or $x$. In the following, we will study the behavior of these quadrupole susceptibilities upon changing magnetic field strength for three special field directions.

- $H \parallel [001]$:

Figure 13 shows the staggered part of the static quadrupole susceptibility, $\chi^{Q_{\mu}}$ as a function of magnetic field applied along $[001]$ direction. Note that the staggered part here refers to the component with $q = 0$ that has an odd parity for exchange of $A$ and $B$ sites, instead of finite-$q$ component. The most prominent feature is divergence at two phase boundaries. The divergence at higher field takes place at the transition between phases III and IV, while the divergence at lower field concurs with the transition between phases I and II at $H_c^{(1)} \approx 0.03H_c(001)$. The staggered order parameter, $(Q_{x}^A) - (Q_{x}^B)$, is zero in the phases II and IV, and this continuously emerges upon moving into the phases I and III. The divergence of $\chi^{Q_{x}}$ is a consequence of this continuous phase transition. Another prominent feature is a large jump at $H_c^{(2)} \sim 0.3H_c(001)$. This is due to the first-order phase transition between the phases II and III. Just
above $H^{(2)}_c$ in the phase III, the quadrupole moments are aligned almost parallel to $Q_z$, and their size is large $|\langle Q_{x,y}^A \rangle| \sim 1$, as shown in Fig. 7(a). Therefore, their fluctuations are suppressed and this leads to a reduction of $\chi_{x,y}^{Q_z}$. The quadrupole order is completely different in the phase II, which is below $H^{(2)}_c$. The quadrupole moments are aligned to $\pm Q_y$ direction. Therefore, their transverse fluctuations contribute to $\chi_{x,y}^{Q_z}$, and its value is quite large.

Singularity is found also in the uniform part of the static susceptibility, $\chi_{A,B}^{Q_z}$, as shown in Fig. 14, although this singularity is weaker than that in the staggered part $\chi_{x,y}^{Q_z}$. At the transition point between the phases IV and III, the uniform susceptibility does not diverge but shows a kink. See the (red) line near $H \sim H_c(001)$. The absence of divergence comes from the fact that the corresponding static quantity $\langle Q_{x,y}^A \rangle + \langle Q_{x,y}^B \rangle$ is not an order parameter in either of the phases III and IV. However, this quantity couples to the order parameter and this leads to a kink singularity in its field dependence. This is similar to the singularity in uniform susceptibility of antiferromagnets at the Neel temperature. This kink behavior is enhanced with lowering temperature. The transition between the phases III and II is first order, and $\chi_{A,B}^{Q_z}$ shows a small jump there. The transition between the phases II and I is special, and the uniform susceptibility also diverges. This is because in the phase I $|\langle Q_{x,y}^A \rangle| \neq |\langle Q_{x,y}^B \rangle|$, while both vanish in the phase II. Therefore, not only the staggered part but also the uniform part have fluctuations that diverge with approaching the transition point, which leads to $\chi_{\pm} \rightarrow \infty$. As for $\chi_{A,B}^{Q_z}$, it is suppressed in collinear phases with $\langle Q_y \rangle = 0$ such as in the phases II and IV, while enhanced in the phases I and III. This is natural, since longitudinal fluctuations are expected weaker than transverse ones.

- **$H \parallel [110]$**: Figure 15 shows $\chi_{\pm}^{Q_z}$ at $T = 0$ and for $H \parallel [110]$. In addition to the divergence in $\chi_{x,y}^{Q_z}$ at the critical field, one can see a dip in $\chi_{x,y}^{Q_z}$ at low fields. Indeed, $\langle Q_y \rangle$ shows a non-monotonic behavior in the low-field regime as shown in the inset of Fig. 15, and more directly, the weight of the lowest-energy eigen mode related to $Q_x^A + Q_x^B$ vanishes at the magnetic field where $\chi_{x,y}^{Q_z}$ is a minimum, while the change in eigenenergy is monotonic as shown in Fig. 10.

- **$H \parallel [111]$**: For $H \parallel [111]$, there is only one transition and the susceptibilities show unusual magnetic-field dependence near the critical field. To be specific, we choose the $(x^2 - y^2)$ domain in the ordered phase [see Fig. 6 (c)]. Figure 16 shows that not only the staggered components $\chi_{\pm,y}^{Q_x}$ but also the uniform component $\chi_{\pm}^{Q_x}$ diverge at the critical field $H_c(111)$. It is interesting to note that $\chi_{\pm}^{Q_x}$ diverges only in the ordered phase. The singularities of static $\chi_{\pm}^{Q_x}$ are summarized in Table I. Note that the strong singularity for $\chi^{Q_x} \propto |\delta H|^{-2}$ in the ordered phase makes a striking contrast to the conventional mean-field divergence $\sim |\delta H|^{-1}$ in the other field directions. We will investigate the origin for these unusual behaviors in the next subsection.

**Table I. Singularity of the quadrupolar susceptibilities near the critical field $H_c(111)$ for $H \parallel [111]$ and those near the critical temperature $T_c$ at $H = 0$.** Here, $\delta H = H - H_c$ and $\delta T = T - T_c$.

| $H \parallel [111]$ | $H < H_c$ | $H > H_c$ | $T < T_c$ | $T > T_c$ |
|---------------------|-----------|-----------|----------|----------|
| $\chi_{+}^{Q_x}$    | $|\delta H|^{-2}$ | $\delta H^{-1}$ | $|\delta T|^{-2}$ | $\delta T^{-1}$ |
| $\chi_{-}^{Q_x}$    | $|\delta H|^{-1}$ | $\delta H^{-1}$ | $|\delta T|^{-1}$ | $\delta T^{-1}$ |
| $\chi_{A}^{Q_z}$    | $\sim$ const. | $\sim -\delta H$ | $\sim$ const. | $\sim \delta T$ |
| $\chi_{B}^{Q_z}$    | $|\delta H|^{-1}$ | $\sim$ const. | $\sim \delta H$ | $\sim |\delta T|^{-1}$ | $\sim $ const. | $\sim \delta T$ |
will analyze the local susceptibility $\chi$. Here, $F_\text{loc}$ is the free energy at the stationary point. In Appendix ~G, we obtain $\chi^A_{\text{loc}}$ and $\chi^B_{\text{loc}}$, which appear in several Pr 1-2-20 compounds. As for Pr$_2$T$_2$Al$_{20}$, it is suggested that the ordered state is ferro quadrupole.\cite{10,14,28} We briefly discuss below properties of $\Gamma_3$ ferro quadrupole order.

Also for the ferro quadrupole case, the discussion on $O^2_2(Q_z)$ order in Sect. 2.2 holds and it is generally accompanied by a finite $O^1_2(Q_z)$ component. Neutron scattering experiment suggests that the order is ferro $O^2_2$,\cite{14} and,

$\delta h = g - a$ is the control parameter representing the distance from the critical point, and

$$
\gamma^A_{\text{loc}}(Q_x) = -\langle Q_x^A \rangle = q_s,
$$

$\gamma^A_{\text{loc}}(Q_z) = -\langle Q_z^A \rangle = q_t$. Here, $q_s$ and $q_t$ are given by Eqs. (G-4) and (G-6). The free energy $F^A_{\text{AFQ}}$ is expanded up to the second order in the fluctuation $\delta Q^s = Q^s - (Q^s)$ and we obtain

$$
F^A_{\text{AFQ}} = F^A_{\text{AFQ}} + \frac{1}{2} \delta Q^s \left( \gamma^A_{\text{loc}} \right)^{-1} \delta Q^s.
$$

Here, $F^A_{\text{AFQ}}$ is the free energy at the stationary point. In this domain, $\gamma^B_{\text{loc}}$ is identical to $\gamma^A$, except the sign of the off-diagonal elements. In terms of the parameters in Appendix ~G, we obtain

$$
\left( \gamma^A_{\text{loc}} \right)_{zz} \sim t_1 \delta h^{1/2} + t_2 \delta h^{3/2},
$$

$$
\left( \gamma^A_{\text{loc}} \right)_{\mu\mu} \sim \frac{1}{g} + c^{(1)}_\mu \delta h + c^{(2)}_\mu \delta h^2,
$$

with $\tilde{b} = b - \gamma^2/g$. Pay attention to the relation

$$
\gamma^A_{\text{loc}}(Q_x) = \frac{1}{2} g t_1^2,
$$

and this is the key to the unusual singularities. This results in a decrease of control parameter $g - a$ can be also driven by temperature, i.e., $\delta h = g - a(H, T)$. Therefore, the same singularities appears at $|H| = H_c(111)$ for $H || [111]$ and at the critical temperature for $H = 0$ by regarding $\delta h \propto \delta H$ or $\propto \delta T$ as shown in Table I. Indeed, we have checked this by microscopic mean-field calculation as shown in Fig. 17. The result of $\chi_{\text{loc}}^z$ and $\chi_{\text{loc}}^x$ are very unique and interesting. When the anisotropy is decreased $\gamma \rightarrow 0$, the amplitude of the divergence of $\chi_{\text{loc}}$ itself diverges as $1/\gamma^2$. In isotropic systems, we know that the transverse susceptibility should be finite in the whole region of its ordered phase as a consequence of gapless Goldstone mode. The behavior found here is in this sense consistent.

4. Discussions

In this section, we will discuss several topics relevant to Pr-based 1-2-20 compounds based on the results in this paper.

4.1 Ferro quadrupole order

In this paper, we have studied antiferro quadrupole orders, which appear in several Pr 1-2-20 compounds. As for Pr$_2$T$_2$Al$_{20}$, it is suggested that the ordered state is ferro quadrupole.\cite{6,14,28} We briefly discuss below properties of $\Gamma_3$ ferro quadrupole order.

Also for the ferro quadrupole case, the discussion on $O^2_2(Q_z)$ order in Sect. 2.2 holds and it is generally accompanied by a finite $O^1_2(Q_z)$ component. Neutron scattering experiment suggests that the order is ferro $O^2_2$,\cite{14} and,
in this case, there is no induced $O_2^2$ moment from our discussions in Sect. 2.2.

An important difference from the antiferro quadrupole order is the order of the transition. It is generally first-order as predicted by the Landau theory. The Landau free energy $F_{Q\chi}$ is given as

$$F_{Q\chi} \sim \frac{1}{2} a |Q|^2 + \frac{1}{3} \gamma Q_z (Q_z^2 - 3 Q_x^2) + \frac{1}{4} b |Q|^4. \quad (28)$$

Here, $a$, $b$, and $\gamma$ are constants and $Q$ is the uniform quadrupole moment. Note that for antiferro quadrupole case $Q_{AF}$, the third-order term including three $Q_{AF}$'s is not present due to the inversion symmetry ($A \leftrightarrow B$). The possibility of the first-order transition for the antiferro case is discussed in Appendix G.

The third-order anisotropy $\gamma$ is generally finite unless microscopic parameters are finely tuned. Thus, the transition should be first-order in general cases.\textsuperscript{31} The order of the transition can be controlled by, for example, applying magnetic field. Since the quadrupole couples with magnetic field through Eq. (8), there appears a linear term in $F_{Q\chi}$, leading to a finite moment $\langle Q \rangle$ induced. Then, the situation is similar to the classical liquid-gas transition and it is possible to tune the system to a second-order transition point and also crossover regime by varying the magnetic field and temperature.

Recently, Matsubayashi et al., observed that the superconducting transition temperature for PrTi$_2$Al$_{20}$ is enhanced near the region where the ferro quadrupole order disappears under pressure.\textsuperscript{8} We expect that this is due to critical or strongly enhanced quadrupole fluctuations of orbital degrees of freedom. However, if the order is ferro quadrupole, the transition is generally first order as discussed before. Then, fluctuations are not so particularly enhanced near the transition, unless the transition is very weak first order. For quantitative comparison with experimental data, we need more elaborate calculations with parameter tuning, which is left for a future study.

4.2 Softening in elastic constants in PrIr$_2$Zn$_{20}$

Uniform quadrupole susceptibility is measured indirectly by ultrasonic experiments through the coupling of elastic constant and quadrupole susceptibility.\textsuperscript{32} In systems with $T_d$ symmetry, one measures the elastic constants $c_{11} - c_{12}$ and the $c_{44}$ to detect $\Gamma_3$ and $\Gamma_5$ quadrupoles, respectively. $c_{11} - c_{12}$ gives information about uniform quadrupole susceptibilities in $\Gamma_3$ sector: $\chi_{Qz,Qx}^{\Gamma_3}$, while $c_{44}$ does about $\Gamma_5$ quadrupoles, which are due to the excited states in the 1-2-20 compounds. In PrIr$_2$Zn$_{20}$, the elastic constants exhibit unusual behaviors as a function of magnetic field and temperature.\textsuperscript{10} In this subsection, we discuss two aspects of them.

For $H = 0$, the elastic constants exhibit softening near the transition temperature both in the $c_{11} - c_{12}$ and the $c_{44}$ modes. Since the CEF ground state is the $\Gamma_3$ doublet, the softening in $c_{11} - c_{12}$ is due to its degeneracy, which leads to $-1/T$ at low temperature for $T > T_c$ (note that this does not diverge at $T_c$, since the transition occurs in the antiferro quadrupole sector). However, that in $c_{44}$ mode cannot be explained by a simple picture, since the excited states are in high energy above $\sim 30$ K and there is no $\Gamma_5$ in the direct product $\Gamma_3 \otimes \Gamma_3$. See, Appendix D. As a source of the softening in the $c_{44}$ mode, the effects of mode-mode coupling might be important in this compound. For $c_{11} - c_{12}$ mode, our result in Sects. 3.2.1 and 3.2.2 demonstrates that one of $\chi_{Qx}^{\Gamma_3}$ and $\chi_{Qz}^{\Gamma_3}$ susceptibilities depending on its domain diverges in the ordered phase toward the critical temperature and this is consistent with the experiment.

Under magnetic fields, the elastic constants also exhibit softening as a function of the magnetic field near the high-field critical point.\textsuperscript{10} When the magnetic field is applied in [100] direction, $c_{11}$ (a part of $\Gamma_3$ mode) shows strong softening as a function of magnetic field and also of temperature at 5 T. In addition, there are two anomalies below 5 T, suggesting the existence of multiple phases under the magnetic field.

For other directions, the elastic constant in $\Gamma_3$ mode also shows softening. Our mean-field result is consistent with those for $H \parallel [111]$ in the ordered phase, while in other cases the origin of the softening is beyond the

Fig. 17. (Color online) Quadrupole susceptibility near critical points. (a) $H \parallel [111]$ at $T = 0$. (b) $H = 0$. 

\[ \text{Fig. 17. (Color online) Quadrupole susceptibility near critical points. (a) } H \parallel [111] \text{ at } T = 0. \text{ (b) } H = 0. \]
mean-field approximation. In addition, there are several anomalies for \( \mathbf{H} \parallel [110] \) and [111].\(^{10,11}\) Further experimental works will clarify the nature of the anomalies and the whole \( T-H \) phase diagram.

It is noted that the number of phases for \( \mathbf{H} \parallel [001] \) suggested in these experiments is consistent with the present results, which is also consistent with the early analysis by Onimaru.\(^{24}\) Thus, one can expect that the strong softening around 5 T is related to the quantum critical point of antiferro quadrupole order between the phase-III and the phase-IV. This is a promising scenario and we need to carry out more elaborate calculations beyond the mean-field approximation, since the diverging susceptibility is not the uniform quadrupole susceptibility but the antiferro quadrupole one at \( H_c(001) \) for \( \mathbf{H} \parallel [001] \).

It is also instructive to point out that the uniform quadrupole susceptibility diverges when the sizes of corresponding quadrupole moments at two sublattices are different and they vanish at the transition. This situation is realized between the phase-I and the phase-II. The origin of the enhancement in the uniform quadrupole susceptibility near the transition between the phase-II and the phase-III is also related to this.

### 4.3 Thermo-electric power

Recently, Izawa et al., observed strong enhancement in thermo-electric power \( S \) in \( \text{PrIr}_2\text{Zn}_20 \) as a function of temperature under high magnetic fields.\(^{33}\) The peak position coincides with the peak position of specific heat.\(^{34}\) With decreasing magnetic field, the peak position shifts to a lower temperature and seems to vanish at the critical field \( \sim 5 \) T. This suggests that the peak position is related to some energy scale of dynamics. A candidate of this energy scale is the “spin”-wave gap at \( \mathbf{q} = \mathbf{0} \) as discussed in Sect. 3.1.2. This explains the \( \mathbf{H} \) dependence of specific heat peak position and the fact that the peak temperature vanishes at the critical field. Since in Kondo systems, a peak appears around the Kondo temperature,\(^{35,36}\) to clarify which energy scale determines the peak in \( S \), one needs to carry out more elaborate calculations for non-magnetic \( \Gamma_3 \) systems including both the on-site Kondo screening and inter-site correlations.

### 4.4 Other intersite interactions

In the present study, we have studied the canonical and minimal model with only quadrupole coupling, and have not included magnetic interactions or other non-magnetic ones. To quantitatively reproduce the phase diagram observed in the experiments, it is necessary to include other interaction, \( e.g., \) magnetic dipole interaction and also to carry out calculations beyond the mean-field approximation. Here, we examine the types of possible interactions based on symmetry arguments. See, details in Appendix H.

In Pr-based 1-2-20 compounds, Pr ions form a diamond lattice structure. In the following, we list some of the nearest-neighbor interactions possible in this case.

First, as for the quadrupole-quadrupole interactions, only one type is possible, and this is the one used in the present paper.

Second, as for the dipole-dipole interactions, there are two types allowed and they are given as

\[
g_1 \mathbf{J}(i) \cdot \mathbf{J}(j) + g_2 \left( \mathbf{r}_{ji} \cdot \mathbf{J}(i) \right) \left( \mathbf{r}_{ji} \cdot \mathbf{J}(j) \right).
\]

(29)

Here, \( i \) and \( j \) are nearest neighbors on different sublattices and \( \mathbf{r}_{ji} = \mathbf{r}_{ji}/|\mathbf{r}_{ji}| \) is the unit vector from \( i \) to \( j \). The first term is isotropic in both of \( \mathbf{J} \) space and real space, while the second is anisotropic in both spaces.

Thirdly, as for the octupole moments, in addition to trivial \( T_{xyz}(i)T_{xyz}(j) \) type interaction, the \( T_{xyz} \) octupole can couple with dipole moments as

\[
g_3 \left\{ T_{xyz}(i) \left[ \mathbf{r}_{ji} \cdot \mathbf{J}(j) \right] + T_{xyz}(j) \left[ \mathbf{r}_{ji} \cdot \mathbf{J}(i) \right] \right\}.
\]

(30)

There are many others, but we stop here and leave them in future publications.

It is noted that the interactions listed above include directional ones, \( i.e., \) those including \( \mathbf{r}_{ji} \). These anisotropic interactions are in general important in the f-electron systems and might lead to different ground states from the simple \( \Gamma_3-\Gamma_3 \) model. In order to determine these coupling constants, inelastic neutron scattering is powerful and one can compare the spin-wave dispersions between the experiments and the theory.

### 4.5 Interactions with phonons

Quadrupole moments are located at the center of a cage and they couple with local phonons of the cage atoms. In particular for the \( \Gamma_3 \)-type mode of displacements denoted as \( \xi(z,i) = [\xi_x(i), \xi_y(i), \xi_z(i)] \) (see Fig. 18), this couples linearly with the quadrupole at the center as \( \mathbf{Q}(i) \cdot \xi(i) \).

It would be more interesting to consider 16c site displacements in the 1-2-20 compounds. The 16c site (Zn or Al) is located at the middle of a nearest-neighbor Pr-Pr bond. The first-principle calculations\(^{37}\) for La compounds suggest that its atom oscillation is highly anharmonic and anisotropic with the hard axis along the bond direction. We denote the displacement of this oscillation...
at the center of the \( ij \) bond as \( x_{ij} \equiv (x_{ij}, y_{ij}, z_{ij}) \). It can couple with the quadrupole pair as

\[
g_{ij} \mathbf{Q}(i) - \mathbf{Q}(j) \cdot \mathbf{x}_\perp(ij),
\]

where \( \mathbf{x}_\perp(ij) = [x_{ij}^x, x_{ij}^y, x_{ij}^z] \equiv [(2r_{ji}^x - r_{ji}^x - r_{ji}^y)/\sqrt{6}, (r_{ji}^x - r_{ji}^y - r_{ji}^y)/\sqrt{2}] \) is the transverse component perpendicular to the bond direction. The direction in the plane is determined by the type of the quadrupole order. This also causes inversion symmetry breaking, since the 16c site is an inversion center.

Concerning the displacement \( \mathbf{x}_\perp(ij) \), it is also interesting that this induces the Dzyaloshinskii-Moriya interactions. This is given by

\[
\mathbf{D}_{ij} \cdot [\mathbf{J}(i) \times \mathbf{J}(j)],
\]

where the Dzyaloshinskii-Moriya vector is \( \mathbf{D}_{ij} \propto \mathbf{x}_\perp(ij) \times \hat{r}_{ji} \) in the lowest order in the displacement. This term favors incommensurate magnetic ordered states in general. There are many other interactions induced by \( \mathbf{x}_\perp(ij) \), but we leave them for future studies.

5. Summary

We have investigated antiferro quadrupole orders in the systems where local ground state is a non-Kramers \( \Gamma_3 \) doublet. We have considered this system on a diamond lattice to discuss orders in Pr-based 1-2-20 compounds, but most of the results in the present study also hold for general bipartite lattices with cubic symmetry. We have analyzed a minimal model for antiferro quadrupole orders based on the mean-field approximation and the quantum fluctuations are also analyzed via “spin”-wave calculations.

We have clarified how anisotropy in crystalline-electric-field potential affects the quadrupole order parameter \( \mathbf{Q} \), and thus, the phase diagrams under magnetic fields. The third-order nontrivial coupling in the quadrupoles is essential to explain it. One important consequence is that there is no pure \( O_2^0 \) antiferro quadrupole order without fine tuning of control parameters and the \( O_2^0 \) antiferro quadrupole order is accompanied by ferro \( O_2^0 \) quadrupole moments.

The magnetic field-temperature phase diagram shows varieties of phases. They are explained by competitions between the nonlinear Zeeman coupling (8) and antiferro quadrupole inter-site coupling \( \lambda \). For \( \mathbf{H} \parallel [001] \), three ordered phases appear apart from the high-field phase where the quadrupole moments align as determined by the nonlinear Zeeman coupling. The first is a low-field \( O_2^0 \) antiferro quadrupole phase. The second is a collinear \( O_2^0 \) antiferro quadrupole state. The third is a canted phase. For \( \mathbf{H} \parallel [110] \) and [111], there is only one ordered phase and it is a canted state.

To examine excitation dynamics of quadrupole moments, we have analyzed excitation spectra by using “spin”-wave approximation. At the phase boundaries of the second-order transition, there appears a critical mode with linear energy dispersion \( \omega \sim |\mathbf{q}| \) at the \( \Gamma \) point.

We have discovered unusual singularities at \( T_c \) for \( \mathbf{H} = 0 \) and also at the critical magnetic field along \( [111] \) direction, \( H_c(111) \), and clarified their origin. One staggered quadrupole susceptibility shows a stronger divergence than conventional mean-field one, and more interestingly, one uniform quadrupole susceptibility also exhibits divergence, although the ordered phase is not ferro quadrupole one. This can partially explain the softening in the ultrasonic experiments, but for the complete understanding, we need further investigations.

We have also proposed that a possible origin of enhanced thermo-electric power in the high-field phase is related to this low-energy quadrupole excitation. This scenario is consistent with the fact that the position of Schottky peak of the specific heat \( C(T) \) at high fields roughly coincides the peak position in the thermo-electric power.

As for possible inter-site couplings in the 1-2-20 compounds, we have shown that there exist various directional couplings. Important ones are the dipole-dipole interactions and dipole-octupole interactions. Quadrupole-phonon interactions are also presented and we have shown that the atoms at the 16c site should displace in a way determined by the quadrupole order pattern. This indicates that if the 1-2-20 system shows an antiferro quadrupole order, the inversion symmetry of the lattice structure should be broken at the same time, and as a result, the Dzyaloshinskii-Moriya interactions are induced. We have shown the form of the Dzyaloshinskii-Moriya vector in terms of the displacement at the 16c site. In the present paper, we have concentrated on analyzing a simple quadrupole-quadrupole model. For more quantitative comparison with experimental data, these interactions would be important.

In summary, we have investigated antiferro quadrupole order in \( \Gamma_3 \) non-Kramers doublet systems. We have pointed out that there is no pure \( O_2^0 \) antiferro quadrupole order from general arguments and the mean-field phase
diagram and excitation spectra have been demonstrated. We have also discovered unusual singularities at \( T = T_c \) for \( \mathbf{H} = 0 \) and also the critical field along [111] direction. In the final part, we have presented a list of some nontrivial interactions in the 1-2-20 compounds, which would be important for further theoretical and experimental investigations.

Acknowledgement

The authors would thank K. Izawa, T. Onimaru, and T. Sakakibara for fruitful discussions. K. H. thanks H. Kusunose for his valuable comment on the CEF Hamiltonian. This work was supported by a Grant-in-Aid for Scientific Research (No. 30456199) from the Japan Society for the Promotion of Science.

Appendix A: Wavefunctions

In this Appendix, we list single-site wavefunctions classified by the irreducible representations in the \( T_d \) group used in this paper.

First, let us introduce notations. For Pr ions, a main configuration of f-electrons is the \( J = 4 \) multiplet and its nine levels split as \( \Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5 \) due to \( H_{CEF} \). Two components of \( \Gamma_3 \) doublet are denoted by \( \{u, v\} \) and components of \( \Gamma_4 \) and \( \Gamma_5 \) triplets are written as \{\( X, Y, Z \)\} and \{\( X, Y, Z \)\}, respectively. Representative forms for the irreducible representations in terms of spatial coordinates \( (x, y, z) \) are given as

\[
u \sim 3z^2 - r^2, \quad v \sim \sqrt{3}(x^2 - y^2),
\]

\[
\tilde{X} \sim x(y^2 - z^2), \quad \tilde{Y} \sim y(z^2 - x^2), \quad \tilde{Z} \sim z(x^2 - y^2),
\]

\[
X \sim x, \quad Y \sim y, \quad Z \sim z,
\]

which \( r^2 = x^2 + y^2 + z^2 \). Note that, in \( T_d \) symmetry, \( xyz \) belongs to \( \Gamma_1 \), and thus, \( x \sim yz, y \sim zx, \) and \( z \sim xy \). The spatial coordinate vector \( (x, y, z) \) is \( \Gamma_5 \), while an angular momentum \( \mathbf{J} \) belongs to \( \Gamma_4 \).

Using the above notations, the wavefunctions are given as

\[
|\Gamma_1\rangle = \frac{1}{\sqrt{12}} \left[ \sqrt{5} \left(|4\rangle + |-4\rangle\right) + \sqrt{7} |0\rangle \right],
\]

\[
|\Gamma_3u\rangle = \frac{1}{\sqrt{12}} \left[ \sqrt{7} \left(|4\rangle + |-4\rangle\right) - \sqrt{5} |0\rangle \right],
\]

\[
|\Gamma_3v\rangle = \frac{1}{\sqrt{2}} \left(|2\rangle + |-2\rangle\right),
\]

\[
|\Gamma_4\tilde{X}\rangle = \frac{1}{4i} \left[ \sqrt{7} \left(|1\rangle + |-1\rangle\right) + (|3\rangle + |-3\rangle) \right],
\]

\[
|\Gamma_4\tilde{Y}\rangle = -\frac{1}{4} \left[ \sqrt{7} \left(|1\rangle - |-1\rangle\right) - (|3\rangle - |-3\rangle) \right],
\]

\[
|\Gamma_4\tilde{Z}\rangle = \frac{1}{\sqrt{2i}} \left(|4\rangle - |-4\rangle\right),
\]

\[
|\Gamma_5X\rangle = \frac{1}{4i} \left[ (|1\rangle + |-1\rangle) - \sqrt{7} (|3\rangle + |-3\rangle) \right].
\]

\[
|\Gamma_3Y\rangle = \frac{1}{4} \left[ (|1\rangle - |-1\rangle) + \sqrt{7} (|3\rangle - |-3\rangle) \right],
\]

\[
|\Gamma_5Z\rangle = \frac{1}{\sqrt{2i}} \left(|2\rangle - |-2\rangle\right).
\]

Here, \( |J_z\rangle \) is state with the z-component of the angular momentum \( J_z \) and \( J = 4 \).

Appendix B: Crystalline electric field Hamiltonian

Here, we comment on two representations of the local CEF Hamiltonian. The conventional representation is in terms of Stevens operators and it reads for \( J = 4 \) ion in CEF of \( T_d \) symmetry as

\[
H_{CEF} = \sum_i \left\{ B^0_4 [O^0_4(i) + 5O^1_4(i)] + B^0_6 [O^0_6(i) - 21O^1_6(i)] \right\}
\]

Here, \( O^m_4 \)'s are the Stevens operators and \( B^m_6 \)'s are constants. This form has been widely used to investigate CEF states in f-electron systems, but we have found that this is equivalent with the one represented by only two operators, and they are quadrupole moments defined as \( Q_x = \sqrt{3}O^2_4/8 \) and \( Q_z = O^2_6/8 \). This new representation is Eq. (1) shown in Sect. 2.1. Equation (1) explicitly shows the two invariances of \( \Gamma_3 \) quadrupole operators we consider. Apart from a trivial constant, Eq. (B-1) reduces to Eq. (1) and the parameters are related as

\[
\epsilon_2 = \frac{640}{3} \left( B^0_4 - 126B^0_6 \right), \quad \epsilon_3 = -\frac{78848}{9} B^0_6.
\]

Appendix C: Mean-field ground-state energy for \( \mathbf{H} = 0 \)

In this Appendix, we discuss the ground-state energy for \( \mathbf{H} = 0 \) on the basis of two-sublattice mean-field approximation. Since there are no matrix elements in the quadrupole operators between \( \Gamma_{1,3} \) and \( \Gamma_{4,5} \) states, the relevant Hilbert space here is spanned by \( \Gamma_3 \) and \( \Gamma_1 \) in our analysis.

First, let us show matrix forms of quadrupole operators in basis \{\( |\Gamma_1\rangle, |\Gamma_3u\rangle, |\Gamma_3v\rangle \}:

\[
Q_z = \begin{pmatrix} 0 & 0 & a \\ a & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad Q_x = \begin{pmatrix} 0 & 0 & a \\ a & -1 & 0 \\ 0 & 0 & -a \end{pmatrix}
\]

where \( a = \sqrt{35}/2 \). The basis wavefunctions are explained in Appendix A.

We approximate the intersite interactions by a mean field of quadrupole \( \mathbf{h} = -z\lambda(Q) = -q \mathbf{Q} \). Here, \( \langle \mathbf{Q} \rangle \) is the thermal average on the nearest neighbor sites and \( z \) is the number of the nearest-neighbor sites. Thus, the mean-field Hamiltonian at one site is written as

\[
H_{1\text{site}} = \begin{pmatrix} E_1 & a_q z & a_q x \\ a_q z & q_x & -q_z \\ a_q x & -q_z & q_x \end{pmatrix},
\]

\[
(\text{C-2})
\]
where \((q_s, q_z) = z\lambda(\langle Q_z \rangle, \langle Q_z \rangle) = q(\cos \theta, \sin \theta)\). The angle parameter is \(0 \leq \theta < 2\pi\) and \(q = \sqrt{q_s^2 + q_z^2}\). Let us first diagonalize the \(\Gamma_3\) sector. This is done by using the following new basis:

\[
|\Gamma_3^+\rangle = \cos \frac{\theta}{2} |\Gamma_3u\rangle - \sin \frac{\theta}{2} |\Gamma_3v\rangle, \\
|\Gamma_3^-\rangle = \sin \frac{\theta}{2} |\Gamma_3u\rangle + \cos \frac{\theta}{2} |\Gamma_3v\rangle.
\]  

(3.3)  

(3.4)

Then, in terms of \(|\langle \Gamma_1 \rangle, |\Gamma_3^+ \rangle, |\Gamma_3^- \rangle\rangle\), \(H_{\text{site}}\) reads as

\[
H_{\text{site}} = \begin{pmatrix}
E_1 \\
0 \\
0
\end{pmatrix}.
\]

(3.6)

We are interested in situation where \(E_1 \gg z\lambda(\langle Q \rangle) = q\) and obtain the ground-state energy of \(H_{\text{site}}\) perturbatively as a series of the small parameter \(q/E_1\).

\[
\frac{E_{\text{gs}}}{E_1} = -\left(\frac{q}{E_1}\right) - \frac{35}{4}\left(\sin^2 \frac{3\theta}{2}\right) \left(\frac{q}{E_1}\right)^2 + \frac{35}{4}\left(\sin^2 \frac{3\theta}{2}\right) - \frac{35}{32}\sin^2 \frac{3\theta}{2} \left(\frac{q}{E_1}\right)^3 + \cdots.
\]

(3.6)

We finally show a cubic invariant in the triple product \(\Gamma_3 \otimes \Gamma_3 \otimes \Gamma_3\), which is directly related to Eq. (3):

\[
\begin{align*}
\Gamma_3 \otimes \Gamma_3 \otimes \Gamma_3 &= \Gamma_1 \otimes \Gamma_1 \otimes \Gamma_1 \\
\Gamma_1 : (uu' + vv')u'' - (uv' + vu')v'' \\
\rightarrow u(u^2 - 3v^2) & \quad \text{for } \Gamma_3 = \Gamma_3 = \Gamma_3.
\end{align*}
\]

Appendix E: Landau free energy for quadrupole moment

To study quadrupole anisotropy, we will in this Appendix calculate the corresponding Landau free energy \(F(Q)\) for a single site at magnetic field \(H = 0\), starting from the microscopic model. We first consider the case of finite temperature, and secondly study the zero-temperature case, which needs a special care.

We will calculate the quadrupole Landau free energy \(F(Q)\) for a single site for a given temperature \(T = \beta^{-1}\), with starting from the microscopic CEF Hamiltonian Eq. (1). To this end, we include to the Hamiltonian a coupling to conjugate field \(h = (h_s, h_z) = h(\cos \theta, \sin \theta)\) and obtain its related free energy \(\tilde{F}(h)\):

\[
\tilde{F}(h) = -\frac{1}{\beta} \log \tilde{Z}(h) = -\frac{1}{\beta} \log \text{Tr} e^{-\beta (\tilde{H}_{\text{CEF}} - h \cdot \hat{Q})}.
\]

(E-1)

The unperturbed Hamiltonian is a \(9 \times 9\) matrix, and consists of the \(\Gamma_3\) ground-state doublet and excited states, \(\Gamma_1\) singlet and two triplets, \(\Gamma_4\) and \(\Gamma_5\). With setting the ground-state energy zero \(E_3 = 0\), the energies of these excited multiplets are denoted as \(E_1, E_4, E_5\), respectively.

Using a standard technique, we first expand \(\tilde{Z}(h)\) in \(h\),

\[
\tilde{Z}(h) = Z_0 + d_2 h^2 + d_3 h^3 + d_4 h^4 + \cdots.
\]

(2.2)

Here, the unperturbed partition function is \(Z_0 = 2 + e^{-\beta E_1} + 3(e^{-\beta E_4} + e^{-\beta E_5})\). The first-order term vanishes, and this means that the thermal average of moment vanishes at any finite temperature, unless the inter-site interactions are switched on. It will turn out that the expansion up to the fourth order is sufficient for studying quadrupole anisotropy. Since the operators \(\hat{Q}\) are block-diagonal in the CEF bases in Appendix A, the expansion...
is easy but the results are not so simple. The second- and the fourth-order terms are isotropic with respect to the field direction θ, while the third-order term depends as cos 3θ and we denote $d_4 = d_3 \cos 3\theta$. The explicit forms of \{d_n\} are given as

$$
\frac{d_2}{\beta^2} = 1 + \frac{35}{4} \frac{1 - e^{-\beta E_1}}{\beta E_1} + \frac{3}{16} \left(7^2 e^{-\beta E_4} + 2^2 e^{-\beta E_5}\right)
+ \frac{63 e^{-\beta E_5} - e^{-\beta E_4}}{\beta(E_4 - E_5)},
$$
(E-3)

$$
\frac{d_3}{\beta^3} = 35 \left[ -\frac{1}{\beta E_1} - \frac{1 - e^{-\beta E_1}}{\beta^2 E_1^2} \right]
- \frac{1}{27} \left[ 2(7^2 e^{-\beta E_4} - 8 e^{-\beta E_5}) + \frac{2}{3^4} \left( \frac{e^{-\beta E_4} - e^{-\beta E_5}}{\beta(E_4 - E_5)} \right) - 3 \frac{e^{-\beta E_4} - e^{-\beta E_5}}{\beta^2(E_4 - E_5)^2} \right],
$$
(E-4)

$$
\frac{d_4}{\beta^4} = \frac{1}{2^5 \cdot 3} \left[ 8 + 420 \frac{1}{\beta E_1} + 105 \frac{27 + 35 e^{-\beta E_1}}{\beta^2 E_1^2} \right.
- \frac{6510}{2^{10}} \frac{1 - e^{-\beta E_1}}{\beta E_3^3} + \frac{3}{2^{10}} \left[ (7^2 e^{-\beta E_4} + 2^4 e^{-\beta E_5})
+ 21 \frac{7^2 e^{-\beta E_4} - 4 e^{-\beta E_5}}{\beta(E_4 - E_5)}
- \frac{3^3 \cdot 7 (7^2 e^{-\beta E_4} + 9 e^{-\beta E_5})}{4} - \frac{9 \cdot 7 \cdot 3^9 e^{-\beta E_5}}{2 (\beta^2(E_4 - E_5)^2) \right)
+ 9 \frac{1}{\beta^2 E_1^2} \right].
$$
(E-5)

Converting the moments \{d_n\} into cumulants, the free energy is obtained as a series of $h$,

$$
\tilde{F}(h) \sim F_0 - \frac{1}{2} \chi h^2 - \frac{1}{3} \kappa_3 h_z(h_z^2 - 3h_x^2) + \frac{1}{4} \kappa_4 h^4 ,
$$
(E-6)

with $F_0 = -\beta^{-1} \log Z_0$ and the coefficients are

$$
\chi = \frac{2}{\beta} \frac{d_2}{Z_0}, \quad \kappa_3 = \frac{3}{\beta} \frac{d_3}{Z_0},
$$

$$
\kappa_4 = \frac{4}{\beta} \left[ \frac{1}{2} \left( \frac{d_4}{Z_0} \right)^2 - \frac{d_4}{Z_0} \right] = \frac{\beta}{2 \chi^2} - \frac{4}{\beta} \frac{d_4}{Z_0}.
$$
(E-7)

The thermal average of the quadrupole moment is calculated as $Q = \langle Q_x, Q_z \rangle = \langle Q \cos \varphi, \sin \varphi \rangle = -\partial \tilde{F}(h)/\partial h$ and the result is

$$
Q \sim \chi h + \kappa_3 h_z \cos 2\theta - \sin 2\theta - \kappa_4 h^2 h.
$$
(E-8)

This shows that the second-order coefficient $\chi$ is the linear susceptibility of quadrupole and isotropic, and also that the third-order contribution tilts the moment away from the field direction.

The next step is to invert the relation and obtain for a given $Q$ its corresponding $h(Q)$. This is easily done in the polar representation and the result is

$$
h \sim \frac{Q}{\chi} \frac{\kappa_3 Q^2}{\chi^3} \cos 3\varphi + \left[ \frac{\kappa_3^2}{\chi^2} (1 + \frac{5}{2} \sin^2 3\varphi) + \frac{\kappa_4}{\chi} \right] \frac{Q^3}{\chi^3},
$$
(E-9)

$$
\varphi \sim \varphi + \frac{\kappa_3 Q}{\chi^2} \sin 3\varphi.
$$
(E-10)

Now, combining all these, we can obtain the Landau free energy of quadrupole moment. We perform the Legendre transformation, $F(\mathbf{Q}) = F(h(\mathbf{Q}))+\mathbf{Q} \cdot \mathbf{h}(\mathbf{Q})$ and obtain

$$
F(\mathbf{Q}) \sim F_0 + \frac{35}{8 E_1} h^2 \left[ 1 + \frac{8 h_z^2 - 3 h_x^2}{h^3} \right]
$$
(E-11)

As predicted by the symmetry argument, anisotropy is due to the third-order term.

With approaching zero temperature, the linear susceptibility diverges as $\chi \propto \beta = 1/T$. Therefore, all the coefficients in the expansion above vanish, since $\kappa_3 \propto \beta$ and $\kappa_4 \propto \beta^3$. This indicates that the expansion at zero temperature is not regular around $Q = 0$. In the $\Gamma_3$ ground-state doublet, the modulus of quadrupole moment is $Q = 1$. Therefore, at zero temperature, we need expansion starting from $Q = 1$ not 0.

At zero temperature, it is sufficient to consider the ground states and the excited $\Gamma_1$ singlet. This is because $\Gamma_1$ is the only state that is connected to the ground state by matrix elements of $Q$. Solving the eigenvalue equation of the $3 \times 3$ Hamiltonian matrix, we obtain the exact ground state energy and its expansion in $h$ reads

$$
E_0(h) \sim -h - \frac{35}{8 E_1} h^2 \left[ 1 + \frac{8 h_z^2 - 3 h_x^2}{h^3} \right].
$$
(E-12)

This result is different from the expansion of the free energy in two points. First, $E_0$ has the term of order $h^3$. This implies the presence of spontaneous moment when the field $h$ is switched off. Secondly, the anisotropy appears in the order $h^2$ instead of $h^3$, although the dependence on field direction is common with the finite-temperature case.

The quadrupole moment is again obtained by $Q = -\partial E_0(h)/\partial h$ and the result in the polar representation is

$$
Q \sim 1 + \frac{35}{2 E_1} h \cos^2 \frac{3 \theta}{2} + \frac{105^2}{2^7 E_1^2} h^2 \sin^2 3\theta
$$
(E-13)

$$
\varphi \sim \varphi - \frac{105}{8 E_1} h \sin 3\theta.
$$
(E-14)

As we noted above, the quadrupole moment deviates from $Q = 1$ not 0 upon applying field at zero temperature. One should note that the correction terms vanish, when the field angle is $\theta \sim \frac{3}{2} \pi \times (\text{integer})$. This is also the case in the all orders in $h$. This is because the ground state does not change at all in this case upon increasing $h$.

The next step is the inversion of the relation $Q(\mathbf{h})$ and
we get the field strength and angle as
\[
\frac{h}{E_1} \sim \frac{Q - 1}{35 \cos^2 \frac{3\varphi}{2}} + \frac{945}{16} \left( \frac{Q - 1}{35 \cos^2 \frac{3\varphi}{2}} \right)^2 \sin^2 \frac{3\varphi}{2}, \quad (E-15)
\]
\[
\theta \sim \varphi + \frac{3}{2}(Q - 1) \tan \frac{3\varphi}{2}. \quad (E-16)
\]
Note that the small parameter in expansions is \((Q - 1)/(\frac{35}{2} \cos^2 \frac{3\varphi}{2})\).

Following the same procedure as for the Landau free energy at finite temperature, we obtain the zero-temperature energy of the quadrupole moment. The result is
\[
\frac{E(Q)}{E_1} \sim \frac{1}{35} \frac{(Q - 1)^2}{\cos^2 \frac{3\varphi}{2}} - \frac{1}{70} \frac{(Q - 1)^3}{\cos^4 \frac{3\varphi}{2}} \left( 2547 - 2555 \cos^2 \frac{3\varphi}{2} \right). \quad (E-17)
\]
The zero-temperature result has two essential differences. First, the anisotropy starts to appear in the second order in \((Q - 1)\), and secondly, the angle dependence is not a single harmonic like \(\cos 3\varphi\). These are evidences of the fact that the anisotropy at zero temperature cannot be represented by an analytic form in \(Q\), even if only small deviations are concerned.

Appendix F: Mean-field theory for susceptibility of a two-sublattice system

We explain in this Appendix a method of calculating susceptibility in a system with the two sublattices \(A\) and \(B\). The input of the method is local susceptibility at one site of each sublattice, \(\chi_{\text{loc}}^s\) \((s=A\ or\ B)\). We prepare its exact value by either an analytic or numerical method. This is easy since the local Hilbert space is small, nine dimensions in our case. Let us employ a mean-field theory and derive a formula that gives the susceptibility of the entire system from the local susceptibilities. To be specific, we will consider the response of quadrupole moment \(Q^s\) with respect to its conjugate field \(\bar{h}^s\).

In the mean-field theory, quadrupole moment at each site feels an effective field that consists of the molecular fields contributed by its neighbor sites and an external conjugate field. This is represented by the following mean-field Hamiltonian
\[
H_{\text{MF}} = H_{\text{loc}} - (\bar{h}^s - g\langle Q^s \rangle) \cdot Q^s = H_0^s - \bar{h}^s \cdot Q^s. \quad (F-1)
\]
Here, the intersite coupling is \(g = z\lambda\) and \(s = A\ or\ B\) with \(\bar{A} = B\ and\ vice\ versa\). The on-site part \(H_{\text{loc}}^s\) is the CEF Hamiltonian \(H_{\text{CEF}}\) plus the Zeeman coupling to magnetic field if it is applied. It does not matter if the magnetic field depends on the sublattices or not, and the following results hold. \(H_0^s\) is the unperturbed part, when concerned is the linear response to external fields \(h^{A,B}\), and this already includes the contribution of the molecular fields in ordered phases.

Now, let us examine the linear response of \(Q\) at each sublattice. There are two points. The first is that the susceptibility is a \(2\times2\) matrix in \(Q\) space and also a \(2\times2\) matrix in the sublattice space
\[
\delta Q^s_{\mu} = \sum_{s,\mu} \chi_{\mu\mu'}^{ss'} h^{s'}_{\mu'} \mu, \mu' \in \{x, z\}. \quad (F-2)
\]
Here, \(\delta Q^s_{\mu}\) denote the induced moments due to the external fields, and we will calculate \(\chi_{\mu\mu'}^{ss'}\). The second point is important and the core idea of the mean-field theory: the induced moments modifies the molecular fields, and this can be represented by the renormalization of the external fields. Since we know exactly the local response at each sublattice, they constitute self-consistency conditions
\[
\delta Q^s = \chi_{\text{loc}}^s (\bar{h}^s - g\delta Q^s). \quad (F-3)
\]
Here, under-bar denotes a \(2\times2\) matrix, and the orbital-space degrees of freedom are thus represented by vector and matrix for simplicity.

It is straightforward to solve these and we obtain
\[
\chi^s = (1 - g^2 \chi_{\text{loc}}^s)^{-1} \chi_{\text{loc}}^s, \quad (F-4)
\]
\[
\chi^s = -g(1 - g^2 \chi_{\text{loc}}^s)^{-1} \chi_{\text{loc}}^s. \quad (F-5)
\]
The uniform and staggered susceptibilities are given as
\[
\chi^+ = \chi^{AA} + \chi^{BB} \pm (\chi^{AB} + \chi^{BA}), \quad (F-6)
\]
\[
= \sum_{s=A,B} (1 - g^2 \chi_{\text{loc}}^s)^{-1} \chi_{\text{loc}}^s (1 \mp g \chi_{\text{loc}}^s). \quad (F-7)
\]
If a staggered order is present, it induces the cross responses
\[
\chi^+ = \chi^{AA} - \chi^{BB} \mp (\chi^{AB} - \chi^{BA}). \quad (F-8)
\]
Here, \(\chi^+\ and\ \chi^-\ take - and + sign, respectively. Beware that these are not symmetric in the internal \(Q\) space, and the correct symmetry is \((\chi^+)_{\mu\mu'} = (\chi^-)_{\mu'\mu}\).

Appendix G: Landau theory of antiferro quadrupole order

In this Appendix, we study the Landau free energy for the antiferro quadrupole order and find its minimum point. As discussed in details in Appendix E, the single-site free energy is given by Eq. (E-11). Adding the intersite interaction, we set up a minimal form of the total free energy
\[
F_{\text{tot}} = \sum_{s=A,B} \left[ \frac{1}{2} a|Q^s|^2 - \frac{1}{3} \gamma Q^s_{z}(Q^s_{z} + 3Q^s_{z}) \right] + g Q^A \cdot Q^B. \quad (G-1)
\]
Here, \(a, b, \gamma,\ and g\ are all positive phenomenological constants and we will consider the transition with the change of \(a\). This free energy (G-1) is appropriate for \(H = 0\) and also for \(H \parallel [111]\), where the magnetic field does not di-
Here, the new factor is \( F_{\text{tot}} \) is invariant upon simultaneous rotation of \( Q^{A,B} \) by the angle \( \pm 2\pi / 3 \), but not invariant for inversion \( Q^{A,B} \rightarrow -Q^{A,B} \) due to the \( \gamma \) term.

For simplicity, we focus on the the case of \( |Q^A| = |Q^B| \). This corresponds to the mean-field solutions for \( H = 0 \) and \( H || [111] \). Parameterizing \( Q^* = (Q_x^*, Q_y^*) = q(\cos \theta_x, \sin \theta_x) \), the free energy is now a function of the two angles and the common amplitude

\[
F_{\text{tot}} = a q^2 + \frac{1}{2} b q^4 + g q^2 R(\theta_A, \theta_B). \tag{G-2}
\]

Here, the new factor is

\[
R(\theta_A, \theta_B) \equiv \cos(\theta_A - \theta_B) - \frac{\gamma}{3g} (\cos 3\theta_A + \cos 3\theta_B).
\tag{G-3}
\]

We minimize \( F_{\text{tot}} \) in two steps; we first minimize \( R \) for a given \( q \) and secondly minimize \( R \) with the whole respect to \( q \). \( R \) is minimized for a nearly antiparallel configuration of the two quadrupole moments;

\[
\theta_{A,B} = \pm \left( \frac{\pi}{2} + \frac{\gamma}{2g} q \right), \quad R_{\text{min}} \sim -1 - \frac{\gamma^2}{2g} q^2. \tag{G-4}
\]

There are two other solutions, but they agree to the above one by symmetry operation of \( \pm 2\pi / 3 \) rotation.

Inserting this result to Eq. (G-2), we find the function to be minimized is a standard \( \phi^4 \)-model with modified coefficients

\[
F_{\text{tot}} \sim \tilde{a} q^2 + \frac{1}{2} \tilde{b} q^4, \quad \tilde{a} \equiv a - g, \quad \text{and} \quad \tilde{b} \equiv b - \gamma^2 / g. \tag{G-5}
\]

Here, \( \tilde{b} > 0 \) if the anisotropy is not so strong, and we first consider this case. Then, the transition is continuous. Finite moments start to appear when \( a \) becomes smaller than the critical value \( a_c = g \), and their amplitude is the mean-field result of the \( \phi^3 \)-model, \( q \sim |\tilde{a}| / |\tilde{b}|^{1/2} \). Including higher-order corrections in the calculations above, we obtain the result up to the next order

\[
q \sim \sqrt{\frac{|\tilde{a}|}{\tilde{b}}} \left( 1 - \frac{\gamma^4}{2\tilde{b}^2 g^4 |\tilde{a}|} \right). \tag{G-6}
\]

In the case of this continuous transition, the angle between \( Q^{A,B} \) starts from \( \pi \) and gradually deforms with the growth of their amplitude as shown by Eq. (G-4).

When the anisotropy is strong \( \tilde{b} < 0 \), we need to include the next-order term in \( q \).

\[
F_{\text{tot}} \sim \tilde{a} q^2 + \frac{1}{2} \tilde{b} q^4 + \frac{\gamma^2}{3g} q^6. \tag{G-7}
\]

This is the \( \phi^5 \)-model and describes a first-order transition upon varying \( a \), when \( \tilde{b} < 0 \). This transition takes place at

\[
a_\# \sim g \left( 1 + \frac{3\tilde{b}^2 g^2}{16 \gamma^4} \right) > a_c, \tag{G-8}
\]

and there the order parameter jumps to

\[
\bar{q}_\# \sim \sqrt{\frac{3|\tilde{b}| g^3}{4\gamma^4}}. \tag{G-9}
\]

Note that in the case that the moments \( Q^{A,B} \) are not completely antiparallel at the transition point,

\[
\Delta \theta \equiv \theta_A - \theta_B - \pi \sim \sqrt{\frac{3|\tilde{b}| g}{4\gamma^2}}. \tag{G-10}
\]

Even when the anisotropy is very strong, the result (G-9) is still valid, but the angle deformation approaches \( \Delta \theta \rightarrow \frac{\pi}{2} \).

### Appendix H: How to make invariant form

In this Appendix, we will discuss a general method to construct interactions that are invariant under a given point group. Although the following discussion is essentially the same as that done by Sakai et al,\(^{38}\) we show some details of the calculations.

Let us consider site \( i \) and its nearest neighbor sites \( j = 1, 2, 3, \) and \( 4 \) in a diamond lattice structure. The relative positions of the nearest neighbors (\( j = 1, 2, 3, \) and \( 4 \)) are \( (111)/4, (111)/4, (111)/4, \) and \( (111)/4 \) for \( j = 1, 2, 3, 4 \), respectively, where we set the lattice constant to unity.

See, Fig. 19. A general form of interactions between the nearest-neighbors is

\[
V_i = \sum_{\mu \nu} \sum_j \lambda_{ij}^{\mu \nu} A_i^\mu B_j^\nu. \tag{H-1}
\]

Here, \( \lambda_{ij}^{\mu \nu} \) is the coupling constant and \( A^\mu (B^\nu) \) transforms as one of the irreducible representations \( \mu (\nu) \) for local \( T_d \) point group without changing the site index. We represent the local point group operation by \( R_{\text{loc}} \) and also symmetry operation around the \( i \) site on the site index \( j \) by \( R_{\text{site}} \).

Now, we change the representations \( \mu \) and \( \nu \), which are not irreducible with respect to the index of irreducible representation for \( A \otimes B \). We denote this index as \( l \) and Eq. (H-1) is now given as

\[
V_i = \sum_{j=1}^{4} \sum_l \lambda_{ij}^l [A_i \otimes B_j]_l \equiv \sum_{j=1}^{4} \sum_l \lambda_{ij}^l C_{ijl}. \tag{H-2}
\]

This is further symmetrized by taking a following representation instead of \( j \):

\[
V_i = \sum_l \lambda_{ii}^l C_{ii} + \sum_l \bar{C}^l \cdot \bar{C}_{ii}, \tag{H-3}
\]

\[
\lambda_{ii}^l = \frac{1}{2} \sum_{j=1}^{4} \lambda_{ij}^l, \quad \lambda_{ii}^l = \frac{1}{2} (\lambda_{ij}^l - \lambda_{ij}^l + \lambda_{ij}^l - \lambda_{ij}^l), \tag{H-4}
\]

\[
\lambda_{ii}^l = \frac{1}{2} (\lambda_{ij}^l - \lambda_{ij}^l - \lambda_{ij}^l + \lambda_{ij}^l), \quad \lambda_{ii}^l = \frac{1}{2} (\lambda_{ij}^l + \lambda_{ij}^l - \lambda_{ij}^l - \lambda_{ij}^l). \tag{H-5}
\]
Note that
\[ (\tilde{\lambda})_u = \sum_{j=1}^{4} \tilde{U}_{uj} \lambda^j = \frac{\sqrt{3}}{2} \sum_{j=1}^{4} (\tilde{r}_{ij})_u \lambda^j, \] (H-6)
where \( \tilde{r}_{ij} \) is the unit vector from \( i \) to \( j \), and similar definitions for \( \tilde{C}_{ij} \) and \( \tilde{C}_{ij} u \) as \( \tilde{U}_{ij} \). The site indices of \( \tilde{C}_{ij} \) transform as \( \Gamma_1 \) under the operations \( R_{site} \), and that of \( \tilde{C}_{ij} \) as \( \Gamma_5 \) and \( \lambda \)'s do not transform under symmetry operations \( R_{site} \) because they are just coupling constants. Since under the operations \( R_{loc} \), different irreducible representations in \( l \) do not mix, we can analyze \( l \) in \( \Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4 \) and \( \Gamma_5 \), separately. The result is very simple and there are only two couplings: \( \lambda^{1s} \) and \( \lambda^{1o} \). The latter is given by \( \lambda^{X} = \lambda^{1s}(1, 0, 0), \lambda^{Y} = \lambda^{1s}(0, 1, 0), \lambda^{Z} = \lambda^{1s}(0, 0, 1) \), leading to
\[ V_i = \lambda^{1s} \sum_{j=1}^{4} C_{ij} \Gamma_1 + \lambda^{1o} \sum_{j=1}^{4} \tilde{r}_{ij} \cdot \left( C_{ijX} \Gamma_1 + C_{ijY} \Gamma_1 + C_{ijZ} \Gamma_1 \right) . \] (H-7)

Equation (H-7) indicates that we need to construct \( \Gamma_1 \) or \( \Gamma_5 \) representations by a given set of operators \( A \) and \( B \). Finally, since the above derivation does not include the fact that the bond center of the diamond lattice structure is the inversion center of the system, interactions obtained should be symmetrized with respect to the inversion operations. Even when the number of operators included increases, the above discussion is still valid by regarding \( C_{ij} = [A_i \otimes A_i' \otimes \cdots \otimes B_j \otimes B_j' \otimes \cdots] \).

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\[ Q^2_{2x}(i) - O^2_{2x}(i) \propto Q^2_{2y}(i) - 3Q^2_{2z}(i) \propto \cdots \rightarrow Q^2(i) \sin 3\theta(i). \] (H-8)
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