Quadrupole Susceptibility of Gd-Based Filled Skutterudite Compounds

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(Received May 2, 2014)

Abstract

It is shown that quadrupole susceptibility can be detected in Gd compounds contrary to our textbook knowledge that Gd$^{3+}$ ion induces pure spin moment due to the Hund’s rules in an LS coupling scheme. The ground-state multiplet of Gd$^{3+}$ is always characterized by $J=7/2$, where $J$ denotes total angular momentum, but in a $j$-$j$ coupling scheme, one $f$ electron in $j=7/2$ octet carries quadrupole moment, while other six electrons fully occupy $j=5/2$ sextet, where $j$ denotes one-electron total angular momentum. For realistic values of Coulomb interaction and spin-orbit coupling, the ground-state wavefunction is found to contain significant amount of the $j$-$j$ coupling component. From the evaluation of quadrupole susceptibility in a simple mean-field approximation, we point out a possibility to detect the softening of elastic constant in Gd-based filled skutterudites.

KEYWORDS: Quadrupole, Gadolinium, Filled skutterudites, Wigner-Eckart theorem.

1. Introduction

Recently, multipole phenomena have attracted much attention in the research field of strongly correlated $f$-electron systems. In general, multipole indicates spin-orbital complex degree of freedom, which is considered to be active in $f$-electron materials due to the strong spin-orbit coupling of $f$ electrons. However, when orbital degeneracy is lifted, for instance, due to the effect of crystal potential with low symmetry, only spin degree of freedom often remains. Thus, $f$-electron compounds with high symmetry are important for the research of multipole phenomena. In this sense, filled skutterudite compounds LnT$_x$X$_{12}$ (Ln: lanthanide, T: transition metal, X: pnictogen) with cubic structure of T$_h$ point group have provided us ideal stages for multipole physics. Here we pick up Gd-based compounds. In general, Gd ion takes the trivalent state in compounds, leading to the $4f^7$ system. In an LS coupling scheme, due to the Hund’s rules, electron configuration is determined so as to maximize total spin angular momentum $S$, indicating $S=7/2$ for Gd$^{3+}$. Since seven $f$ orbitals are singly occupied, total orbital angular momentum $L$ is zero in this case. Then, the total angular momentum $J$ of the ground state is given by $J=S=7/2$. The ground-state multiplet is generally affected by a crystalline electric field (CEF) potential, but the octet of Gd ion is not changed at all, since the CEF potentials act only on charge, not on spin, and the octet with $J=S=7/2$ and $L=0$ is spherically symmetric state. Namely, in the LS coupling scheme, there is no CEF splitting in the ground-state multiplet and we cannot expect to observe the response of higher-rank multipole in Gd-based compounds.

Note here that the LS coupling scheme is exact in the limit of $U \gg \lambda$, where $U$ denotes the magnitude of Hund’s rule interaction and $\lambda$ is spin-orbit coupling. In actual materials, $U$ is larger than $\lambda$, but $\lambda/U$ is not equal to zero. Thus, the effect of a $j$-$j$ coupling scheme should appear, more or less, in the ground-state wavefunction. For Gd$^{3+}$ ion, the ground state in the $j$-$j$ coupling scheme is also characterized by $J=7/2$, but it is composed of fully occupied $j=5/2$ sextet and one electron in $j=7/2$ octet, where $j$ indicates one-electron total angular momentum. Since one $f$ electron in the $j=7/2$ octet possesses orbital degree of freedom, we can observe the CEF level splitting even for Gd compounds in the $j$-$j$ coupling scheme. For actual rare-earth compounds, $U$ is about a few eV, while $\lambda$ is several thousand Kelvin, indicating that $\lambda/U$ is in the order of 0.1. Namely, the actual materials are in the intermediate situation between the LS and $j$-$j$ coupling schemes. Thus, the ground state of Gd compounds includes the contribution of the $j$-$j$ coupling scheme and the quadrupole susceptibility is expected to be significant in contrast to our knowledge on the basis of the LS coupling scheme.

In this paper, it is shown that quadrupole susceptibility can be detected in Gd compounds, although it has been simply believed that Gd$^{3+}$ ion induces pure spin moment due to the Hund’s rules. It is found that the $j$-$j$ coupling component appears in the ground-state wavefunction for realistic values of Coulomb interaction and spin-orbit coupling. With the use of the CEF parameters determined from PrOs$_4$Sb$_{12}$, we evaluate the quadrupole susceptibility for Gd-based filled skutterudite compounds and discuss the detection of the softening of elastic constant.

The organization of this paper is as follows. In Sec. 2, we define the local $f$-electron Hamiltonian and explain the definition of multipole in the form of one-body operator. In Sec. 3, we discuss the CEF states and determine the parameters from the experimental results of PrOs$_4$Sb$_{12}$. In Sec. 4, we evaluate quadrupole susceptibility in a simple mean-field theory and discuss the detection of the elastic constant for Gd-based filled skutterudites. Finally, in Sec. 5, we summarize this paper. Throughout this paper, we use such units as $\hbar=k_B=1$.

2. Local Hamiltonian and Multipole Operator

2.1 Local Hamiltonian

First we define the local $f$-electron Hamiltonian as

$$H_{loc} = H_C + H_{so} + H_{CEF},$$

where $H_C$ denotes Coulomb interaction term, $H_{so}$ is a spin-orbit coupling term, and $H_{CEF}$ indicates crystalline electric field (CEF) potential term. Among them, $H_C$ is given by

$$H_C = \sum_{m_1=\cdots=m_4} \sum_{\sigma,\sigma'} I_{m_1m_2m_3m_4}\sigma_{k_1}\sigma_{k_2}\sigma_{k_3}\sigma_{k_4},$$

(2)
where $\sigma=\pm 1\,(-1)$ for up (down) spin, $f_{\sigma m}$ is the annihilation operator for $f$ electron with spin $\sigma$ and $z$-component $m$ of angular momentum $\ell=3$ at an atomic site $i$, and the Coulomb integral $I_{m_1 m_2 m_3 m_4}$ is given by

$$I_{m_1 m_2 m_3 m_4} = \sum_{k=0}^{6} F^k c_k(m_1, m_4)c_k(m_2, m_3).$$  

(3)

Here $F^k$ indicates the Slater-Condon parameter and $c_k$ is the Gaunt coefficient. Note that the sum is limited by the Wigner-Eckart theorem to $k=0, 2, 4,$ and $6$. Although the Slater-Condon parameters should be determined for the material from the experimental results, here we simply assume the ratio among the Slater-Condon parameters as physically reasonable value, given by

$$F^0 = 10U, \quad F^2 = 5U, \quad F^4 = 3U, \quad F^6 = U,$$  

(4)

where $U$ denotes the scale of Hund’s rule interaction among $f$ orbitals, which should be in the order of a few $\text{eV}$. The spin-orbit coupling term $H_{so}$ is expressed as

$$H_{so} = \lambda \sum_{i,m\sigma,m',\sigma'} \zeta_{i,m\sigma,m',\sigma} f^\dagger_{i,\sigma} f_{i,\sigma'},$$  

(5)

where $\lambda$ is the spin-orbit interaction, and the matrix element $\zeta$ is given by

$$\zeta_{i,m\sigma,m',\sigma} = \frac{m\sigma/2}{\sqrt{(\ell+1)-m(m+\sigma)/2}},$$  

(6)

and zero for other cases.

Finally, the CEF term $H_{CEF}$ is expressed as

$$H_{CEF} = \sum_{i,m\sigma,m'} B_{m,m'} f^\dagger_{i,\sigma} f_{i,m',\sigma},$$  

(7)

where $B_{m,m'}$ denotes the CEF potential for $f$ electrons from the ligand ions, which is determined from the table of Hutchings for angular momentum $\ell=3$. For the filled skutterudite compounds with $T_h$ symmetry, $B_{m,m'}$ is expressed by using three CEF parameters, $B^0_0, B^1_1, B^2_2$, as

$$B_{3,3} = B_{-3,-3} = 180 B^0_0 + 180 B^0_0,$$

$$B_{2,2} = B_{-2,-2} = -420 B^0_0 - 1080 B^0_0,$$

$$B_{1,1} = B_{-1,-1} = 60 B^0_0 + 2700 B^0_0,$$

$$B_{0,0} = 360 B^0_0 - 3600 B^0_0,$$

$$B_{3,1} = B_{-3,1} = 60 \sqrt{15} (B^0_0 - 21 B^0_0),$$

$$B_{2,0} = B_{-2,0} = 30 B^0_0 + 7560 B^0_0,$$

$$B_{1,-1} = B_{-1,-3} = 360 B^0_0. $$

(8)

Note the relation of $B_{m,m'}=B_{m',m}$. Following the traditional notation, we define $B^0_0, B^1_1, B^2_2$ as

$$B^0_0 = W_x/F(4),$$

$$B^1_1 = W(1-|x|)/F(6),$$

$$B^2_2 = W_y/F(6),$$

(9)

where $x$ and $y$ specify the CEF scheme for $T_h$ point group, while $W$ determines the energy scale for the CEF potential. As for $F(4), F(6)$, and $F^4(6)$, we choose $F(4)=15, F(6)=180$, and $F^4(6)=24$ for $\ell=3$.  

### 2.2 Definition of multipole operator

Next we define multipole as spin-orbital density in the form of one-body operator from the viewpoint of multipole expansion of electron density in electromagnetism. On the basis of this definition of the multipole operator, we have developed microscopic theories for multipole-related phenomena. For instance, octupole ordering in $\text{NpO}_2$ has been clarified by evaluating multipole interaction with the use of the standard perturbation method in terms of electron hopping. We have also discussed possible multipole states of filled skutterudites by analyzing multipole susceptibility of a multiorbital Anderson model based on the $j-j$ coupling scheme. Quite recently, a microscopic theory for multipole ordering from an itinerant picture has been developed on the basis of a seven orbital Hubbard model with spin-orbit coupling.

The multipole operator $\hat{T}$ is expressed in the second-quantized form as

$$\hat{T}^{(k)}_{j\gamma j',\mu j'\gamma'} = \sum_{q,m\sigma,m'\sigma'} G^{(k)}_{j\gamma j',q} T_{m,m',\sigma,\sigma'}^{(k,q)} f^\dagger_{i,\sigma} f_{i,m',\sigma'},$$  

(10)

where $k$ is a rank of multipole, $q$ denotes an integer between $-k$ and $k$, $\gamma$ is a label to express $O_h$ irreducible representation, $G^{(k)}_{j\gamma j',q}$ is the transformation matrix between spherical and cubic harmonics, and $T_{m,m',\sigma,\sigma'}^{(k,q)}$, can be calculated by using the Wigner-Eckart theorem as

$$T_{m,m',\sigma,\sigma'}^{(k,q)} = \sum_{i\mu\mu'} \langle j|\hat{T}^{(k)}_{j\gamma j',q}|i\mu\mu'\rangle \times \langle j\mu|\hat{T}^{(k,q)}_{j\gamma j',q}|i\mu\mu'\rangle.$$

(11)

Here $\ell=3$, $s=1/2$, $j=\ell\pm s$, $\mu$ denotes the $z$-component of $j$, $\langle j\mu|\hat{T}^{(k)}_{j\gamma j',q}|i\mu\mu'\rangle$ indicates the Clebsch-Gordan coefficient, and $\langle j|\hat{T}^{(k,q)}_{j\gamma j',q}|j\mu\mu'\rangle$ is the reduced matrix element for spherical tensor operator, given by

$$\langle j|\hat{T}^{(k,q)}_{j\gamma j',q}|j\rangle = \frac{1}{2k^2} \sqrt{(2j+k+1)!/(2j-k)!}.$$

(12)

We note that $k\leq2j$ and the highest rank is $2j$. Namely, for $f$ electrons, we can treat the multipoles up to rank $7$ in the present definition.

In this paper, we define the multipole operator in the one-body form on the analogy of the multipole expansion theory of electromagnetic potential, but some readers may cast questions about the validity of the present definition. Since the multipole operators have been traditionally defined by the Stevens’ operator equivalent in the space of the Hund’s-rule multiplet characterized by the total angular momentum $J$, the present definition seem to be different from such a traditional one at a first glance. Concerning this point, we provide detailed comments in the following. Hereafter the Stevens’ operator equivalent is simply called the Stevens operator.

First of all, we reply to the above question in a simple manner. In one word, the present definition of multipole operator is related to the Stevens operator through the Wigner-Eckart theorem as

$$\langle n, J, M|\hat{T}^{(k)}_{j\gamma j',q}|n, J, M'\rangle = c_{n,\ell}(U, \lambda) \sum_q G^{(k)}_{j\gamma j',q} O^{(k)}_{\ell}(J; M, M'),$$

(13)
In the limit of large $U$, the $3^+$ ion in the Gd compounds. The extent of the effect of quadrupole will be discussed in the next section.

From a mathematical viewpoint, the relation eq. (13) just expresses the Wigner-Eckart theorem, but it contains physically important message concerning the multipole. Since the $J$-multiplet of $f^{n_0}$-electron system is given by the appropriate superposition of $n$-body states, the Stevens operator is considered to be given by the expression of multipole in the many-body form, in sharp contrast to the present definition of one-body form. However, for $f^{n_0}$-electron systems, eq. (13) means that the expectation value of the multipole operator in the present definition is in proportion to the Stevens operator and the effect of interactions is included only in the proportional coefficient $c$. When we impose the orthonormal condition on the multipole operator, the difference in the normalization is absorbed in the proportional coefficient. Namely, the multipole in the present definition is equivalent to the Stevens operator, except for the proportional coefficient. Thus, it is possible to use one of the definitions of multipole, one-body or many-body form, depending on the problem, but we point out some advantages to use the multipole in the one-body form.

The Stevens operator is considered to be suitable for localized situation, which is well described by the $LS$ coupling scheme. First we construct the Hund’s-rule ground state characterized by spin moment $S$ and angular momentum $L$ for $f^{n_0}$-electron systems. Then, we include the effect of spin-orbit coupling to form the multiplet characterized by total angular momentum $J$, which is given by $J=|L−S|$ and $J=L+S$ for $n<7$ and $n>7$, respectively. In such a case, it seems to be natural to define the multipole by the Stevens operator given by eq. (14). However, it is difficult to consider itinerant situation in the $LS$ coupling scheme, since $J$ is changed by charge fluctuations. In contrast, the present definition of multipole can be used both for itinerant and localized cases, since it is defined as the one-body density operator. This is one of advantages of the present definition of multipole.

When we define multipole in the one-body density operator, the effect of Coulomb interaction and spin-orbit coupling is automatically included in the proportional coefficient. Thus, in the present definition of multipole, we can discuss the relative change of multipole moment in the wide range of Coulomb interaction and spin-orbit coupling from $\lambda/U=0$ ($LS$ coupling scheme) to $\lambda/U=\infty$ ($jj$ coupling scheme). This is another advantage of the one-body definition of multipole. It is true that from a symmetry viewpoint, we can continue to use the Stevens operator even if we deviate from the $LS$ coupling scheme, since the ground state multiplet is always characterized by the same total angular momentum when we change $U$ and/or $\lambda$. However, the coefficient $c$ in eq. (13) is changed by the interactions, but this point is not included in the Stevens operator. This is easily understood when we recall the CEF potential for the case of $n=2$, in which the ground state multiplet is characterized by $J=4$. The CEF potentials are expressed by using the fourth- and sixth-order Stevens operators, but the sixth-order one vanishes in the $jj$ coupling regime, since the CEF term is originally given by the sum of one-electron electrostatic potential and the sixth-order terms do not appear for one electron in the $j=5/2$ states which are accommodated in the limit of large $\lambda$.

Here we should mention that there is a disadvantage concerning the limitation of the rank of multipole in the present

where $n$ is the local $f$-electron number, $J$ is the total angular momentum of the ground state multiplet, $M$ is the $z$-component of $J$, $|n, J, M\rangle$ denotes the degenerate ground states of $H_C + H_{so}$, $c$ denotes a proportional coefficient depending on $n, J, k, U$, and $\lambda$, and $O_K^c(J; M, M')$ is the matrix element of Stevens operator $\hat{O}_K^c$, given by

$$O_K^c(J; M, M') = \frac{\langle J || T^{(c)} || J \rangle}{\sqrt{2J+1}} \langle JM | JM' kq \rangle. \quad (14)$$

Here the reduced matrix element is given by eq. (12), in which $j$ is replaced with $J$. We can numerically calculate all the matrix elements of the Stevens operator for arbitrary numbers of $J$ and $k$, but for some low-order multipole, it is convenient to use the symmetrized polynomials of $J_{\alpha}$, where $J_{\alpha}$ ($\alpha=x$, $y$, and $z$) is the $\alpha$ component of total angular momentum $J$.

In Fig. 1, we depict the coefficients $c$ for the case of $n=7$, corresponding to Gd$^{3+}$ ion. We note that the coefficients do not depend only on the ratio of $\lambda/U$, but even if the values of $U$ and $\lambda$ have been individually changed so as to keep the ratio, we have not found significant difference in the results. Note also that in the present case of $n=7$, the ground state multiplet is characterized by $J=7/2$ and the highest multipole is rank 7 in any case. As naively expected, we find that only dipole moment remains in the limit of the $LS$ coupling scheme for large $U$, since the total angular momentum $J$ of the ground-state multipole is purely composed of seven spins. In the limit of large $\lambda$, all the coefficients converge to unity, since the ground state is essentially expressed by one electron in the $j=7/2$ octet and the one-body multipole expression perfectly agrees with the Stevens operator in the one-electron case. It is interesting to mention that this fact is also related to Yb$^{3+}$ with one hole in the $j=7/2$ octet.

It should be noted that around at $\lambda/U=0.1$ to $0.2$, corresponding to the region for realistic values of actual materials, the coefficients for multipoles other than dipole rapidly increase, although the magnitude of the coefficient depends on individual values of $U$ and $\lambda$. In particular, it is impressive that the coefficient for quadrupole seems to be larger than we have naively expected, since the realistic situation with $\lambda/U=0.1$ to $0.2$ has been believed to be well described by the $LS$ coupling scheme. This result strongly suggests that quadrupole degree of freedom cannot be simply neglected in the calculation of the multipole effect in the $\lambda/U=0.1$ to $0.2$ regime.
definition of the multipole in the one-body form. As mentioned in the previous subsection, we can treat the multipoles up to rank 7 in the present multipole definition. In order to treat higher multipoles with \( k \geq 8 \), it is necessary to define the multipole in the many-body operator form, since the Stevens operator with the many-body form can treat all possible multipoles up to rank 2\( J \) in the multiplet characterized by \( J \). Nevertheless we believe that the present multipole definition with one-body form keeps an advantage, since in actuality, it is very rare to treat higher-order multipoles with \( k \geq 8 \).

3. Crystalline Electric Field States

3.1 Effective Hamiltonian

The local CEF state can be determined by the diagonalization of the local Hamiltonian eq. (1), but in order to understand how the CEF states are changed due to the competition between the Coulomb interaction and spin-orbit coupling, i.e., the \( LS \) and \( j-j \) coupling schemes, it is useful to derive the effective Hamiltonian \( H_{\text{eff}} \) from eq. (1) with the use of the Stevens operator eq. (14). We express \( H_{\text{eff}} \) as

\[
H_{\text{eff}}(n, J) = B_0^0(n, J)(\hat{O}_0^0 + 5\hat{O}_4^0) + B_0^0(n, J)(\hat{O}_0^0 - 21\hat{O}_6^0) + B_0^0(n, J)(\hat{O}_0^0 - \hat{O}_0^0),
\]

where \( \hat{O}_0^0 \) is the Stevens operator of which matrix elements for \( n \) and \( J \) are given by eq. (14) and \( B_0^0(n, J) \) denotes the CEF parameter for the multiplet specified by \( n \) and \( J \).

The effects of \( U \) and \( \lambda \) appear in the CEF parameters, \( B_0^0(n, J), B_0^0(n, J) \), and \( B_0^0(n, J) \), which are expressed by

\[
\begin{align*}
B_0^0(n, J) &= k_4(n, J)B_4^0, \\
B_0^0(n, J) &= k_6(n, J)B_6^0, \\
B_0^0(n, J) &= k_6(n, J)B_6^0,
\end{align*}
\]

where \( B_4^0 \), \( B_6^0 \), and \( B_6^0 \) for one \( f \) electron with \( \ell = 3 \) are given by eq. (9) and \( k_4(n, J) \) and \( k_6(n, J) \) are given by

\[
k_4(n, J) = \beta_j^{(n)} / \beta_\ell, \quad k_6(n, J) = \gamma_j^{(n)} / \gamma_\ell,
\]

respectively. Here \( \beta_j^{(n)} \) and \( \gamma_j^{(n)} \) are the so-called Stevens factors, which are coefficients appearing in the method of Stevens’ operator equivalent.\(^{29}\) Note that in general, \( \beta_j^{(n)} \) and \( \gamma_j^{(n)} \) depend on the Coulomb interaction and spin-orbit coupling, since they are determined by the nature of the ground-state multiplet specified by \( J \).

For one \( f \) electron with \( \ell = 3 \), \( \beta_\ell \) and \( \gamma_\ell \) are given by

\[
\begin{align*}
\beta_\ell &= \frac{2}{11 \cdot 45}, \\
\gamma_\ell &= -\frac{4}{9 \cdot 13 \cdot 33},
\end{align*}
\]

respectively. For the ground state of \( n = 7 \) and \( J = 7/2 \), in the limit of \( U \to \infty \), i.e., in the \( LS \) coupling scheme, we obtain \( k_4(n, J) = k_6(n, J) = 0 \), suggesting that the CEF potentials do not work for \( f^7 \) states with \( J = S = 7/2 \) in the \( LS \) coupling scheme. On the other hand, in the limit of \( \lambda = \infty \), i.e., in the \( j-j \) coupling scheme, we obtain \( k_4(n, J) = 3/7 \) and \( k_6(n, J) = 1/7 \) from the Stevens factors\(^{29}\)

\[
\beta_{7/2}^{(n)} = \frac{2}{11 \cdot 77}, \quad \gamma_{7/2}^{(n)} = -\frac{4}{13 \cdot 33 \cdot 63}.
\]

Note that the absolute values of \( \beta_{7/2}^{(n)} \) and \( \gamma_{7/2}^{(n)} \) in the \( j-j \) coupling scheme are equal to those for \( \text{Yb}^{3+} \) ion with one hole in \( j = 7/2 \) octet, although the signs are just inverted.

For the intermediate coupling region in which both \( U \) and \( \lambda \) are finite, we numerically evaluate \( k_4(n, J) \) and \( k_6(n, J) \) by deriving \( H_{\text{eff}} \) from the local Hamiltonian \( H_{\text{loc}} \). By using the ground state \( |n, J, M \rangle \) of \( H_{\text{so}} \) and \( H_{\text{C}} \), we evaluate the matrix elements of the effective Hamiltonian as

\[
H_{\text{eff}}(n, J, M, M') = \langle n, J, M | H_{\text{CEF}} | n, J, M' \rangle,
\]

where we assume that \( |W| \) is much smaller than both \( U \) and \( \lambda \). Since the matrix elements of the Stevens operator have been already listed for each value of \( J \), we can numerically obtain \( B_0^0(n, J), B_0^0(n, J), \) and \( B_0^0(n, J) \) from eq. (20) for any values of \( U \) and \( \lambda \) for a given value of \( n \).

In Fig. 2, we show \( k_4(n, J) \) and \( k_6(n, J) \) for \( n = 7 \) and \( J = 7/2 \) as functions of \( \lambda/U \). In order to draw this figure, we numerically evaluate the matrix element eq. (20) for \( |W| = 10^{-4} \) eV. Concerning \( U \) and \( \lambda \) for \( \lambda/U < 1 \), we fix \( \lambda \) as \( \lambda = 1.0 \) and increase \( U \), while for \( \lambda/U > 1 \), we fix \( U \) as \( U = 1.0 \) and increase \( \lambda \). As mentioned in Fig. 1, we have not found significant difference in the results, even when we individually change the values of \( U \) and \( \lambda \) by keeping the ratio.

As mentioned above, we obtain \( k_4(n, J) = k_6(n, J) = 0 \) for small \( \lambda/U \), while we find \( k_4(n, J) = k_6(n, J) = 3/7 \) for large \( \lambda/U \). In the region of \( \lambda/U = 0.1 \sim 1.0 \), we observe rapid increases of both \( k_4(n, J) \) and \( k_6(n, J) \) from zeros to the values of the \( j-j \) coupling limit. In this sense, for actual values of \( \lambda \) and \( U \), we expect the appearance of the CEF effect even for the case of \( n = 7 \). The quantitative argument of the CEF potentials will be discussed in the next subsection.

Finally, we note the difference in the increasing behavior of \( k_4(n, J) \) and \( k_6(n, J) \). Although \( k_4(n, J) \) monotonically increases from zero to \( 3/7 \), \( k_6(n, J) \) does not change monotonically, but it forms a peak around at \( \lambda/U \approx 1.0 \). In particular, \( k_6(n, J) \) is slightly larger than \( 1/7 \), which is the value of the \( j-j \) coupling limit. In the region of \( \lambda/U = 0.1 \sim 1.0 \), the effect of \( k_6(n, J) \) is relatively larger than that of \( k_4(n, J) \).

3.2 CEF parameters

Before proceeding to the evaluation of quadrupole susceptibility, it is necessary to determine the CEF parameters in \( H_{\text{CEF}} \). For the purpose, as typical material, we consider
filled skutterudite compounds. As for the CEF parameters of PrO$_3$Sb$_{12}$, it has been confirmed that the ground state is $\Gamma_1^+$ singlet state and the first CEF excited state is $\Gamma_4^{(2)+}$ triplet with small excitation energy of about 10 K. $^{5-7}$ Note that since filled skutterudite compounds crystallize in the cubic structure with $T_d$ symmetry, two triplet states of $\Gamma_4^+$ and $\Gamma_5^+$ in $O_h$ symmetry are mixed with each other, leading to two $\Gamma_4^+$ states. $^{10}$

In order to reproduce the CEF energy scheme which has been experimentally determined, $^{5-7}$ we perform the optimization of $W$, $x$, and $y$ in $H_{\text{CEF}}$ of eq. (1) for $U=1.0$ eV. Note that $\lambda$ is set as the value which has been experimentally found. $^{32}$ For Pr$^{3+}$ ion, we use $\lambda=0.094$ eV. After the optimization, we find $W=-0.69$ meV, $x=0.22$, and $y=1.08$. We note that these CEF parameters determine the CEF potentials for one $f$-electron state of eq. (9), not for $f^2$-states of $J=4$ of eqs. (15) and (16). In Fig. 3(a), we show the CEF energies vs. $x$ for $W=-0.69$ meV and $y=1.08$. The vertical broken line denotes the position of $x=0.22$, at which we find $E(\Gamma_4^{(2)+})-E(\Gamma_1^+)=7.9K$, $E(\Gamma_4^{(1)+})-E(\Gamma_1^+)=134.9K$, and $E(\Gamma_4^{(2)+})-E(\Gamma_4^{(1)+})=205.4K$, where $E(\Gamma_i)$ denotes the eigenenergy of the CEF state characterized by the irreducible representation of $\Gamma_i$. These excitation energies reproduce well the experimental CEF energy scheme of PrO$_3$Sb$_{12}$. $^{5-7}$

Here it is instructive to consider the CEF potentials in eq. (16) of the effective model for $n=2$ and $J=4$. After some algebraic calculations with the use of the above optimized values of $W$, $x$, and $y$, we obtain $B_i^0(n=2, J=4)=2.29 \times 10^{-2}$K, $B_i^0(n=2, J=4)=1.33 \times 10^{-3}$K, and $B_i^0(n=2, J=4)=1.38 \times 10^{-2}$K. In the analysis of the experimental results, $^5$ the CEF potentials for the states of $n=2$ and $J=4$ have been found to be $A_4=2.37 \times 10^{-2}$K, $A_6=1.32 \times 10^{-3}$K, and $A_i^0=1.08 \times 10^{-2}$K, where $A_4$, $A_6$, and $A_i^0$ used in Ref. 5 denote $B_i^0(n=2, J=4)$, $B_i^0(n=2, J=4)$, and $B_i^0(n=2, J=4)$ in our notation, respectively. The CEF potentials for the states of $n=2$ and $J=4$ obtained by considering both finite spin-orbit coupling and Coulomb interactions are totally similar to those obtained in the $LS$ coupling scheme in which the Coulomb interactions are assumed to be infinite, although there exist deviations between two groups of the CEF potentials due to the effect of finite Coulomb interactions. This fact indicates that the CEF states of $n=2$ are well described by the $LS$ coupling scheme.

Next we show the CEF energy scheme for Gd-based filled skutterudites by using the same CEF parameters. Since the CEF potentials work on $f$ orbital, as easily understood from $H_{\text{CEF}}$, there is no reason to change the CEF parameters when we replace the rare-earth ion with another one in the same environment due to the same ligand ions. Note that $\lambda$ is determined from the experimental value and we set $\lambda=0.18$ eV for Gd ion. In Fig. 3(b), we show the CEF energies vs. $T$ for $n=7$ with the use of the same parameters as those in Fig. 3(a), except for the spin-orbit coupling. Note that the magnitude of the CEF splitting is obviously smaller than that of Fig. 3(a), but we observe the CEF excitation in the order of a few Kelvin. In the present parameters, we find that at $x=0.22$, the ground state is $\Gamma_6^{7+}$ quartet and the excited states are two types of $\Gamma_5^{6-}$ doublets. Note that two different doublets $\Gamma_6^5$ and $\Gamma_7^5$ in $O_h$ symmetry are mixed with each other, leading to two $\Gamma_5^5$ doublet states. Note also that $\Gamma_5^5$ quartet in $O_h$ symmetry is expressed by $\Gamma_6^{7+}$ in $T_d$ symmetry. $^{10}$

In the $LS$ coupling scheme, there is no CEF splitting for the case of $n=7$, since the octet of $J=7/2$ is composed of $S=7/2$ and $L=0$. However, as emphasized in the discussion of multipole partner, the actual situation is in the middle of the $LS$ and $j-j$ coupling schemes. Thus, in contrast to our knowledge on the basis of the $LS$ coupling scheme, we observe the CEF splitting due to the effect of the $j-j$ coupling component in the wavefunction. This point will be discussed again for the quadrupole susceptibility.

4. Quadrupole Susceptibility

Now we discuss the quadrupole susceptibility, which can be detected by the measurement of elastic constant $C$. In general, we consider the strain fields $\epsilon_u$ and $\epsilon_v$, which are coupled with quadrupoles $Q_{uu}=\hat{T}^{(2)}_{4,3z^2-r^2}$ and $Q_{uv}=\hat{T}^{(2)}_{4,x^2-y^2}$, respectively. In the notation of the Stevens operator, these are expressed by $(2J_2^2-J_2^4-J_2^6)/2$ and $(3J_2^2-J_2^4)/2$, respectively. $^{30,31}$

By following the standard formalism to calculate the elastic constant, we add the coupling term between strain and quadrupole to $H_{\text{loc}}$, expressed as

$$H = H_{\text{loc}} + H_{\text{QS}} + H_{\text{QQ}},$$

where $H_{\text{QS}}$ and $H_{\text{QQ}}$ denote quadrupole-strain interaction and inter-site quadrupole interaction terms, respectively. We express them as

$$H_{\text{QS}} = -g \sum_i (Q_{uu}\epsilon_u + Q_{uv}\epsilon_v),$$

$$H_{\text{QQ}} = -\lambda \sum_{ij} (Q_{uu}Q_{uv} + Q_{uv}Q_{uu}).$$
and
\[ H_{QQ} = -g' \sum_{(i,j)} (\hat{Q}_{ii} \hat{Q}_{jj} + \hat{Q}_{ij} \hat{Q}_{ji}), \]

where \( g \) and \( g' \), respectively, denote quadrupole-strain and inter-site quadrupole couplings and \((i,j)\) indicates the pair of nearest neighbor atomic sites.

The elastic constant \( C \) is usually expressed with the use of quadrupole susceptibility \( \chi_Q \) as \( C = -Ng^2\chi_Q \), where \( N \) denotes the number of rare-earth ion in the unit volume. By considering only the strain field of \( \varepsilon \), we estimate \( \chi_Q \) in a simple mean-field approximation, in which we express \( H_{QQ}^{MF} \) as
\[ H_{QQ}^{MF} = -g' \sum_{(i,j)} \hat{Q}_{ii} \langle \hat{Q}_{ij} \rangle, \]

where \( \langle \cdot \rangle \) denotes the operation to take thermal average. Then, we obtain \( \chi_Q \) in the mean-field approximation as
\[ \chi_Q = \frac{1}{1 - g' \chi}, \]

where \( \chi \) is the on-site quadrupole susceptibility determined from \( H_{loc} \), given by
\[ \chi = \frac{1}{Z} \sum_{n,m} e^{-E_n/T} - e^{-E_m/T} \left[ \frac{\langle n | \hat{Q}_v | m \rangle}{E_n - E_m} \right]^2. \]

Here we suppress the site dependence of \( \hat{Q}_{vi} \), \( Z \) is the partition function given by \( Z = \sum_n e^{-E_n/T} \), \( E_n \) denotes the eigenenergy of the \( n \)-th eigenstate \( |n\rangle \) of \( H_{loc} \), and \( \langle \hat{Q} \rangle = \sum_n e^{-E_n/T} \langle n | \hat{Q} | m \rangle / Z \).

In Fig. 4(a), we depict \(-\chi_Q \) vs. \( T \) for \( n=2 \) corresponding to \( \text{PrOs}_4\text{Sb}_{12} \) for several values of \( g' \) with the use of \( U=1.0 \text{ eV}, \lambda=0.094 \text{ eV} \) (experimental value), and the CEF parameters determined in the previous subsection. For \( g'=0 \), we find a minimum in \(-\chi_Q \) at \( T \approx 3 \text{ K} \) due to the suppression of the Curie term. Then, at low enough temperatures, the quadrupole susceptibility is dominated by the Van Vleck term due to the off-diagonal term stemming from the quasi-degenerate \( \Gamma_1 \) singlet and \( \Gamma_1^{(2)} \) triplet \(,33,34 \) which are characteristic to \( \text{PrOs}_4\text{Sb}_{12} \). When we increase the value of \( g' \) up to \( 1 \text{ K} \) as shown in Fig. 4(a), we do not find significant changes in the temperature dependence, although the absolute value is slightly suppressed.

We remark that the characteristic behavior of \(-\chi_Q \) for \( g'=0 \) has been obtained in the analysis of the experimental results in the \( LS \) coupling scheme.\(,33,34 \) The experimental results on the elastic constant for \( \text{PrOs}_4\text{Sb}_{12} \) have been well explained by such calculation results. Here it is emphasized that we correctly reproduce the previous results by using the definition of multipole in the one-electron density operator form. Note, however, that the absolute value of \(-\chi_Q \) for \( g'=0 \) is different from that in the previous result, although the shape of the temperature dependence agrees quite well with the previous one. An important origin of such difference is due to the difference in the wavefunction. Another origin is due to the normalization of the multipole operator, which will be commented later. In any case, for the purpose to reproduce the experimental results with the calculation one, we adjust the value of \( g \), which is just a fitting parameter, since it is not determined solely from the theoretical calculations in the present framework. Thus, in this paper, we do not take care of the difference in the absolute values between the present \( \chi_Q \) and the previous results. However, it is meaningful to consider the relative difference between the results for \( n=2 \) and \( n=7 \) in the same calculation framework.

In Fig. 4(b), we depict \(-\chi_Q \) vs. \( T \) for \( n=7 \) corresponding to Cd-based filled skutterudite compounds for several values of \( g' \) with the use of \( U=1.0 \text{ eV}, \lambda=0.18 \text{ eV} \) (experimental value), and the same CEF parameters as those for \( \text{PrOs}_4\text{Sb}_{12} \). The results are similar to those for Ce compounds with \( \Gamma_8 \) quartet ground state. This point is intuitively understood from the similarity between \( \text{Ce}^{3+} \) ion with one electron in the \( j=5/2 \) sextet and \( \text{Gd}^{3+} \) ion with one electron in the \( j=7/2 \) octet in the limit of the \( j-j \) coupling scheme, when quartet ground state appears due to the CEF potentials.

Note that as easily understood from the difference in the vertical scales between Figs. 4(a) and 4(b), the absolute value of the quadrupole susceptibility for \( n=7 \) is larger than that for \( n=2 \), mainly due to the contribution of the Curie term. When we increase \( g' \) in the order of \( 1 \text{ K} \), the magnitude of the quadrupole susceptibility is totally suppressed, but it is still possible to observe the softening in the elastic constant, which is determined by the quadrupole susceptibility. For the case of \( \text{PrOs}_4\text{Sb}_{12} \), the fitting to the experimental results has been done for \( g'=0 \),\(,33,34 \) but at the present stage, we cannot determine the magnitude of \( g' \) in order to discuss the absolute value of \(-\chi_Q \) of Gd-based filled skutterudites. An important message which we emphasize here is that it is possible to observe the softening of elastic constant even in Gd-based filled...
skutterudite compounds contrary to our knowledge on the basis of the $LS$ coupling scheme.

5. Discussion and Summary

We have evaluated the quadrupole susceptibility for realistic values of Coulomb interaction and spin-orbit coupling for Pr- and Gd-based filled skutterudite compounds. In particular, we have pointed out a possibility that the softening of the elastic constant can be observed for Gd compounds.

Concerning previous research on elastic properties of Gd compounds, we notice the measurement of elastic constant in rare-earth hexaborides.\textsuperscript{35,36} No anomaly has been reported in GdB\textsubscript{6} due to the elastic constant measurement, except for the signal at a temperature of the antiferromagnetic phase transition. In this sense, it may be difficult to observe actually the softening of elastic constant in Gd compounds with the cubic structure. However, we believe that it is worthwhile to perform more precise ultrasonic experiments in Gd compounds, in particular, for Gd-based filled skutterudites.

Here we also remark that Eu\textsuperscript{2+} also contains seven $f$ electrons. Thus, we expect the appearance of the softening of elastic constant in Eu compounds.\textsuperscript{36} Note, however, that valence fluctuation between divalent and trivalent states is considered to be strong in europium. It may be also difficult to detect the softening of elastic constant in Eu compounds, but we hope that precise ultrasonic experiments in Eu compounds will be done in near future.

In the evaluation of the quadrupole susceptibility, we have not considered the competition among different types of multipoles. Since we have concentrated only on the measurement of the elastic constant, the quadrupole susceptibility has been evaluated. However, for Gd compounds, we have frequently observed an antiferromagnetic phase in the low-temperature region. When the Néel temperature is so high, it may be difficult to detect the softening of the elastic constant in the paramagnetic phase. In such a case, it is interesting to consider the anisotropy of magnetization in the antiferromagnetic phase due to the effect of quadrupole degree of freedom. It is one of future problems to estimate the extent of the anisotropy of magnetization in Gd compounds.

If we intend to show explicitly the occurrence of the antiferromagnetic phase, it is necessary to perform the optimization of multipole susceptibility.\textsuperscript{23,27} Then, we conclude that the multipole state with the largest eigenvalue of the susceptibility matrix is realized when we decrease the temperature. Such calculations have been actually performed for the seven-orbital Anderson model with the use of a numerical renormalization group technique.\textsuperscript{21} For the case of Gd ion, it has been shown that the dipole state exhibits the maximum eigenvalue and the eigenstate of the second largest eigenvalue is characterized by quadrupole. As for the extension of the calculations to the periodic systems,\textsuperscript{27} it is another future issue.

In this paper, we have considered the coupling between quadrupole and the strain for the elastic constant. However, from the symmetry viewpoint, it is necessary to include also the effect of hexadecapoles. In fact, for the explanation of the temperature dependence of the elastic constant of PrM\textsubscript{6} with $\Gamma\textsubscript{3}$ doublet ground state, a crucial role of hexadecapole has been emphasized.\textsuperscript{37} Also in Gd-based compounds, such higher-order multipoles may play some roles for the explanation of the behavior of elastic constant. If we will successfully observe the softening of the elastic constant in Gd-based filled skutterudites, it may be necessary to include the effect of hexadecapole to explain precisely the temperature dependence of the elastic constant. It is also another future problem.

Finally, we provide a comment on the normalization of the multipole operator. In the present paper, since we have considered only the quadrupole susceptibility, it is not necessary to pay attention to the normalization of the multipole operator. However, if we consider the diagonalization of the multipole susceptibility matrix, it is inevitable to define the normalization. A natural way is to redefine each multipole operator so as to satisfy the orthonormal condition of $\text{Tr}\{\hat{T}_{\gamma}^{(k)}\hat{T}_{\gamma'}^{(k')}\} = \delta_{kk'}\delta_{\gamma\gamma'}$.\textsuperscript{38} Note again that we have not considered such re-definition in the present paper.

In summary, we have found that the $j-j$ coupling component significantly appears in the ground-state wavefunction for $n=7$ with $J=7/2$ even for realistic values of Coulomb interaction and spin-orbit coupling. With the use of the CEF parameters determined from Pr\textsubscript{0.8}Sb\textsubscript{1.2}, we have evaluated the quadrupole susceptibility for Gd-based filled skutterudites. We have emphasized that the softening of the elastic constant can be detected in Gd compounds. We expect that ultrasonic experiments will be performed in Gd-based filled skutterudite compounds in a future.

Acknowledgement

We thank Y. Aoki, Y. Nakanishi, Y. Nemoto, H. Sato, T. Goto, T. Yanagisawa, and Y. Yoshizawa for discussion and comments. This work has been supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Heavy Electrons” (No. 20102008) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan. The computation in this work has been done using the facilities of the Supercomputer Center of Institute for Solid State Physics, University of Tokyo.

\begin{thebibliography}{99}

1. T. Hotta: Rep. Prog. Phys. 69 (2006) 2061.
2. Y. Kuramoto, H. Kusunose, and A. Kiss: J. Phys. Soc. Jpn. 78 (2009) 072001.
3. P. Santini, S. Carretta, G. Amoretti, R. Caciuﬃno, N. Malmagni, and G. H. Lander: Rev. Mod. Phys. 81 (2009) 807.
4. H. Sato, H. Sugawara, Y. Aoki, and H. Harima: Handbook of Magnetic Materials Volume 18, ed. K. H. J. Buschow, pp. 1-110, Elsevier, Amsterdam, 2009.
5. M. Kohgi, K. Iwasa, M. Nakajima, N. Metoki, S. Araki, N. Bernhoeft, J.-M. Mignot, A. Gukasov, H. Sato, Y. Aoki, and H. Sugawara: J. Phys. Soc. Jpn. 72 (2003) 1002.
6. K. Kuwahara, K. Iwasa, M. Kohgi, K. Kaneko, S. Araki, N. Metoki, H. Sugawara, Y. Aoki, and H. Sato: J. Phys. Soc. Jpn. 73 (2004) 1438.
7. E. A. Goremychkin, R. Osborn, E. D. Bauer, M. B. Maple, N. A. Fredrick, W. M. Yuhasz, F. M. Woodward and J. W. Lynn: Phys. Rev. Lett. 93 (2004) 157003.
8. J. C. Slater: Quantum Theory of Atomic Structure, (McGraw-Hill, New York, 1960).
9. M. T. Hutchings: Solid State Phys. 16 (1964) 227.
10. K. Takegahara, H. Harima and A. Yanase: J. Phys. Soc. Jpn. 70 (2001) 1190.
11. K. R. Lea, M. J. M. Leask and W. P. Wolf: J. Phys. Chem. Solids 23 (1962) 1381.
12. K. Kubo and T. Hotta: Phys. Rev. B 71 (2005) 140404(R).
13. K. Kubo and T. Hotta: Phys. Rev. B 72 (2005) 132411.
14. K. Kubo and T. Hotta: Phys. Rev. B 72 (2005) 144401.
15. T. Hotta: Phys. Rev. Lett. 94 (2005) 067003.
\end{thebibliography}
16) T. Hotta: J. Phys. Soc. Jpn. 74 (2005) 1275.
17) T. Hotta: J. Phys. Soc. Jpn. 74 (2005) 2425.
18) T. Hotta and H. Harima: J. Phys. Soc. Jpn. 75 (2006) 124711.
19) T. Hotta: J. Magn. Magn. Mater. 310 (2007) 1691.
20) T. Hotta: J. Phys. Soc. Jpn. 76 (2007) 034713.
21) T. Hotta: J. Phys. Soc. Jpn. 76 (2007) 083705.
22) T. Hotta: J. Phys. Soc. Jpn. 77 (2008) 074716.
23) T. Hotta: Proc. Int. Conf. New Quantum Phenomena in Skutterudite and Related Systems (Skutterudite 2007), J. Phys. Soc. Jpn. 77 (2008) Suppl. A, p. 96.
24) T. Hotta: J. Phys.: Conf. Ser. 150 (2009) 042061.
25) T. Hotta: Phys. Rev. B 80 (2009) 024408.
26) T. Hotta: J. Phys. Soc. Jpn. 79 (2010) 094705.
27) T. Hotta: Phys. Res. Int. 2012 (2012) 762798.
28) T. Inui, Y. Tanabe and Y. Onodera: Group Theory and Its Applications in Physics, (Springer, Berlin, 1996).
29) K. W. H. Stevens: Proc. Phys. Soc. A65 (1952) 209.
30) R. Shiina, H. Shiba and P. Thalmeier: J. Phys. Soc. Jpn. 66 (1997) 1741.
31) R. Shiina: J. Phys. Soc. Jpn. 73 (2004) 2257.
32) S. Hüfner: Optical Spectra of Transparent Rare Earth Compounds, (Academic Press, New York, 1978).
33) T. Goto, Y. Nemoto, K. Sakai, K. Onuki, T. Yamaguchi, M. Akatsu, T. Yanagisawa, H. Sugawara, and H. Sato: Physica B 359-361 (2005) 822.
34) T. Goto, Y. Nemoto, K. Onuki, K. Sakai, T. Yamaguchi, M. Akatsu, T. Yanagisawa, H. Sugawara, and H. Sato: J. Phys. Soc. Jpn. 74 (2005) 263.
35) S. Nakamura, T. Goto, S. Kunii, K. Iwashita, and A. Tamaki: J. Phys. Soc. Jpn. 63 (1994) 623.
36) Y. Nakanishi: private communications.
37) K. Araki, Y. Nemoto, M. Akatsu, S. Jumonji, T. Goto, H. S. Suzuki, H. Tanida, and S. Takagi: Phys. Rev. B 84 (2011) 045110.
38) K. Kubo and T. Hotta: J. Phys. Soc. Jpn. 75 (2006) 013702.