Crystal Field Excitations of Filled Skutterudite 
PrRu$_4$P$_{12}$ by Raman Scattering

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Abstract. Raman scattering spectra of single crystalline PrRu$_4$P$_{12}$ have been measured in the temperature region between 4.6 K and 300 K. Additional peaks appear below metal-insulator transition temperature. Among these peaks, CEF excitations for two different Pr ion sites can be assigned from the results of magnetic field (H≤8T) dependence and polarization dependence. From the energy of CEF excitations in Raman spectra, we have re-determined CEF energy levels for Pr$_1$ and Pr$_2$ ions. From the result of CEF level schemes and the different atomic displacement of Ru around Pr$_1$ and Pr$_2$, Pr$_1$ ion is affected by a strong positive point charge potential of Ru, and Pr$_2$ ion feels strong p-f hybridization.

1. Introduction

Ternary compounds of filled skutterudite RT$_4$X$_{12}$ (R:rare-earth, T:transition metal, and X:pnictogen) have attracted much attention, because the compounds show a variety of novel physical properties, such as an unconventional superconductivity, a multipole ordering and so on. Among a great number of skutterudite compounds, PrRu$_4$P$_{12}$ shows metal-insulator (M-I) transition at T$_{M-I}$=63K.[1] The transition is accompanied with the structural change from metallic Im$ar{3}$ to insulating Pm$ar{3}$.[2].

The charge-density-wave formation due to the Fermi surface nesting is proposed as a mechanism of the M-I transition by the band calculation,[3] the importance of the Pr 4f-electron contribution to the transition has also been pointed out,[4], and the antiferrohexadecapole order is recently proposed.[5] In the experimental approach to elucidate the mechanism, Iwasa et al. observed crystal electric field (CEF) excitations by inelastic neutron scattering,[6] and they determined the CEF energy levels for two different Pr ion sites, such as $\Gamma_1(0\text{meV})$-$\Gamma_4^{(2)}(8.07\text{meV})$-$\Gamma_4^{(1)}(9.18\text{meV})$-$\Gamma_{23}(15.71\text{meV})$ for Pr$_1$, and $\Gamma_4^{(2)}(0\text{meV})$-$\Gamma_1(3.12\text{meV})$-$\Gamma_4^{(1)}(13.88\text{meV})$-$\Gamma_{23}(20.13\text{meV})$ for Pr$_2$, at T=5K. This result well reproduces the physical properties such as an induce magnetic moment or magnetic susceptibility.

On the other hand, our group have performed Raman scattering experiment in order to clarify the lattice and electronic state at the M-I transition.[7] In the Raman spectra of PrRu$_4$P$_{12}$, 8 Raman active phonons and two CEF excitations are observed at room temperature. With decreasing temperature, the additional phonons due to the structural phase transition appear below T$_{M-I}$. In addition, the CEF excitation peaks split into two different CEF state for Pr$_1$
and Pr2. The result of CEF levels by Raman scattering agrees with that by inelastic neutron scattering. In this report, to check the assignment of CEF excitations, we have measured the magnetic field dependence and polarization dependence of the Raman scattering spectra.

Single crystal sample of PrRu$_4$P$_{12}$ was synthesized by Sn-flux method. The Raman scattering measurements were performed in a quasi-backscattering geometry. An Ar ion laser with the wavelength of 514.5 nm was employed as an excitation beam and its typical power was $\sim 10$ mW at the specimen. The scattered light was analyzed by a triple grating spectrometer and the analyzed light was detected by a Liq.N$_2$-cooled CCD detector. Eight phonons, $\Gamma_R = 2A_g + 2E_g + 4T_g$ are Raman active in the skutterudite structure $Im\bar{3}$. The peaks with symmetry of $A_g/\Gamma_1$, $E_g/\Gamma_{23}$, and $T_g/\Gamma_4$ can be selectively observed by polarization dependence of incident and scattered light as following polarization geometries: $A_g/\Gamma_1$ appear at the $(x,x)$ geometry, $E_g/\Gamma_{23}$ at $(x,x)$ and $(x+y,x-y)$, and $T_g/\Gamma_4$ in $(x,y)$. In the notation of $(\alpha,\beta)$, $\alpha$ and $\beta$ are the polarization directions of incident and scattered light, respectively. Hereafter, we use $A_g$, $E_g$, and $T_g$ for phonons, and $\Gamma_1$, $\Gamma_{23}$, and $\Gamma_4$ for CEF excitations.

![Figure 1](image_url)

**Figure 1.** $(x,y)$ and $(x+y,x-y)$ Raman scattering spectra of PrRu$_4$P$_{12}$ measured at room temperature ($T>T_{M-I}$) and $T=5K$ ($T<T_{M-I}$). The closed triangles are phonons for metallic phase, and open triangles are additional peaks below $T>T_{M-I}$. The solid and dotted vertical lines at a bottom of the figure denote the energy of expected CEF excitations for Pr1 and Pr2, respectively, derived from the result of neutron experiment. P$_1$~P$_6$ peaks are CEF excitations assigned in this work. (see in text)

### 2. Results and Discussions

Figure 1 shows Raman spectra of PrRu$_4$P$_{12}$ measured at below and above $T_{M-I}$. In this figure, representative spectra with $(x,y)$ and $(x+y,x-y)$ are shown. As shown in the figure, $2E_g$ and $4T_g$ phonons (closed triangles) are observed in the spectra measured at room temperature. New peaks (open triangles) appear below $T_{M-I}$. Among these new peaks, the peaks observed at higher energy than 200 cm$^{-1}$ are phonons, which is originated from the structural change to lower symmetry ($Pm\bar{3}$). On the other hand, new peaks below 180 cm$^{-1}$ can be assigned as the CEF excitation of Pr ions, since the energies of all peaks observed below 180 cm$^{-1}$ agree with those of the CEF excitations measured by neutron experiment as shown in the figure. In addition, each peak satisfies the polarization selection rule for corresponding CEF excitation.

To check the assignment of CEF excitations, we have measured Raman scattering spectra under magnetic field, because the CEF excitations including the triplet $\Gamma_4$ state are expected to
split or shift by magnetic field. Figure 2 shows the magnetic field dependence of \((x, x)\) Raman spectra in lower energy region. With increasing magnetic field, increase of peak intensity (dotted arrows), peak splitting (solid arrows), and energy shift (triangles) have been observed. These peaks were already assigned as the excitations of \(\Gamma_4^{(1)}\) for 76 cm\(^{-1}\) peak, \(\Gamma_4^{(2)}\) for 115 cm\(^{-1}\), and \(\Gamma_1\) for 139 cm\(^{-1}\).[7] The estimated Zeeman splitting for each Pr ions is by about 20 cm\(^{-1}\) at \(H=8T\) for \(\Gamma_4^{(2)}\), and the other states slightly split by about 4\(\sim\)5 cm\(^{-1}\) and 1\(\sim\)2 cm\(^{-1}\) for \(\Gamma_4^{(1)}\) and \(\Gamma_{23}\), respectively. These estimated Zeeman splitting quantitatively reproduce the behavior of CEF excitations spectra, taking into account for the selection rule under magnetic field.

Figure 2. Magnetic field dependence of \((x, x)\) Raman spectra of PrRu\(_4\)P\(_{12}\) measured at \(T=4.6K\).

Figure 3 shows Raman spectra of \((x, y)\) and \((y, x)\) measured at \(T=5K\) and room temperature. The peaks denoted by arrows have different intensity between \((x, y)\) and \((y, x)\) spectra.

Taking account of these newly CEF peaks, we have re-determined CEF energy levels, as shown in figure 4. From the comparison of the CEF schemes between by neutron and Raman experiments, there is a qualitative difference for the level scheme of Pr1, that is, \(\Gamma_1\) and \(\Gamma_{23}\).
for neutron and $\Gamma_1^{-1} - \Gamma_4^{-1} - \Gamma_23 - \Gamma_4^{(2)}$ for Raman.

The CEF level scheme for $4f^2(Pr^{3+})$ state in Pr-filled skutterudites was recently studied by Otsuki et al.[9] In the case of a point charge potential, the scheme $\Gamma_1^{-1} - \Gamma_4^{(1)} - \Gamma_23 - \Gamma_4^{(2)}$ is favored under the condition of positive valence of transition-metal ions. On the other hand, $p-f$ hybridization stabilizes the $\Gamma_4^{(2)}$ triplet as the ground state.

Below $T_{M-I}$, the interatomic distance of Pr1-Ru and Pr2-Ru becomes shorter and longer than that of Pr-Ru above $T_{M-I}$, because of the atomic displacement for Ru is $\delta > 0$ for $(1/4+\delta, 1/4+\delta, 1/4+\delta)$. [6] Therefore, it seems that the electronic state of the transition metal strongly affects on the Pr1 ion below $T_{M-I}$. This suggests that the energy scheme for Pr1 tends to become $\Gamma_1^{-1} - \Gamma_4^{(1)} - \Gamma_23 - \Gamma_4^{(2)}$ easily. At the same time, $\Gamma_4^{(2)}$ ground state is stabilized for Pr2 ion, because the Pr2 ion feels weak point charge potential of transition metal and relatively strong $p-f$ hybridization. From the results of CEF level scheme by Raman scattering, we obtain the good reproducibility for magnetic properties, such as magnetization or induced magnetic moment. The difference of CEF level schemes between neutron and Raman experiment does not affect to these properties, because this difference is shown in $E \geq 10\text{meV}$ ($\simeq 100\text{K}$) from the ground state.

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[1] Sekine C, et al. 1997 Phys. Rev. Lett. 79 3218
[2] Lee C H, et al. 2001 J. Phys. Condens. Matter 13 L45
[3] Harima H, et al. 2003 Acta Phys. Polonica B 34 1189
[4] Lee C H, et al. 2004 Phys. Rev. B 70 153105
[5] Takimoto T 2006 J. Phys. Soc. Jpn. 75 0347141
[6] Iwasa K, 2005 Phys. Rev. B 72 024414
[7] Ogita N, et al. 2005 Physica B 359-361 847
[8] Schaack G 2000 Light Scattering in Solids VII ed Cardona M and Güntherodt (Berlin Springer) p24
[9] Otsuki J, Kusunose H and Kuramoto Y 2005 J. Phys. Soc. Jpn. 74 200