Microscopic Aspects of Multipole Properties of Filled Skutterudites

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Abstract

We discuss low-temperature multipole states of Nd-based filled skutterudites by analyzing a multiorbital Anderson model with the use of a numerical renormalization group method. In order to determine the multipole state, we take a procedure to maximize the multipole susceptibility matrix. Then, it is found that the dominant multipole state is characterized by the mixture of 4u magnetic and 5u octupole moments. The secondary state is specified by 2u octupole. When we further take into account the coupling between f electrons in degenerate $\Gamma_7$ ($e_u$) orbitals and dynamical Jahn-Teller phonons with $E_g$ symmetry, quadrupole fluctuations become significant at low temperatures in the mixed multipole state with 4u magnetic and 5u octupole moments. Finally, we briefly discuss possible relevance of the present results to actual Nd-based filled skutterudite compounds.

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1. Introduction

Recently, magnetism and superconductivity of rare-earth and actinide compounds have attracted renewed attention in the research field of condensed matter physics [1]. In particular, filled skutterudites, expressed as $\text{RT}_4\text{X}_{12}$ with rare-earth atom R, transition metal atom T, and pnictogen X, provide us a platform for systematic research of magnetism and superconductivity of $f^n$-electron systems with $n \geq 2$ [2,3], where $n$ denotes the number of $f$ electrons.

Since $\text{RT}_4\text{X}_{12}$ crystallizes in the cubic structure with high symmetry of $T_h$ point group [4], orbital degeneracy remains in general. Due to the strong spin-orbit coupling in $f$ electrons, spin-orbital complex degrees of freedom, i.e., multipoles, become active in filled skutterudites. For instance, a second-order phase transition at 6.5K in $\text{PrFe}_4\text{P}_{12}$ [5] has been considered to be due to antiferro quadrupole ordering [6]. Note that a possibility of antiferro hexadecapole order has been also suggested in $\text{PrFe}_4\text{P}_{12}$ [7]. In $\text{NdFe}_4\text{P}_{12}$, a significant role of quadrupole at low temperatures has been suggested from the measurement of elastic constant [8]. A possibility of octupole ordering in $\text{SmRu}_4\text{P}_{12}$ has been also pointed out from the elastic constant measurement [9]. Note that the octupole scenario in $\text{SmRu}_4\text{P}_{12}$ has been supported by muon spin relaxation [10] and $^{31}\text{P}$ NMR experiments [11]. Quite recently, a possibility of antiferro hexadecapole order has been proposed to understand metal-insulator transition of $\text{PrRu}_4\text{P}_{12}$ [12].

Another characteristic issue of filled skutterudites is rattling, i.e., anharmonic vibrations of rare-earth atom around the off-center position inside the pnictogen cage. Effects of rattling on low-temperature $f$-electron states have been recently discussed actively, in particular, with relevance to magnetically robust heavy-fermion phenomenon observed in $\text{SmOs}_4\text{Sb}_{12}$ [13,14]. Concerning the symmetry of vibrations, a possibility of degenerate $E_g$ mode has been suggested in $\text{PrOs}_4\text{Sb}_{12}$ [15]. Since there exists linear coupling between $f$ electrons in degenerate $\Gamma_{67}$ ($e_u$) orbitals and vibration mode with $E_g$ symmetry, the present author has pointed out quasi-Kondo phenomenon due to dynamical Jahn-Teller (JT) phonons [16,17].

In this paper, we focus on the case of $n=3$ as typical example to study low-temperature multipole properties and the effect of JT phonons on the multipole state of filled skutterudites. The multiorbital Anderson model constructed based on a $j$-$j$ coupling scheme is analyzed by a numerical renormalization group method. Note that the multipole state is determined by the maximization of the multipole susceptibility. It is found that the primary multipole state is characterized by the mixture of 4u magnetic and 5u octupole moments, while the secondary state is specified by...
The modified CEF potential is expressed as a sum of potential and Coulomb interaction terms as perturbations. The coupling term as an unperturbed part, while the CEF potential for angular momentum \( \ell \) is given by

\[
H_{\text{loc}} = \sum_{m,m',\sigma} (B_{m,m} \delta_{\sigma \sigma'} + \lambda \zeta_{m,m,m',\sigma'}) f_m^{\dagger} f_{m'}^{\dagger} \delta_{\sigma \sigma'},
\]

where \( B_{m,m} \) is the annihilation operator for \( f \) electrons with spin \( \sigma \) and angular momentum \( m(=\pm 3, \cdots, 3) \), \( \sigma'=\pm 1 \) for up (down) spin, \( B_{m,m'} \) is the crystalline electric field (CEF) potential for angular momentum \( \ell=3 \), \( \delta_{\sigma \sigma'} \) is the Kronecker’s delta, and \( \lambda \) is the spin-orbit coupling. The matrix element \( \zeta_{m,m',\sigma'} \) is given by

\[
\zeta_{m,\pm 1, m, \pm 1} = \pm m/2, \\
\zeta_{m, \mp 1, m, \pm 1} = \sqrt{12 - m(m \pm 1)/2},
\]

and for the zeroth order cases. The Coulomb integral \( I_{m_1,m_2,m_3,m_4} \) is expressed by the combination of four Slater-Condon parameters, \( F^0, F^2, F^4, \) and \( F^6 \) [19]. In this paper, we set \( F^0=10 \), \( F^2=5 \), \( F^4=3 \), and \( F^6=1 \) in the unit of \( eV \). For the \( T_h \) point group, \( B_{m,m} \) is given by three CEF parameters, \( B_{4}^{0}, B_{6}^{0}, \) and \( B_{8}^{0} \) [4,18]. In the traditional formalism [20,21], they are expressed as

\[
B_{4}^{0} = Wx/15, \quad B_{6}^{0} = W(1 - |x|)/180, \quad B_{8}^{0} = W y/24.
\]

where \( x \) and \( y \) specify the CEF scheme for the \( T_h \) point group, while \( W \) determines an energy scale for the CEF potential.

The local Hamiltonian \( H_{\text{loc}} \) can provide us exact information on local \( f \)-electron states, irrespectively of the values of Coulomb interactions and spin-orbit coupling [18]. However, since \( H_{\text{loc}} \) includes seven orbitals, we are immediately faced with difficulties for further study of many-body phenomena in \( f \)-electron systems. Thus, it is natural to consider the effective model which describes well low-energy states of \( H_{\text{loc}} \). For the purpose, we have proposed to exploit a \( j-j \) coupling scheme [22,23]. We set the spin-orbit coupling term as an unperturbed part, while the CEF potential and Coulomb interaction terms as perturbations. Then, we obtain the effective model of \( H_{\text{loc}} \) as [23]

\[
H_{\text{eff}} = \sum_{\mu, \nu} \tilde{B}_{\mu, \nu} f_{\mu}^{\dagger} f_{\nu}^{\dagger} + \sum_{\mu_1, \mu_2, \mu_3, \mu_4} \tilde{I}_{\mu_1, \mu_2, \mu_3, \mu_4} f_{\mu_1}^{\dagger} f_{\mu_2}^{\dagger} f_{\mu_3} f_{\mu_4},
\]

where \( \tilde{B}_{\mu, \nu} \) is the annihilation operator for \( f \) electron with angular momentum \( \mu(=\pm 5/2, \cdots, 5/2) \) in the \( j=5/2 \) sextet. The modified CEF potential is expressed as

\[
\tilde{B}_{\mu, \nu} = \tilde{B}_{\mu, \nu}^{(0)} + \tilde{B}_{\mu, \nu}^{(1)},
\]

where \( \tilde{B}_{\mu, \nu}^{(0)} \) denotes the CEF potential for \( j=5/2 \) and \( \tilde{B}_{\mu, \nu}^{(1)} \) is the correction in the order of \( W^2/\lambda \). The effective interaction in eq. (4) is given by

\[
\tilde{I}_{\mu_1, \mu_2, \mu_3, \mu_4} = \tilde{I}_{\mu_1, \mu_2, \mu_3, \mu_4}^{(0)} + \tilde{I}_{\mu_1, \mu_2, \mu_3, \mu_4}^{(1)},
\]

where \( \tilde{I}_{\mu_1, \mu_2, \mu_3, \mu_4}^{(0)} \) is expressed by three Racah parameters, \( E_0, E_1, \) and \( E_2, \) which are related to the Slater-Condon parameters. Explicit expressions of \( \tilde{I}^{(0)} \) by using \( E_0, E_1, \) and \( E_2 \) are shown in Ref. [22].

On the other hand, \( \tilde{I}^{(1)} \) is the correction term in the order of \( 1/\lambda \). Details on this term have been discussed in Ref. [23]. Here, three comments are in order. (i) Effects of \( B_{6}^0 \) and \( B_{8}^0 \) are included as two-body potentials in \( \tilde{I}^{(1)} \). (ii) The lowest-order energy of \( \tilde{I}^{(1)} \) is \( |W|/J_H \), where \( J_H \) denotes the original Hund’s rule interaction among \( f \) electrons. (iii) The parameter space in which \( H_{\text{eff}} \) works is determined by the conditions for the weak CEF, i.e., \( |W|/J_H \ll 1 \) and \( |W|J_H/\lambda \ll E_2 \). Since \( E_2 \) is the effective Hund’s rule interaction in the \( j-j \) coupling scheme, estimated as \( E_2 \sim J_H/49 \) [22], we obtain \( |W|/\lambda \ll 0.02 \). Thus, it is allowed to use \( H_{\text{eff}} \) even for \( \lambda \) in the order of 0.1 eV [23], when \( |W| \) is set as a realistic value in the order of \( 10^{-4} \) eV for actual \( f \)-electron materials.

Now we consider the hybridization between \( f \) and conduction electrons. From the band-structure calculations, it has been revealed that the main conduction band of filled skutterudites is \( a_u \) with \( xyz \) symmetry [24], which is hybridized with \( f \) electrons in the \( \Gamma_5 \) state with \( a_u \) symmetry. In order to specify the \( f \)-electron state, we introduce “orbital” index which distinguishes three kinds of the Kramers doublets, two \( \Gamma_5^{\pm} \) and one \( \Gamma_5^{-} \). Here “a” and “b” denote the two \( \Gamma_5^{\pm} \)’s and “c” indicates the \( \Gamma_5^{-} \).

Then, the multiorbital Anderson model is given by

\[
H = \sum_{k \sigma} \varepsilon_k c_k^{\dagger} c_{k \sigma} + \sum_{k \sigma} (V c_k^{\dagger} f_{k \sigma} + \text{h.c.}) + H_{\text{eff}} + H_{\text{eph}},
\]

where \( \varepsilon_k \) is the dispersion of \( a_u \) conduction electrons with \( \Gamma_5 \) symmetry, \( f_{k \sigma} \) is the annihilation operator of \( f \) electrons on the impurity site with pseudospin \( \sigma \) and orbital \( \gamma \), \( c_{k \sigma} \) is the annihilation operator for conduction electrons with momentum \( k \) and pseudo-spin \( \sigma \), and \( V \) is the hybridization between conduction and \( f \) electrons with \( a_u \) symmetry. Throughout this paper, we set \( V=0.05 \) eV. Note that the energy unit of \( H \) is half of the bandwidth of the conduction band, which is considered to be in the order of 1 eV, since the bandwidth has been typically estimated as 2.7 eV for \( \text{PrRu}_4\text{P}_{12} \) [25]. Thus, the energy unit of \( H \) is taken as eV. To set the local \( f \)-electron number as \( n=3 \), we adjust the \( f \)-electron chemical potential.

The last term in eq. (7) denotes the electron-phonon coupling. Here, the effect of \( E_g \) rattling is included as relative vibration of surrounding atoms. We remark that localized \( \Gamma_5^{-} \) orbitals with \( a_u \) symmetry have linear coupling with JT phonons with \( E_g \) symmetry, since the symmetric representation of \( e_u \times e_u \) includes \( E_g \). Then, \( H_{\text{eph}} \) is given by
\[ H_{\text{eph}} = g(Q_2 \tau_x + Q_3 \tau_z) + (P_2^2 + P_3^2)/2 \]
\[ + (\omega^2/2)(Q_2^2 + Q_3^2) + b(Q_3^3 - 2Q_2^3Q_3) , \]
(8)
where \( g \) is the electron-phonon coupling constant, \( Q_2 \) and \( Q_3 \) are normal coordinates for \((x^2 - y^2)\)- and \((3z^2 - r^2)\)-type JT phonons, respectively, \( P_2 \) and \( P_3 \) are corresponding canonical momenta, \( \tau_x = \sum \sigma (f_{1\sigma} f_{1\sigma} + f_{3\sigma} f_{3\sigma} \), \( \tau_z = \sum \sigma (f_{1\sigma} f_{1\sigma} - f_{3\sigma} f_{3\sigma} \), \( \omega \) is the frequency of local JT phonons, and \( b \) indicates the cubic anharmonicity. Note that the reduced mass of JT modes is set as unity. Here we introduce non-dimensional electron-phonon coupling constant \( \alpha \) and the anharmonic energy \( \beta \) as \( \alpha = g^2/(2\omega^2) \) and \( \beta = b/(2\omega)^{3/2} \), respectively.

3. Multipole Susceptibility

In order to clarify the magnetic properties at low temperatures, we usually discuss the magnetic susceptibility, but in more general, it is necessary to consider the susceptibility of multipole moments such as dipole, quadrupole, and octupole. The multipole operator is given in the second-quantized form as
\[ X_\gamma = \sum_{\mu, \nu} (X_\gamma)_{\mu\nu} \hat{a}^\dagger \mu \hat{a}^\dagger \nu , \]
where \( X \) denotes the symbol of multipole with the symmetry of \( \Gamma_\gamma \) and \( \gamma \) indicates a set of indices for the irreducible representation. For \( j=5/2 \), we can define multipole operators up to rank 5 in general, but we are primarily interested in multipole properties from the \( \Gamma_5 \) quartet. Thus, we consider multipole moments up to rank 3 in \( \Gamma_0 \) symmetry.

Now we show explicit forms of multipole operators [26,27]. As for dipole moments with \( \Gamma_{4u} \) symmetry, the operators are expressed as
\[ J_{4ux} = J_x, \quad J_{4uy} = J_y, \quad J_{4uz} = J_z, \]
(10)
where \( J_x, J_y, \) and \( J_z \) are three angular momentum operators for \( j=5/2 \), respectively. Concerning multipole moments, they are classified into \( \Gamma_3 \) and \( \Gamma_5 \). We express the \( \Gamma_3 \) quadrupole operators as
\[ O_{3gu} = (2J_y^2 - J_z^2)^1/2, \quad O_{3gv} = \sqrt{3}(J_x^2 - J_y^2)^1/2. \]
(11)
For the \( \Gamma_5 \) quadrupole, we have the three operators
\[ O_{5g\xi} = \sqrt{3}J_yJ_\xi/2, \]
\[ O_{5g\eta} = \sqrt{3}J_xJ_\eta/2, \]
\[ O_{5g\zeta} = \sqrt{3}J_xJ_\zeta/2, \]
(12)
where the bar denotes the operation of taking all possible permutations in terms of cartesian components.

Octupole moments are classified into three types as \( \Gamma_{2u}, \Gamma_{4u}, \) and \( \Gamma_{5u} \). Among them, \( \Gamma_{2u} \) octupole is written as
\[ T_{2u} = \sqrt{15}J_xJ_yJ_z/6. \]
(13)
For the \( \Gamma_{4u} \) octupole, we express the operators as
\[ T_{4ux} = (2J_y^3 - J_zJ_x^2 - J_yJ_z^2)^1/2, \]
\[ T_{4uy} = (2J_y^3 - J_yJ_z^2 - J_y^2J_z)^1/2, \]
\[ T_{4uz} = (2J_z^3 - J_zJ_x^2 - J_zJ_y^2)^1/2, \]
(14)
while \( \Gamma_{5u} \) octupole operators are given by
\[ T_{5ux} = \sqrt{15}(J_xJ_yJ_z)^1/6, \]
\[ T_{5uy} = \sqrt{15}(J_yJ_zJ_x)^1/6, \]
\[ T_{5uz} = \sqrt{15}(J_zJ_xJ_y)^1/6. \]
(15)
Note that we redefine the multipole moments so as to satisfy the orthonormal condition \( \text{Tr}(X_\gamma X_\gamma') = \delta_{\gamma\gamma'} \) [28].

In principle, the multipole susceptibility can be evaluated in the linear response theory [27], but we should note that the multipole moments belonging to the same symmetry can be mixed. In order to determine the coefficient of such a mixed multipole moment, it is necessary to find the optimized multipole state which maximizes the susceptibility. Namely, we define the multipole operator as
\[ M = \sum_\gamma p_\gamma X_\gamma, \]
(16)
where the coefficient \( p_\gamma \) is determined by the eigenstate with the maximum eigenvalue of the susceptibility matrix, given by
\[ \chi_{\gamma\gamma'} = \frac{1}{Z} \sum_{n,m} \frac{e^{-E_n/T} - e^{-E_m/T}}{E_m - E_n} \langle n|X_\gamma|m\rangle \langle m|X_\gamma'|n\rangle. \]
(17)
Here \( E_n \) is the eigenenergy for the \( n \)-th eigenstate \( |n\rangle \), \( T \) is a temperature, and \( Z \) is the partition function given by \( Z = \sum e^{-E_n/T} \).

In order to evaluate \( \chi_{\gamma\gamma'} \) as well as an entropy \( S_{\text{imp}} \) and a specific heat \( C_{\text{imp}} \) of \( f \) electrons, we resort to the numerical renormalization group (NRG) method [29,30], in which momentum space is logarithmically discretized to include efficiently the conduction electrons near the Fermi energy. In actual calculations, we introduce a cut-off \( \Lambda \) for the logarithmic discretization of the conduction band. Due to the limitation of computer resources, we keep \( m \) low-energy states. In this paper, we set \( \Lambda = 5 \) and \( m = 3000 \). Note that the temperature \( T \) is defined as \( T = \Lambda^{-(N-1)/2} \) in the NRG calculation, where \( N \) is the number of the renormalization step. The phonon basis for each JT mode is truncated at a finite number \( N_{\text{ph}} \), which is set as \( N_{\text{ph}} = 20 \) in this paper.

4. Results

First let us discuss the CEF states on the basis of \( H_{\text{eff}} \). In Figs. 1(a) and 1(b), we show the CEF energy levels for \( n=2 \) and 3, respectively. Here we set \( \lambda = 0.1 \) eV, \( W = -6 \times 10^{-4} \) eV, and \( \gamma = 0.3 \). Since the effects of \( B_6^0 \) and \( B_8^0 \) are included in \( H_{\text{eff}} \) as two-body potentials, \( H_{\text{eff}} \) can reproduce well the
CEF energy levels of the local Hamiltonian \( H \) in the realistic intermediate coupling region with \( \lambda/J \) in the order of 0.1. As for details, see Ref. [23].

In order to determine the value of \( x \) for Nd-based filled skutterudites, here we recall that in PrOs\(_4\)Sb\(_{12}\), the ground state is \( \Gamma_1^+ \) singlet and the excited state is \( \Gamma_4^+ \) triplet with small excitation energy as large as 10 K [31,32,33,34,35]. Such a situation is well reproduced by choosing \( x=0.4 \) for \( n=2 \) in Fig. 1(a). Now we change rare-earth ion from Pr\(^{3+}\) to Nd\(^{3+}\). In principle, it is not necessary to modify the CEF parameters even if rare-earth ion is changed, since the CEF potential is given by the sum of electrostatic potentials from ligand anions. Note, however, that the CEF potentials may be changed due to the substitution of T and/or X in RT\(_4\)X\(_{12}\).

When we set \( x=0.4 \) for \( n=3 \) in Fig. 1(b), it is observed that the ground state for \( n=3 \) at \( x=0.4 \) is \( \Gamma_6^\pm \) quartet and the first excited state is \( \Gamma_5^- \) doublet with the excitation energy of 0.02 eV. Experiments for NdOs\(_4\)Sb\(_{12}\) have suggested \( \Gamma_6^\pm \) ground and \( \Gamma_5^- \) excited states with the excitation energy of 220 K [36]. It should be remarked that the theoretical CEF energy levels for \( n=3 \) agree well with experimental results for NdOs\(_4\)Sb\(_{12}\), by using the CEF parameters deduced from the CEF energy levels for PrOs\(_4\)Sb\(_{12}\). We note that in NdFe\(_4\)P\(_{12}\), both the ground and first excited states have been found to be \( \Gamma_6^\pm \) quartet with the excitation energy of 222 K [8]. However, in any case, the ground state quartet is well separated from the first excited state both for NdOs\(_4\)Sb\(_{12}\) and NdFe\(_4\)P\(_{12}\). In such a situation, it is considered that low-temperature multipole properties are not sensitive to the first excited state. Thus, in the following discussion, we fix \( x=0.4 \).

For the purpose to understand the CEF energy levels of NdFe\(_4\)P\(_{12}\), it is necessary to consider first those of PrFe\(_4\)P\(_{12}\). Here we note that the hybridization effect has been considered to play an important role to understand the difference in the CEF energy states among Pr-based filled skutterudites [37,38,39]. In order to determine the CEF energy levels of NdFe\(_4\)P\(_{12}\), it is also important to include the effect of hybridization for the case of \( n=3 \). Such calculations can be done, in principle, by using the effective model \( H_{\text{eff}} \) on the basis of the \( j-j \) coupling scheme. It is one of future problems.

Now we proceed to the NRG results of \( H \). First let us consider the case without the coupling between \( f \) electrons and JT phonons. In Fig. 2(a), we show the multipole susceptibility \( \chi \). The dominant multipole moment in the low-temperature region is the mixture of 4u magnetic and 5u octupole, given by

\[
M_a = p_a J_{4ua} + q_a T_{4ua} + r_a T_{5ua},
\]

where we find that \( p_a=0.989, q_a=-0.0258 \), and \( r_a=-0.146 \) for \( a=x, y, \) and \( z \). The mixture of 4u and 5u moments is characteristic of \( T_h \) symmetry. In fact, when we calculate the multipole susceptibility for \( O_h \) symmetry (\( y=0 \)) using the same parameters except for \( y \), we actually find that \( r_a=0 \). It is one of important features of filled skutterudites with \( T_h \) symmetry that 4u magnetic moment is accompanied with 5u octupole. Note that the magnitude of \( r_a \) depends on parameters. The secondary multipole state is given by 2u octupole. We also find another mixture of 4u magnetic and 5u octupole moments, with reduced magnitude of susceptibility. In Fig. 2(b), we show entropy and specific heat. At low temperatures, there remains an entropy of log 4, originating from localized \( \Gamma_6^- \) quartet, since we consider the hybridization between \( a_u \) conduction band and \( \Gamma_5^- \) state. In actuality, there should exist a finite hybridization between \( a_u \) conduction bands and \( \Gamma_6^- \) states, even if the value is not large compared with that between \( a_u \) conduction and \( \Gamma_5^- \) electrons. Thus, the entropy of log 4 should be eventually released.

Next we include the effect of dynamical JT phonons, but before proceeding to the numerical results, let us consider intuitively what happens. In the \( j-j \) coupling picture, we accommodate three electrons into the one-electron levels with \( \Gamma_5^- \) and \( \Gamma_6^- \). Note that \( \Gamma_5^- \) is lower than \( \Gamma_6^- \), since the ground state of \( n=2 \) is \( \Gamma_1^+ \) singlet, which is mainly composed of doubly occupied \( \Gamma_5^- \). When we accommodate one more electron, it should be put into \( \Gamma_6^- \). Thus, the \( \Gamma_6^- \) quartet ground state is obtained. Intuitively, the 4-fold degeneracy is understood by the combination of spin and orbital degrees of freedom.

Here we consider the JT potential in the adiabatic approximation. Note that in actuality, the potential is not static, but it dynamically changes to follow the electron motion. For \( \beta=0 \), the potential is continuously degenerate along the circle of the bottom of the Mexican-hat potential. Thus, we obtain double degeneracy in the vibronic state concerning the rotational JT modes along clockwise and anti-clockwise directions. When a temperature becomes
The situation in the low-temperature region is well described when the temperature is decreased, such vibrations are also suppressed and the specific rotational JT modes are released, while there still remains spin degree of freedom in the localized Γ4u+5u quartet. In fact, at low temperatures, magnetic susceptibility becomes dominant. Note that χ for Mz is slightly larger than those for Mx and My.

Around at T=10⁻³, we find a peak in the specific heat, since an entropy of log 2 is released. As mentioned above, this is considered to be quasi-Kondo behavior, originating from the suppression of the rotational mode of dynamical JT phonons [16]. In this case, the entropy of log 2 concerning orbital degree of freedom coupled with JT phonons is released, while there still remains spin degree of freedom in the localized Γ4u+5u quartet. In fact, at low temperatures, magnetic susceptibility becomes dominant.

In Figs. 3(d) and 3(e), we show multipole susceptibilities, entropy, and specific heat for ω=0.1, α=0.5, and β=−0.002. For T>10⁻⁴, susceptibilities for both 3g quadrupole moments are significant, suggesting that quadrupole fluctuations are dominant in this temperature region. However, when the temperature is decreased, χ₃gᵥ is suppressed, while χ₃gₓ remains at low temperatures. Instead, the mixed multipole with 4u magnetic and 5u octupole moments becomes dominant.

In Figs. 3(f), we show the temperature dependence of average displacements. For T>10⁻⁴, we find √⟨Q₂²⟩≠0 and √⟨Q₃²⟩≠0, suggesting that both Q₂ and Q₃ modes are active. This is consistent with the finite values of susceptibilities for O₃gₓ and O₃gᵥ. Note that the Q₃-type displacement is considered to occur, since ⟨Q₂⟩=0 and ⟨Q₃⟩≠0. In the low-temperature region, we find √⟨Q₂²⟩=⟨Q₂⟩=0, while √⟨Q₃²⟩=|⟨Q₃⟩|≠0, indicating that only Q₂-type JT vibration is active with finite displacement. This is also consistent with the result that χ₃gₓ remains at low temperatures, since the vibration mode is fixed as Q₃-type after the quasi-Kondo phenomenon occurs.

### 5. Discussion and Summary

In this paper, we have clarified that the magnetic state with active quadrupole fluctuations appears in Nd-based filled skutterudites, when we consider the effect of dynamical JT phonons. In fact, the existence of degenerate quadrupole moments has been suggested from the experiment of elastic constant [8]. In Fig. 3(d), in the temperature region of T>10⁻⁴, we have observed that both O₃gₓ and O₃gᵥ become active, although they are not exactly degenerate due to the effect of JT phonons. However, the effect of the magnetic state with active quadrupole fluctuations seems to be consistent with actual Nd-based filled skutterudites. Note that in the present NRG calculations, we cannot conclude the nature of intersite magnetic interaction, ferromagnetic or antiferromagnetic, although Nd-based filled skutterudites are ferromagnets.

In Nd-based filled skutterudites such as NdFe₄P₁₂ [40] and NdRu₄Sb₁₂ [41], peculiar behavior of a resistance min-
imum in the temperature region higher than a Curie temperature $T_C$ has been pointed out. Quite recently, Np-based filled skutterudite NpFe$_4$P$_{12}$ has been synthesized [42]. Since actinide ion is considered to take a tetavalent state in the filled skutterudite structure, NpFe$_4$P$_{12}$ is also classified into the case of $n=3$, except for the difference between 4f and 5f electrons states. In fact, NpFe$_4$P$_{12}$ is also a ferromagnet with $T_C=23$ K and a similar resistance minimum has been observed above $T_C$ [42].

In the present paper, we have observed the quasi-Kondo behavior for the case of $n=3$. When the temperature is decreased, an entropy log 2 originating from the double degeneracy of the vibronic state is released. In other word, this may be quadrupole Kondo phenomenon, since quadrupole (orbital) degrees of freedom are tightly coupled with JT phonons, as understood from Figs. 3(d) and 3(f). It seems to be premature to conclude the mechanism only from the present numerical results, but the quasi-Kondo behavior due to dynamical JT phonons coupled with orbital (quadrupole) degrees of freedom may explain qualitatively the resistance minimum phenomenon in Nd-based filled skutterudites. Further investigations are required.

As mentioned in the introduction, concerning the mechanism of magnetically robust heavy-fermion phenomena observed in SmOs$_2$Sb$_{12}$ [13], a potential role of phonons has been pointed out from the viewpoint of the Kondo effect with non-magnetic origin [14]. In this context, the quasi-Kondo behavior due to the dynamical JT phonons may be a possible candidate to understand magnetically robust heavy-fermion phenomenon. In fact, we have found the quasi-Kondo behavior also for the case of $n=5$, but the details of the results on Sm-based filled skutterudites will be discussed elsewhere [43]. Here we emphasize the common feature between Nd- and Sm-based filled skutterudites with the same $\Gamma^{67}_{67}$ quartet ground states. From this viewpoint, it may be interesting to design the experiment to detect the effect of rattling in Nd-based filled skutterudites.

In summary, we have discussed the multipole state for $n=3$ by analyzing the multipole Anderson model with the use of the NRG method. When we do not consider the coupling between JT phonons and $f$ electrons in $\Gamma^{67}_{67}$ quartet, we have found that the dominant multipole moment is the mixture of 4u magnetic and 5u octupole. The secondary multipole state is 2u octupole. When the coupling with JT phonons is switched and the cubic anharmonicity is included, the magnetic ground state includes significant quadrupole fluctuations and we have found the quasi-Kondo behavior due to the entropy release concerning the rotational JT mode.

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References

[1] See, for instance, J. Phys. Soc. Jpn. Suppl. 75 (2006).
[2] H. Sato et al.: J. Phys.: Condens. Matter 15 (2002) S2063.
[3] Y. Aoki et al.: J. Phys. Soc. Jpn. 74 (2005) 209.
[4] K. Takegahara, H. Harima and A. Yanase: J. Phys. Soc. Jpn. 70 (2001) 1190; ibid. 70 (2001) 3468; ibid. 71 (2002) 372.
[5] Y. Aoki et al.: Phys. Rev. B 65 (2002) 064446.
[6] K. Iwasa et al.: Physica B 312-313 (2002) 834.
[7] Y. Nakanishi et al.: preprint.
[8] Y. Nakanishi et al.: Phys. Rev. B 69 (2004) 064409.
[9] M. Yoshizawa et al.: J. Phys. Soc. Jpn. 74 (2005) 2141.
[10] K. Hachitani et al.: Phys. Rev. B 73 (2006) 052408.
[11] S. Masaki et al.: J. Phys. Soc. Jpn. 75 (2006) 053708.
[12] T. Takimoto: J. Phys. Soc. Jpn. 75 (2006) 034714.
[13] S. Sanada et al.: J. Phys. Soc. Jpn. 74 (2005) 246.
[14] S. Yotsuhashi et al.: J. Phys. Soc. Jpn. 74 (2005) 49.
[15] T. Goto et al.: Phys. Rev. B 69 (2004) 180511(R).
[16] T. Hotta: Phys. Rev. Lett. 95 (2006) 197201.
[17] T. Hotta: Physica B 378-380 (2006) 51.
[18] T. Hotta: J. Phys. Soc. Jpn. 74 (2005) 1275.
[19] T. Hotta: Rep. Prog. Phys. 69 (2006) 2061.
[20] K. R. Lea, M. J. M. Leask and W. P. Wolf: J. Phys. Chem. Solids 23 (1962) 1381.
[21] M. T. Hutchings: Solid State Phys. 16 (1964) 227.
[22] T. Hotta and K. Ueda: Phys. Rev. B 67 (2003) 104518.
[23] T. Hotta and H. Harima: J. Phys. Soc. Jpn. 75 (2006) No. 12, in press. See also cond-mat/0602646.
[24] H. Harima and K. Takegahara: J. Phys.: Condens. Matter 15 (2003) S2081.
[25] H. Harima et al.: J. Phys. Soc. Jpn. Suppl. 71 (2002) 70.
[26] R. Shiina, H. Shiba and P. Thalmeier: J. Phys. Soc. Jpn. 66 (1997) 1741.
[27] T. Hotta: J. Phys. Soc. Jpn. 74 (2005) 2425.
[28] K. Kubo and T. Hotta: J. Phys. Soc. Jpn. 75 (2006) 013702.
[29] K. G. Wilson: Rev. Mod. Phys. 47 (1975) 773.
[30] H. R. Krishna-murthy, J. W. Wilkins and K. G. Wilson: Phys. Rev. B 21 (1980) 1003.
[31] Y. Aoki et al.: J. Phys. Soc. Jpn. 71 (2002) 2098.
[32] M. Kohgi et al.: J. Phys. Soc. Jpn. 72 (2003) 1002.
[33] T. Tayama et al.: J. Phys. Soc. Jpn. 72 (2003) 1516.
[34] K. Kuwahara et al.: J. Phys. Soc. Jpn. 73 (2004) 1438.
[35] E. A. Goremychkin et al.: Phys. Rev. Lett. 93 (2004) 157003.
[36] P.-C. Ho et al.: Phys. Rev. B 73 (2005) 094410.
[37] J. Otsuki, H. Kusunose and Y. Kuramoto: J. Phys. Soc. Jpn. 74 (2005) 200.
[38] Y. Kuramoto et al.: Prog. Theor. Phys. Suppl. 160 (2005) 134.
[39] Y. Kuramoto et al.: J. Phys. Soc. Jpn. Suppl. 75 (2006) 209.
[40] H. Sato et al.: Phys. Rev. B 62 (2000) 15125.
[41] K. Abe et al.: J. Phys.: Condens. Matter 14 (2002) 11757.
[42] Y. Aoki et al.: J. Phys. Soc. Jpn. 75 (2006) 073703.
[43] T. Hotta: preprint.