Temperature evolution of crystal field splitting in Pr-filled skutterudite

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Abstract. Crystal field states of Pr ⁴f electrons of PrOs⁴P₁₂ and PrRu⁴Sb₁₂ were investigated by inelastic neutron scattering. Different spectral widths between two excitations from the ground state singlet to the triplets and their temperature evolutions are well reproduced by the theory based on the exchange coupling between ⁴f and conduction electrons (Becker K W et al. 1977 Z. Physik B 28 9). Shift of level energies by around 1 meV below 60 K were also observed. The results support the p-f hybridization effect in Pr-filled skutterudites.

1. Introduction
Electron hybridization between f and conduction electrons plays a key role in heavy fermion and valence fluctuation etc., and is seen as broad magnetic excitation spectra instead of well-defined crystal-field (CF) excitations of localized f states [1]. Recently, multipolar ordering phenomena in rare-earth filled skutterudite RT₄X₁₂ (R = lanthanide and actinide elements, T = transition metal, and X = pnictogen), crystallizing in the body centered cubic structure (space group Im3 (T₅h)) [2], are found to be given by p-f hybridization between f of R and p of X [3, 4, 5]. PrRu₄P₁₂ is a typical system undergoing a metal-nonmetal transition at $T_{M-I} = 63$ K [6]. The transition is driven by antiferro-type higher-rank multipolar ordering, which is characterized by the two inequivalent Pr-ion CF schemes align in staggered way below $T_{M-I}$ [8]. The CF level splitting and the spectral widths strongly depend on temperature [7]. Because of the Fermi-surface nesting condition [9], this phase transition is interpreted to be a charge-density-wave (CDW) formation with the alternative arrangement of ⁴f electron multipoles [10].

The isostructural material PrOs₄P₁₂ does not undergo any phase transition down to 0.1 K [11], because of no apparent nesting condition of the Fermi surface [12, 13]. The temperature variation of specific heat was not in accordance with the well localized ⁴f state, indicating a hybridization effect as mentioned by Matsuhira et al. [14] We carried out inelastic neutron scattering measurement of PrOs₄P₁₂ in order to identify the hybridization effect, that is not hidden by any phase transition. Details of the study are seen in the preceding article [15]. In addition, we will present results of PrRu₄Sb₁₂ in the normal metallic phase [16], in order to confirm the hybridization effect.

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2. Experimental procedure
Samples for inelastic neutron scattering experiments were synthesized by the flux method [12]. We used a triple-axis thermal neutron spectrometer TOPAN installed at the reactor JRR-3, JAEO, Tokai, Japan, operating in the mode of constant scattered neutron energy of 13.5 meV. Sample temperatures were controlled by a closed-cycle refrigerator.

3. Results and analysis
Figure 1 shows magnetic scattering functions, $S(E)$, of PrOs$_4$P$_{12}$ as a cross section difference between PrOs$_4$P$_{12}$ and LaOs$_4$P$_{12}$. Those of PrRu$_4$Sb$_{12}$ was obtained by subtracting background intensities measured with the empty sample container, so that nonmagnetic contribution may exist and absolute magnetic cross section has not been evaluated yet. Distinct magnetic peaks observed at $\sim$ 4 and $\sim$ 12 meV of PrOs$_4$P$_{12}$ are excitations between CF levels of Pr$^{3+}$ $4f^2$ electrons as discussed later. The spectra of PrRu$_4$Sb$_{12}$ also exhibit the excitation peaks consistent with the previous work [17]. A shoulder-like feature around 15 meV may be due to the nonmagnetic contribution, because such response was not reported in the previous work. The spectral widths of both materials become broader with variation of temperature. This phenomenon reflects characteristic interplay between $4f$ and conduction electrons. The CF Hamiltonian, $H_{\text{CF}} = W \left[ \frac{2}{\beta} (O_0^d + 5O_0^t) + \frac{1}{\beta} |\xi|^2 (O_0^d - 21O_0^t) + \frac{1}{\beta} (O_0^t - O_0^d) \right]$, based on Stevens' operator equivalent [18] was adopted for analyzing the observed spectra. We performed a least-squares fitting analysis of the CF excitation cross sections [19]. The spectral shape was assumed to be a Lorentzian function, and was convoluted with the spectrometer resolution expressed by a Gaussian form (0.85 meV of full width at half maximum at the elastic scattering condition). The results shown by solid lines in figure 1 reproduce the experimental data well. The resultant CF scheme of PrOs$_4$P$_{12}$ is $\Gamma_1$ (singlet, 0 meV) $\rightarrow$ $\Gamma_4^{(2)}$ (triplet, $\sim$ 5 meV) $\rightarrow$ $\Gamma_4^{(1)}$ (triplet, $\sim$ 12 meV) $\rightarrow$ $\Gamma_{23}$ (doublet, $\sim$ 16 meV) in the whole temperature

**Figure 1.** Symbols represent magnetic scattering functions of PrOs$_4$P$_{12}$, and those of PrRu$_4$Sb$_{12}$. Ordinate origin of each temperature data is shifted. Solid lines are results of model fitting for CF scheme.

**Figure 2.** Half widths at half maximum of the excitation spectra for $\Gamma_1$ $\rightarrow$ $\Gamma_4^{(1)}$ (blue squares) and $\Gamma_1$ $\rightarrow$ $\Gamma_4^{(2)}$ (red circles). Lines are the calculated results for PrOs$_4$P$_{12}$ based on the BFK theory.
range, which is consistent with the specific heat study [14]. The CF scheme of PrRu₄Sb₁₂ is also Γ₁ (0 meV) − Γ₄⁽²⁾ (∼ 5.4 meV) − Γ₄⁽¹⁾ (∼ 12.4 meV) − Γ₂₃ (16 − 17 meV).

The intrinsic half widths at half maximum (HWMM) γ(T) for the excitation from Γ₁ to Γ₄⁽²⁾ and that from Γ₁ to Γ₄⁽¹⁾ are depicted by circles and squares, respectively, in figure 2. Increment of γ(T) with increasing temperature, indicates the exchange interaction between f electrons and carrier. It is noticeable that γ(T) for the excitation to Γ₄⁽¹⁾ is much broader than that to Γ₄⁽²⁾. Since the widths of PrOs₄P₁₂ and PrRu₄Sb₁₂ are close, the common mechanism of spectral broadening is expected to be common for the skutterudite compounds.

4. Discussions
The general description of the CF excitation width given by the exchange interaction between 4f and conduction electrons, that was discussed by Becker, Fulde and Keller (BFK) [20], can be applied to the metallic Pr-filled skutterudite. Following this theory, we derived γ(T) for the excitations from the singlet ground state Γ₁ to the triplet in T₉ point group, expressed as

\[ \gamma(T) = 2\pi |J_{ex}N(E_F)|^2 \left( \frac{40d^2}{3} k_B T e^{-\Delta_{CF}/k_BT} + \frac{20d^2}{3} \frac{\Delta_{CF}}{1 - e^{-\Delta_{CF}/k_BT}} + \frac{1}{2} \frac{5 - 4d^2}{k_BT} \right). \] (1)

The parameter d is defined in the triplet wave function form under T₉ \[ |\Gamma_4^{(T₉)}, m\rangle = \sqrt{1 - d^2} |\Gamma_5^{(O₉)}, m\rangle + d |\Gamma_4^{(O₉)}, m\rangle, (m = 1, 2, 3) \], where \( \Gamma_4^{(O₉)} \) and \( \Gamma_5^{(O₉)} \) are triplet eigenfunctions under O₉ point group [21]. \( J_{ex} \) denotes an exchange constant between 4f and conduction electrons multiplied by \( g_J - 1 \), \( N(E_F) \) is the density of states at the Fermi level, and \( \Delta_{CF} \) is the CF splitting energy whose temperature variation was derived by the aforementioned spectral analysis. \( N(E_F) \) is assumed to be constant in the whole temperature range, since no distinct anomaly was seen in electrical resistivity [11, 16]. The values of d and \( \Delta_{CF} \) have already been determined in the spectral analysis.

The temperature dependences of spectral widths of PrOs₄P₁₂ was fitted by equation (1) with a single parameter \( J_{ex}N(E_F) \). The best fit result for HWHM data with the parameter \( J_{ex}N(E_F) = 0.0244 \pm 0.0005 \) is shown by the lines in figure 2. The result is quantitatively consistent with the observation below 30 K, although it deviates from the data in higher temperature region with worse accuracy due to the less statistics. It is notable that the BFK theory agrees with the fact that the width for the excitation to Γ₄⁽¹⁾ is larger than that for Γ₄⁽²⁾. It can be understood that the different shapes of 4f wave functions of the two triplets with respect to the surrounding P cage structure give inequivalent damping of electronic excitation. We conclude that the exchange interaction expected to be p-f hybridization is responsible for the electronic state. The broader spectra of the excitation Γ₁ − Γ₄⁽¹⁾ than that of Γ₁ − Γ₄⁽²⁾ are observed also in PrOs₄Sb₁₂ [22, 23]. Therefore, the hybridization effect is expected to be common for the skutterudite compounds.

The temperature of around 30 K, below which the characteristic shift of CF splitting energies are observed for PrOs₄P₁₂, is comparable to the CF splitting energy between the Γ₁ ground state and the Γ₄⁽¹⁾ first excited state. The thermal population probability of the ground state becomes large below ∼30 K, so that the 4f wave function contributing to p-f hybridization varies thorough this temperature. Therefore, the CF potential given by p-f hybridization depends on temperature, resulting in the shift of the CF splitting energy. On the other hand, the shift of the excitation energy of Γ₄⁽²⁾ from 14 to 44 K is only by 0.03 meV in PrRu₄Sb₁₂. Although it may be due to the higher excitation energy of Γ₄⁽²⁾ for PrRu₄Sb₁₂, more detailed study is necessary.
5. Summary
The intrinsic spectral widths and the temperature evolutions of excitations from the ground state $\Gamma_1$ to the two triplets $\Gamma_4$ of Pr-fille skutterudites are well reproduced by the BFK theory taking into account the exchange interaction between $f$ and conduction electrons. The shift of CF levels indicates that the $f$ state population correlates with the variation of CF potential by $p$-$f$ hybridization. We conclude that $p$-$f$ hybridization is significant commonly for the electronic properties of Pr-fille skutterudites.

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References
[1] Holland-Moritz E and Lander G H 1994 Handbook on the Physics and Chemistry of the Rare Earths vol 19 (Amsterdam: Elsevier Science B V) p 1
[2] Sales B C 2003 Handbook on the Physics and Chemistry of Rare Earths vol 33 (Amsterdam: Elsevier Science B V) p 1
[3] Otsuki J, Kusunose H and Kuramoto Y 2005 J. Phys. Soc. Jpn. 74 200
[4] Otsuki J, Kusunose H and Kuramoto Y 2005 J. Phys. Soc. Jpn. 74 2082
[5] Kuramoto Y 2008 Prog. Theor. Phys. Suppl. 176 77
[6] Sekine C, Uchiyama T, Shirotani I and Yagi T 1997 Phys. Rev. Lett. 79 3218
[7] Iwasa K, Hao L, Kuwahara K, Kohgi M, Saha S R, Sugawara H, Aoki Y, Sato H, Tayama T and Sakakibara T 2005 Phys. Rev. B 72 024414
[8] Iwasa K, Hao L, Hasegawa T, Takagi T, Horiuchi K, Mori Y, Murakami Y, Kuwahara K, Kohgi M, Sugawara H, Saha S R, Aoki Y and Sato H 2005 J. Phys. Soc. Jpn. 74 1930
[9] Harima H and Takegahara K 2002 Physica B 312 – 313 843
[10] Takimoto T 2006 J. Phys. Soc. Jpn. 75 034714
[11] Yuhasz W M, Ho P -C, Sayles T A, Yanagisawa T, Frederick N A, Maple M B, Rogl P and Giester G 2007 J. Phys.: Condens. Matter 19 076212
[12] Sugawara H, Iwahashi Y, Magishi K, Saito T, Koyama K, Harima H, Kikuchi D, Sato H, Endo T, Settai R and Onuki Y 2009 Phys. Rev. B 79 035104
[13] Harima H and Takegahara K 2008 Physica B 403 906
[14] Matsuhira K, Doi Y, Wakeshima M, Hinatsu Y, Kihou K, Sekine C and Shirotani I 2005 Physica B 359 – 361 977
[15] Iwasa K, Saito K, Murakami Y and Sugawara H 2009 Phys. Rev. B 79 235113
[16] Takeda N and Ishikawa M 2000 J. Phys. Soc. Jpn. 69 868
[17] Adroja D T, Park J -G, Goremychkin E A, Takeda N, Ishikawa M, McEwen K A, Osborn R, Hillier A D and Rainford B D 2005 Physica B 359-361 983
[18] Takegahara K, Harima H and Yanase A 2001 J. Phys. Soc. Jpn. 70, 1190
[19] Birgeneau R J 1972 J. Phys. Chem. Solids 33 59
[20] Becker K W, Fulde P and Keller J 1977 Z. Physik B 28 9
[21] Shinya R 2004 J. Phys. Soc. Jpn. 73 2257
[22] Kuwahara K, Iwasa K, Kohgi M, Kaneko K, Metoki N, Raymond S, Méasson M -A, Flouquet J, Sugawara H, Aoki Y and Sato H 2005 Phys. Rev. Lett. 95 107003
[23] Goremychkin E A, Osborn R, Bauer E D, Maple M B, Frederick N A, Yuhasz W M, Woodward F M and Lynn J W 2004 Phys. Rev. Lett. 93 157003