Resonant x-ray scattering study on electronic hybridization in unconventional ordered phase of PrRu$_4$P$_{12}$

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Abstract. PrRu$_4$P$_{12}$, which undergoes a metal-insulator transition at $T_{MI} \sim 63$ K, has been investigated by resonant x-ray scattering technique at the Pr $L_3$-edge, the P $K$-edge, and the Ru $L_3$-edge, in which element and orbital selective electronic states can be clarified. Resonating energy spectra at the 111 reflection were found at the Pr $L_3$-edge and P $K$-edge, while it was not observed at the Rh $L_3$-edge. This is the first observation of quite large resonant signal at the P $K$-edge. This result is considered as a direct evidence for the strong Pr 4$f$ and P 3$p$ hybridization effect on the unconventional ordered phase accompanied by the insulator state.

1. Introduction

Filled skutterudites $RT_4X_{12}$ ($R =$ lanthanide and actinide elements, $T =$ transition metal, $X =$ pnictogen) have attracted great interests because of various physical properties, such as heavy-fermion superconductivity and multipole order [1, 2, 3, 4]. There the $R$ ion is surrounded by the $X$ ions forming an icosahedron, therefore it is expected that the mixing between $p$ state of $X$ ion and $f$ state of $R$ ion is responsible for the various physical properties.

PrRu$_4$P$_{12}$ exhibits a metal-insulator (MI) transition at $T_{MI} \sim 63$ K. X-ray and electron diffraction revealed a structural phase transition from the space group of $I\bar{m}3$ to that of $Pm\bar{3}$ at $T_{MI}$ [5]. Namely the reflections at the $hkl$ with $h + k + \ell =$ odd appear below $T_{MI}$. As an origin of the MI transition, the nesting of the Fermi surface was theoretically proposed [6]. However, LaRu$_4$P$_{12}$ does not show such the MI transition, even though it has a similar electronic structure except for the 4$f$ electrons. It indicates that the 4$f$ electron plays an important role in the MI transition. Then a possibility of antiferro-hexadecapole order of Pr 4$f$ was theoretically proposed as an origin of the band-gap formation [7, 8].

Neutron scattering study on the crystal-field excitations elucidated the presence of strong orbital hybridization between Pr 4$f$ and P 3$p$ ($p - f$ hybridization), which causes the formation of charge-density-wave state associated with staggered 4$f$-electron order below $T_{MI}$ [9]. Accordingly, the $p - f$ hybridization is expected to be essential for the MI transition. On the other hand, photoemission study reported that no notable anomaly was observed across the MI transition [10]. This result indicates that spatial structure of a particular electronic state
relevant to the MI transition should be investigated. Therefore, details of the $p-f$ hybridization effect on the ordered state in PrRu$_4$P$_{12}$ remains an important issue.

Resonant X-ray scattering (RXS) is a powerful tool for observing the spatial ordering of charge, orbital, and spin degrees of freedom [11]. PrRu$_4$P$_{12}$ has also been studied by the RXS to elucidate the unconventional ordered phase below $T_{MI}$ [12], although there was no clear evidence for the resonant features due to the electronic ordering. Furthermore, the RXS technique has a potential to elucidate the hybridized electronic state, since the resonant signal has element and orbital selective information depending on the absorption energy. In this study to investigate the hybridized electronic state below $T_{MI}$, the RXS measurement has been performed at the Pr $L_3$-edge, the P $K$-edge, and the Ru $L_3$-edge.

2. Experiments

Single crystal of PrRu$_4$P$_{12}$ was synthesized with Sn-flux method. The crystal structure is cubic with lattice constant $a = 8.042$ Å at room temperature, which is consistent with previous report [13]. RXS and fluorescence measurements were carried out at BL-4C and BL-11B in Photon Factory, KEK. The incident beams were monochromatized by Si(111) double crystals. The experiments at the Pr $L_3$-edge were performed at BL-4C using a four-circle diffractometer with $\sigma$-polarization incident beam. The experiments at the P $K$-edge and at the Ru $L_3$-edge were performed at BL-11B using an in-vacuum two-circle diffractometer [14] with $\pi$-polarization incident beam. Polarization analysis of the scattered beam was not performed in these measurements.

![Figure 1](image-url)

Figure 1. (a) Fluorescence spectrum at the P $K$-edge. (b) Energy dependence of the scattering intensity at the 111 reflection and at $T = 30$ K.
3. Results and discussion

We have measured the RXS spectrum at the P K-edge to elucidate the P 3p electronic state in the unconventional ordered phase below $T_{MI}$. The fluorescence of PrRu$_4$P$_{12}$ was measured near the P K-edge ($1s \rightarrow 3p$ transition) as shown in Fig. 1(a). The spectrum reflects the unoccupied P 3p electronic state. Energy dependence of the scattering intensity was measured at the 111 reflection and at $T = 30$ K as shown in Fig. 1(b). The strongly resonated peaks were observed near the edge energy, while the scattering intensity exists even at 2135 eV (non-resonant energy). The latter is the Thomson scattering due to the structural distortion at the $T_{MI}$. On the other hand, the resonant signal at the P K-edge reflects the difference in the P 3p electronic states between two P icosahedrons due to the staggered 4f-electron order. The strongest resonant peak exists at 2142 eV, which reflects the 3p state near the Fermi energy. The intensity is about $10^2$ times stronger than that at 2135 eV. This signal at the 111 reflection appears below $T_{MI}$, and no signal was observed above $T_{MI}$.

In order to compare with the resonant intensity at the Pr edge, we have measured the RXS signal at the Pr L$_3$-edge ($2p \rightarrow 5d$ transition). Energy dependence of the scattering intensity was measured at the 111 reflection as shown in Fig. 2(b). The spectrum has a small peak structure at 5961.6 eV, which reflects the staggered Pr 5d-electronic state. The result is consistent with the previous report [12]. The component of the RXS signal is comparable to the Thomson scattering component at 5940 eV (non-resonant energy). It means that the change of the Pr 5d electronic states is much smaller than that of the P 3p state. It is noteworthy that the resonant signal at the Pr L$_3$-edge does not detect the 4f electronic state directly by the dipole transition ($E1$) process. The resonant signal at the quadrupole ($E2$) transition has not been reported so far [12], although a RXS signal associated with a hexadecapole order is theoretically proposed.

![Figure 2](image_url)

**Figure 2.** (a) Fluorescence spectrum at the Pr L$_3$-edge. (Data were taken from Ref. [12].) (b) Energy dependence of the scattering intensity at the 111 reflection and at $T = 9$ K.
Figure 3. (a) Fluorescence spectrum at the Ru $L_3$-edge. (b) Energy dependence of the scattering intensity at the 111 reflection and at $T = 30$ K.

to appear at the $E2$ transition [15].

We have also measured the RXS signal at the Ru $L_3$-edge ($2p \rightarrow 4d$ transition). Since the atomic displacement of Ru on the structural change at $T_{MI}$ is comparable to the displacement of P atoms [16], we examined whether a RXS signal appears at the Ru $L_3$-edge or not. Energy spectrum at the 111 reflection is shown in Fig. 3(b). The intensities simply become weak near the absorption edge energy, and the spectrum is similar to that of the fluorescence (Fig. 3(a)). It indicates that any component of the RXS signal was not detected within the experimental error. Namely the change in the Ru 4$d$ electronic state is quite small, which may indicate a less contribution of the Ru electrons to the unconventional ordered state below $T_{MI}$.

4. Conclusion

We have performed the RXS measurements at the P $K$-edge, the Pr $L_3$-edge, and the Ru $L_3$-edge to elucidate the element and orbital selective electronic states in the unconventional ordered phase below $T_{MI}$. We newly found the strongly resonated peaks near the P $K$-edge, which directly evidence the alternative arrangement of P icosahedrons characterized by inequivalent $3p$ electronic states in the low-temperature $Pm\bar{3}$ phase. Moreover, the strongest resonant peak is considered to originate from the $3p$ state near the Fermi energy. The present result is in accordance with the gap formation accompanying the staggered $4f$ multipole order, which is driven by the strong $p-f$ hybridization. In contrast, because no resonant signal at the Ru $L_3$-edge was observed, the hybridization with the Pr $4f$ electrons is dominated by the phosphorus $p$ electrons. The resonant signal at the Pr $L_3$-edge is also quite weak. This result indicates that the Pr 5$d$ state does not contribute to the ordered state. It is also consistent with the Pr $4f$ electrons play more important roles in the MI transition, because the $L_3$-edge measurement is
not a direct probe for the Pr 4f electrons. Finally, our result at the P K-edge is considered as a direct evidence for the strong Pr 4f and P 3p hybridization effect on the unconventional ordered phase below $T_{MI}$. In future work, the direct observation of the Pr 4f electronic state at the Pr M-edge becomes quite important to understand the $p – f$ hybridization effect.

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