Hybridization and multipole orders of 4f electrons in Pr skutterudites

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Characteristics of hybridization and multipole orders of 4f-electrons in Pr skutterudites are explained in terms of a pseudo-quartet composed of crystalline electric field (CEF) singlet and the triplet. It is shown that the contrasting behaviors observed in PrFe₄P₁₂ and PrOs₄Sb₁₂ are ascribed to the difference in triplet wave functions and the CEF splittings. Since a macroscopic degeneracy remains even in the ordered phase with the Γ₃-type antiferro-quadrupole (AQF) order, a model with strong AQF fluctuation and static monopole/hexadecapole order is proposed for PrFe₄P₁₂. The remaining cubic symmetry explains qualitatively the behavior of staggered magnetization observed by NMR and neutron scattering. For identification of possible hexadecapole orders in PrFe₄P₁₂ and PrRu₄P₁₂, eightfold intensity pattern is predicted in the azimuthal angle scan of resonant X-ray scattering. In PrOs₄Sb₁₂, the ferromagnetic exchange coupling with the conduction band does not lead to magnetic Kondo effect, but a momentum-dependent quadrupole coupling can give rise to enhanced effective mass, which should be sensitive to disorder.

KEYWORDS: quadrupole order, quantum fluctuation, resonant X-ray scattering, skutterudite

1. Introduction

There are puzzling properties in filled Pr skutterudite compounds. In this paper we concern with mechanism of the following behaviors: PrFe₄P₁₂ undergoes a phase transition at 7 K in zero field.¹ The susceptibility shows a cusp at the transition, but there is no Néel order in the ordered phase. Then an antiferro-quadrupole (AQF) order has been considered as a plausible explanation.² Indeed a staggered magnetic moment and the lattice distortion have been found by neutron diffraction.³ However, in contrast with the case of PrOs₄Sb₁₂,⁴ there is no component perpendicular to the field of the staggered moment.⁵ If the order parameter is AFQ, one may naturally expect finite perpendicular component in some directions of the field. Thus proper identification of the order parameter remains to be done. On the other hand, PrOs₄Sb₁₂ has well-defined CEF excitations as seen by neutron scattering,⁶,⁷ and by the Schottky-type anomaly in the specific heat.⁷,⁸ Near the Schottky peak around 2 K, superconductivity sets in with a huge discontinuity in the specific heat. The problem here is the origin of the Cooper pair. More modestly, one may ask the mechanism which produces heavy electrons forming the Cooper pair. These two Pr skutterudites also show contrasting behaviors in the temperature dependence of the resistivity: PrFe₄P₁₂ shows a typical Kondo effect, while PrOs₄Sb₁₂ only a mild shoulder in the temperature dependence.⁹ The inelastic neutron spectrum of PrFe₄P₁₂ is characterized by broad quasi-elastic features like other heavy-fermion systems, without well defined CEF excitations.¹⁰,¹¹

In this paper we propose a possible route toward understanding these fundamental issues. We begin with brief review of our previous results which explain the contrasting behaviors in terms of the character of CEF states. Then we proceed to rather speculative new ideas. These include proposal of a novel multipole order in PrFe₄P₁₂ in which fluctuating quadrupoles are not frozen even in the ordered phase. The frozen multipole is a hexadecapole which should be probed by resonant X-ray scattering. In addition, for PrOs₄Sb₁₂, we propose that the induced quadrupolar fluctuation with moment dependent coupling with conduction band is responsible for the heavy mass.

2. Local electronic states and hybridization effects

2.1 CEF splitting by p-f hybridization

Filled skutterudites RT₄X₁₂ form a bcc structure with the space group Im₃. The R site has the local symmetry Γ₄, which has no four-fold rotation axis.¹¹ In this symmetry, the 4f² Hund’s-rule ground states H₄ of Pr³⁺ split into a singlet Γ₁, a non-magnetic doublet Γ₂₃, and two Γ₄ triplets. Of these, two Γ₄ triplets are written as Γ₄ and Γ₄, which are linear combinations of triplets Γ₄ and Γ₄ in O₆. Under this crystal symmetry, the CEF potential is written as

\[ V_{CEF} = A_4 \left( O_6^4 + 5O_4^1 + A_6^6 \left( O_6^6 - 21O_6^1 \right) + A_6^8 \left( O_6^8 - O_6^8 \right) \right) = W \left[ \frac{O_6^4}{60} \left( 1 - \frac{1}{3} \right) \right] + \frac{O_6^6}{1260} + \frac{O_6^8}{30}, \]

in the standard notation.¹¹ The term γ₀₄ mixes the Γ₄ and Γ₄ triplet states in the point group O₆.

There are two main sources for the CEF splitting: the Coulomb potential from ligands, and hybridization between 4f electrons and ligands. In the point charge model, CEF coefficients A₄, A₆ sixty and A₆ eighty in eq.(1) are determined by coordination of the charge and the radial extension of the 4f wave function. Explicit results have been obtained in ref.14 taking the effective charge Z₁ of a transition ion as the parameter and requiring the charge neutrality with trivalent Pr. To estimate the CEF potential, we use the lattice parameter in PrOs₄Sb₁₂, which gives the Pr-T distance d₁ = 4.03Å with T=Sb, the Pr-X distance dₓ = 3.48Å with X=Os and the X-Pr-X vertical angle θₓ = 49.2°. These data will be used to derive the results presented in Fig.1.

Another important mechanism for CEF splittings is the covalency effect, or hybridization between localized and ligand orbitals. According to band calculation,¹³ the conduction band striding the Fermi level is formed mostly by the molecular orbital α₆ formed by 12 pnictogens around each Pr. The other relevant molecular orbital τₓ form two energy bands around a few eV above the Fermi level, and three a few eV
below. We neglect contributions from $t_d$ bands to CEF splittings because of the larger excitation energy. Therefore we first consider hybridization of the form

$$H_{\text{hyb}} = V_a \sum_\sigma f_\sigma^\dagger c_\sigma + \text{h.c.}, \quad (2)$$

where $c_\sigma$ annihilates a conduction electron in the Wannier orbital with the $a_d$ symmetry at the origin, and $f_\sigma^\dagger$ creates an $4f$ electron with the same ($a_d$) orbital symmetry. We take the hybridization parameter $V_a$ real. Hereafter we adopt the Mulliken notation such as $a_d$ for orbital symmetry, and the Bethe notation such as $\Gamma_1$ for a double-group representation with spin-orbit coupling. In the second-order perturbation theory, the effective interaction is given by

$$H_{\text{eff}} = PH_{\text{hyb}} \frac{1}{E-H_0} QH_{\text{hyb}}P, \quad (3)$$

where $P$ is the projection operator onto $4f^2$ states, and $Q = 1 - P$. We first deal with such part of the second-order hybridization that is diagonal with respect to the conduction states. Diagonalization of $H_{\text{eff}}$ with this constraint gives the CEF wave functions and their energies. We assume the following intermediate states: (i) $4f^1$ and an extra electron in vacant states, and (ii) $4f^3$ and an extra hole in filled states. For simplicity, we neglect the multiplet splittings in both kinds of intermediate states. We note that $4f^1$ and $4f^3$ intermediate states give opposite contributions to the level splitting. Hence the sequence of CEF levels is determined by competition between both intermediate states. The hybridization is parameterized by the Slater-Koster parameters $(pff\pi)$ and $(pff\pi)$. It turns out hybridization with $a_d$ comes only from $(pff\pi)$.

We combine both contributions to CEF splittings by point-charge interaction and by hybridization. To a good approximation we can assume the half-filled $a_d$ band. We introduce a parameter

$$1/\Delta_1 = 1/\Delta_2 - 1/\Delta_3.$$  

Note that $1/\Delta_2 = 0$ in the case of $\Delta_3 = \Delta_1$, and $1/\Delta_3$ becomes negative if $4f^1$ is the dominant intermediate state. For the point charge parameters we tentatively take $Z_i = 2$. Figure 1 shows computed results as a function of strength of hybridization, $(pff\pi)^2/\Delta_1$. It should be emphasized that the the closely lying singlet and triplet are realized only with simultaneous crossing of three levels near $(a)$ should be taken with caution. In other words, only the Coulomb potential is the source of the $y$ parameter in our result. From the study of phase diagram in magnetic field,\textsuperscript{15} it seems that the level $\Gamma_3$ is situated higher in this region. As a result, if high pressure drives the system toward further left in the Fig.1, it is likely that the triplet becomes the ground state instead of the doublet.

It is reasonable that the larger cage in PrOs$_4$Sb$_{12}$ favors the $4f^1$ excited states rather than the $4f^3$ states, the parameter $\Delta_1$ can become smaller, leading to negative $\Delta_1$. Since the hybridization with $a_d$ orbitals alone cannot take into account the parameter $y$ in eq.(1), the simultaneous crossing of three levels near $(a)$ should be taken with caution. In other words, only the Coulomb potential is the source of the $y$ parameter in our result. From the study of phase diagram in magnetic field,\textsuperscript{15} it seems that the level $\Gamma_3$ is situated higher in this region. As a result, if high pressure drives the system toward further left in the Fig.1, it is likely that the triplet becomes the ground state instead of the doublet.

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2.2 Exchange interactions with conduction electrons

We are interested in the matrix element between the singlet and the triplet in the $T_b$ group. As we have seen the triplet is a linear combination of $\Gamma_4$ and $\Gamma_5$ in the $O_h$ group. Hence it is convenient to analyze the symmetry properties of triplets in the cubic case. The direct products of pseudo-quartets can be decomposed as

$$(\Gamma_1 \oplus \Gamma_4) \otimes (\Gamma_1 \oplus \Gamma_4) = \Gamma_1 + 2\Gamma_4 + (\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5), \quad (5)$$

$$(\Gamma_1 \oplus \Gamma_5) \otimes (\Gamma_1 \oplus \Gamma_5) = \Gamma_1 + 2\Gamma_5 + (\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5), \quad (6)$$

where $\Gamma_4$ has the same symmetry as the magnetic moment. The product of $\Gamma_1 \oplus \Gamma_4$ produces newly two $\Gamma_4$ representations, of which one is time-reversal odd and the other is even. The odd representation represents the magnetic moment, while the

![Fig. 1. CEF level structures derived from hybridization and point charge potential as a function of $(pff\pi)^2/\Delta_1$.](image-url)
even one the hexadecapole moment. On the other hand, the pseudo-quartet $\Gamma_1 \oplus \Gamma_3$ does not produce a new $\Gamma_4$ representation. Physically, this means that $\Gamma_4$ as the first excited states gives rise to a van Vleck term in the magnetic susceptibility, while $\Gamma_3$ does not.

It is convenient to introduce the effective moment operators in the pseudo-quartet in $T_a$. In the case of $w = 0$ (pure $\Gamma_3$ triplet), the magnetic moment within $\Gamma_1$ is the only relevant quantity. The vector operator in this case is written as $X^v$. On the other hand, another vector operator $X^o$ is necessary to describe the magnetic moment of van Vleck type. The operator $X^v$ act on the triplet states, and $X^o$ connect the singlet and the triplet. The effective interaction within the pseudo-quartet is given by

$$H_{\text{exc}} = (l_s X^v + l_s X^o) \cdot \frac{1}{2} \sum_{\alpha \beta} c^\dagger_\alpha \vec{s} \sigma_{\alpha \beta} c_\beta.$$

where the conduction electron spin $s_c$ is explicitly written in terms of fermion operators. The coupling constants are proportional to $V^2_d$ and negative. The origin of the ferromagnetic exchange is traced to the Hund rule involving the spin-orbit interaction; the dominant orbital moment is pointing oppositely from the spin moment. In other words, the spin exchange is antiferromagnetic as is usual for a hybridization induced exchange.

Alternatively, one can use the pseudo-spin representation as in ref.19:

$$X^v = S_1 + S_2, \quad X^o = S_1 - S_2,$$

where $S_1$ and $S_2$ are spin 1/2 operators. The pseudo-spin representation naturally leads to commutation rules among $X^v$ and $X^o$. The exchange interaction in terms of pseudo-spins is given by

$$H_{\text{exc}} = (J_1 S_1 + J_2 S_2) \cdot s_c,$$

where $J_1 = I_1 + I_4$ and $J_2 = I_1 - I_4$. It turns out that $J_2$ becomes positive for as $w$ deviates from 0. The emergence of antiferromagnetic exchange is due to the particular CEF level structure in Pr skutterudites. $J_2$ is almost negligible in the pure $\Gamma_5$ case ($w = 0$), and becomes an order of magnitude larger as $w$ increases toward unity, i.e., toward pure $\Gamma_4$. It is likely that the Kondo-type behavior seen in PrFe$_4$P$_{12}$ originates from a $\Gamma_4$-type triplet together with a small singlet-triplet splitting. Numerical results have been reported for dynamical properties of the pseudo-quartet with use of the NCA.

2.3 Quadrupole interactions with conduction electrons

Although the conduction band is of $a_u$ type, it can acquire the coupling with quadrupole moments through mixing with $t_u$-type calcogen bands. We start with the most general form of p-f hybridization as given by

$$H_{\text{hyb}} = \sum_{\Gamma \alpha \beta} \sum_{\nu \sigma} \left[ V_{t_u(\alpha \beta)} f_{\Gamma(\alpha \nu \sigma)} f_{\nu \sigma} + \text{H.c.} \right],$$

where the indices $\alpha, \beta$ distinguish different sets with the same irreducible representation $\Gamma$. A member in the irreducible representation is specified by $\nu$, and $\sigma$ denotes a spin component. Let us consider nine Pr sites making up a body-centered cube each of which is surrounded by 12 pnicogen. A 4f orbital state $3z^2 - r$ for example, in the body centered Pr at $R = (000)$ has hybridization with surrounding pnicogen orbitals $\Gamma = t_{ux}, \nu = z$, for which five different sets have been enumerated. Each $t_u$ molecular orbital mixes with the eight $a_u$ orbitals surrounding Pr corner atoms at $R = (\pm 1, \pm 1, 0)$. Summation over eight sites gives the form factor as

$$F_{\nu}(k) = \frac{\sqrt{3}}{2} \cos k_x \cos k_y \sin k_z,$$

where $k$ is the wave number of the conduction electron. Other components $F_{\nu}(k)$ with $\nu = x, y$ are obtained from the case of $\nu = z$ by cyclic rotation of $k_x, k_y, k_z$. Let us introduce a set $\nu = x, y, z$ of new Wannier orbitals each of which is created by the operator

$$\psi_{\nu \sigma} = \frac{1}{\sqrt{N}} \sum_k F_{\nu}(k) c^\dagger_\nu(k).$$

Then the effective hybridization through $t_u$ orbitals is given by

$$H_t = \frac{1}{\sqrt{N}} \sum_{\nu \sigma} \sum_{\nu \sigma} \left[ V_{t_u(\nu \sigma)} \psi_{\nu \sigma} f_{\nu \sigma} + \text{H.c.} \right],$$

where $\beta$ distinguishes two different sets with the $t_u$ symmetry in 4f orbitals such as $3z^2 - r^2$ and $r^2 - r_y^2$. The effective hybridization parameter $V_{t_u}$ is determined by $V_{t_u(a)}$, the intersite mixing between $t_u(a)$ and $a_u$, and their energy separation.

Following the same line as derivation of the effective magnetic exchange, the second order effects of eq.(12) gives quadrupole coupling. To describe the coupling we introduce the operator $O^y_{\mu \nu}$ where ($\gamma = 1 \rightarrow 5$) represents the quadrupole from the CEF singlet-triplet transition, while ($\gamma = 5 \rightarrow 1$) comes from the intra-triplet transition. We shall argue later that the latter quadrupole operator is a key to understand the strange heavy-fermion behavior found in PrOs$_4$Sb$_{12}$. The effective quadrupole coupling between 4f and conduction electrons is given by

$$H_{\text{quad}} = \sum_{\gamma} \sum_{\mu \nu} \sum_{\nu \sigma} O^y_{\mu \nu} \sum_{\sigma} \psi_{\nu \sigma} \psi_{\nu \sigma}.$$

We shall evaluate these two coupling constants $l^y_{\text{quad}}$ quantitatively in separate work.

3. Fluctuating quadrupoles

3.1 Triplet pair with AFQ interaction

An AFQ order of the $\Gamma_4$-type involving a CEF triplet involves a subtle problem concerning the degeneracy in the ordered phase. The normalization of relevant operators is defined by

$$O^y_0 = 3^{-1/2}[3J_z^2 - J(J + 1)], \quad O^y_2 = J^y_z - J^z_y.$$  

In the case of $\Gamma_4$ triplet, nonzero matrix elements are given by $\langle 0|O^y_0|0\rangle = 28/\sqrt{3}, \langle 0|O^y_2|0\rangle = -14/\sqrt{3}$, and $\langle 0|O^y_2|\pm\rangle = -14$. For identifying the degeneracy problem, which is intimately related to the ordering pattern in PrFe$_4$P$_{12}$, we take a two-site system where the triplet $\Gamma_4$ is present at each site A or B. The interaction Hamiltonian is given by

$$H_{t \Gamma_3} = g_3 (O^y_{2A} O^y_{2B} + O^y_{2A} O^y_{2B}).$$

We recombine three states in the triplet as

$$|z\rangle = |0\rangle, \quad |x\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |−\rangle), \quad |y\rangle = \frac{1}{\sqrt{2}}(|+\rangle − |−\rangle).$$
Then we take the nine-fold basis $|k\rangle_A |l\rangle_B$ for the two sites, where $k, l$ are $x, y$ or $z$. By diagonalization of $H_{13}$ we find that the nine-fold degeneracy splits into six-fold and three-fold degenerate states. With antiferro-type interaction $g_3 > 0$, the ground state is the six-fold multiplet with energy $-196 g_3 / \sqrt{3}$, and the three-fold degenerate excited level has energy $784 g_3 / 3$. The six-fold degeneracy comes from the number of ways to choose different orbitals for $|k\rangle_A |l\rangle_B$ with $k \neq l$. Because of the absence of off-diagonal elements in the two-site Hamiltonian, the mean-field theory at zero temperature becomes exact for the two-site system. The bcc lattice can be separated into A and B sublattices. Then with only the $\Gamma_3$-type intersite interaction, the degenerate ground state of the bcc lattice should be given exactly by the mean-field theory.

Thus a model with nearest-neighbor AFQ interaction of $\Gamma_3$ quadrupoles has a degeneracy with respect to different kinds of quadrupolar patterns. In this sense, the $\Gamma_3$ antiferro-quadrupolar ordering model within the triplet state is similar to the three-state antiferromagnetic Potts model, which possesses a macroscopic degeneracy in the ground state.

3.2 Interaction with conduction spins

We now ask how the degeneracy should be broken in actual PrFe$_2$P$_2$. Experimentally, distortion of Fe sublattice has been observed by X-ray and neutron diffraction. Although the distortion is suggested to be of $O_2^-$-type for each Fe cube, the distortion effects themselves do not exclude a possibility that the actual distortion is of a breathing type as found in PrRu$_2$P$_2$. We consider a situation where conduction electrons cause quantum fluctuations among degenerate AFQ configurations. If the macroscopic degeneracy is removed by this fluctuation mechanism, the cubic symmetry is kept on the average, but a strong two-site AFQ correlation dominates the ground state. In order to pursue the idea qualitatively, we consider a toy model in which a conduction-electron spin is introduced at each site, and each spin has exchange coupling with a triplet. Namely the local interaction $H_{\text{exc}}^{(A)}$ for site A, and $H_{\text{exc}}^{(B)}$ for site B. Let us consider the system

$$H_{\Gamma_3 + \text{exc}} = H_{\Gamma_3} + H_{\text{exc}}^{(A)} + H_{\text{exc}}^{(B)},$$

where we neglect the $\Gamma_1$ singlet for simplicity. According to microscopic theoretical result, we take $I_c < 0$. In the limit $g_3 = 0$, we obtain the quartet ground state and the doublet excited state for each site with separation $3|I_c|/2$. Thus the whole system is 16-fold degenerate in the ground state. The AFQ interaction $g_3$ breaks the degeneracy. In the case of large $g_3 / |I_c|$, on the other hand, the lower manifold of $6 \times 4 = 24$ states has the following level sequence from the ground state: (i) quartet, (ii) octet, (iii) octet, (iv) quartet. The degeneracy of (i) comes from the spin degrees of freedom. Since there is no magnetic interaction between the pair, the Kramers degeneracy at each site cannot be broken. Figure 2 shows the energy levels as a function of $g_3 / |I_c|$ taking the triplet as $\Gamma_4$. The asymptotes for $|g_3 / I_c| \gg 1$ are characterized by the ferromagnetic state with the slope $784/3$ as obtained earlier, and the antiferro-ferromagnetic state with the slope $-196 / \sqrt{3}$. The ratio of the slopes is $-4 / \sqrt{3} \sim -2.3$.

Now we include an intersite magnetic interaction of the form

$$H_{\text{c}2} = J_c \sum_{\langle s \rangle} \langle s \rangle^A \cdot \langle s \rangle^B.$$
3.3 Staggered moments induced by magnetic field

The dominance of quadrupolar moments in the ordered phase in PrFe$_4$P$_{12}$ is indicated by the results of polarized neutron scattering where the induced AFM moments is about 2 times larger for the field direction (001) than for (110). However, there is no component of staggered magnetization perpendicular to the magnetic field. If there is a static quadrupole order, one may naturally expect some anisotropy leading to the perpendicular component. The absence is not due to cancellation by the mixture of quadrupole domains, since NMR has observed a sharp induced staggered field.

If we assume the fluctuating state with no static AFQ order as described by the pair, there is no perpendicular component in the staggered magnetization. In our scenario of fluctuation by the pair, there is no perpendicular component. The absence is not due to cancellation by the mixture of quadrupole domains, since NMR has observed a sharp induced staggered field.

3.4 Uniaxial pressure effect

The quadrupole fluctuation is much affected by uniaxial stress, which serves as valuable probe to identify the nature of electronic states. According to ref. 23, the susceptibility is much enhanced by uniaxial pressure along the magnetic field, while it is insensitive perpendicular to the field. The large anisotropy is common to both ordered and disordered phases. In order to understand the origin of such anisotropy, we have checked how the single-site triplet is affected by uniaxial stress. Provided the uniaxial stress along the $z$-axis favors oblate charge distribution of $4f$ states, the CEF triplet constitutes a scalar in the cubic point group $T_h$ as given by $O_4, O'_6$ and $O''_6$ in eq.(1). Similar multipoles have been postulated as order parameters in PrFe$_4$P$_{12}$. An important difference, however, is the large Néel-like anomaly in the magnetic susceptibility in PrFe$_4$P$_{12}$, and its absence in PrRu$_4$P$_{12}$. We suspect the AFQ interaction is insignificant in PrRu$_4$P$_{12}$.

4. X-ray detection of hexadecapole order

We discuss how to probe possible hexadecapole order transition in PrFe$_4$P$_{12}$ and PrRu$_4$P$_{12}$. The most direct observation should be azimuthal angle scan in resonant X-ray scattering. In the quadrupole scattering process called E2, the staggered order of hexadecapoles contributes to the superlattice scattering. On the other hand, the hexacontatetrapole cannot be probed by the E2 scattering because of its higher rank ($6$). The combination $O''_4 + 5O'_4$ constitutes a scalar in the cubic symmetry, which has a staggered component in the hexadecapole order. We have shown that the amplitude should depend on the azimuthal angle $\psi$ as $\cos 4\psi$ in the $\sigma$-$\sigma'$ channel, and as $\sin 4\psi$ in the $\sigma$-$\pi'$ channel. In the $\sigma$-$\pi'$ channel, the polarization of the light is rotated by $90^\circ$ from the incident beam. These rapid oscillations of the amplitude are not shared by amplitude for other multipoles. In particular, there is no contribution from $O''_4$ in the $\sigma$-$\pi'$ channel. The resulting intensity has the eight-fold pattern ($\propto 1 - \cos 8\psi$) with a minimum at $\psi = 0$. The $\sigma$-$\sigma'$ channel will show a four-fold pattern by combination with $O''_4$. The intensity pattern is illustrated in Fig. 5. In this way resonant X-ray scattering using the E2 transition can identify the hexadecapole order. On the other hand, the non-resonant scattering also has contribution from hexadecapoles with angular momentum $L = 4$, which can be identified by the form factor analysis. Although the monopole contribution should dominate the intensity, one may hope to identify the contribution from $L = 4$ since the quadrupole component $L = 2$ is absent. Identification of the $L = 4$ component provides alternative detection of the hexadecapole order.

![Fig. 4](image1.png) Magnetic susceptibility of an isolated pseudo-quartet under uniaxial pressure $\sigma = 3$ kbar. The parameters are taken as $g_3 = 0.3K$ and $\Delta = 3K$. The middle line shows the susceptibility without uniaxial stress. The unit of $\chi$ is $(g_3\mu_B)^2/T_0$ with $g_J = 4/5$ and $T_0 = 1 K$.

![Fig. 5](image2.png) Predicted azimuthal angle dependence from the hexadecapole order in PrRu$_4$P$_{12}$ and PrFe$_4$P$_{12}$. Assumed are the (001) surface and the $\sigma$-$\pi'$ scattering.
Possible origin of heavy mass in PrOs$_4$Sb$_{12}$

The specific heat of PrOs$_4$Sb$_{12}$ has a conspicuous anomaly of the Schottky type, which has been ascribed to the singlet-triplet CEF splitting. The superconducting transition occurs near the peak of this anomaly with a large jump (~ 1 J/mol·K), which indicates a huge mass of the Cooper pair. If the superconductivity is destroyed by magnetic field, however, the heavy itinerant electrons seem to disappear at lower temperatures. Namely, the specific heat does not have the $\gamma T$ term with large $\gamma$. Figure 6 compares the specific heat of the singlet-triplet CEF model in magnetic field with experimental results. The field of $H = 2T$ already masks the structure from the superconducting transition. It is seen that the discrepancy from the CEF model becomes larger for $T > 1.5K$, and the discrepancy above 4 K grows linearly with $T$, which gives the proportionality constant $\gamma \sim 0.9J/(\text{mol·K}^2)$. In the low temperature end, on the other hand, the Schottky model gives reasonable account of the observed result. We therefore conclude that a fraction of the entropy above ~1K is transferred to the temperature range higher than the maximum of $C(T)$. On the basis of observation above, we speculate that a quadrupole Kondo effect is active in this system where intra-triplet quadrupole excitations scatter conduction electrons. The mass enhancement from the intra-triplet excitation channel should naturally decrease if the thermal population of the triplet becomes small. On the other hand, the singlet-triplet quadrupole channel should saturate below the temperature corresponding to the CEF splitting. The lowest order effect of this latter channel has been discussed by Fulde and Jensen. Since the $\gamma T$ term disappears at low temperature in Fig.6, it seems that the intra-triplet channel is the dominant source of the heavy-fermion behavior. Microscopic study of $I_{\text{quad}}^{(3)}$ in eq.(13) will shed further light on the validity of this hypothesis.

In contrast with the ordinary Kondo-type mechanism, the quadrupole scattering of conduction electrons with the $a_{2u}$ symmetry requires a coherence of Pr atoms of the order of 10 as shown by eq.(11). Hence it should be more sensitive to disorder such as La doping than the ordinary Kondo effect. It should be a difficult but interesting problem how the heavy Cooper pairs survive or disappear in PrOs$_4$Sb$_{12}$ at very low temperature where thermal population of the triplet becomes negligible.

Summary and Outlook

In this paper we have proposed some ideas for understanding the intriguing properties of Pr skutterudites. The key to the understanding is the nature of the triplet CEF states and the singlet-triplet splitting which vary among PrFe$_4$P$_{12}$, PrRu$_4$P$_{12}$ and PrOs$_4$Sb$_{12}$. The difference of CEF states explains the presence of the strong Kondo effect in PrFe$_4$P$_{12}$, and the sharp CEF excitations observed in PrRu$_4$P$_{12}$ and PrOs$_4$Sb$_{12}$. Recently Sm skutterudites have also been actively investigated. In particular, SmOs$_4$Sb$_{12}$ has a large $\gamma T$ term in the specific heat, which is insensitive to magnetic field. We suspect that quadrupolar Kondo effect may be the origin of the heavy mass. In contrast with the case of PrOs$_4$Sb$_{12}$, the quadrupole active states are in the ground CEF level. These ideas can be corroborated only by microscopic calculation based on a realistic model. We plan to test the above ideas in the near future.

The authors thank O. Sakai, K. Iwasa and M. Kohgi for informative discussion. This work was supported partly by Grants-in-Aid for Scientific Research on Priority Area “Skutterudite”, and for Scientific Research (B)15340105 of the Ministry of Education, Culture, Sports, Science and Technology, Japan.