HEAVY FERMION BEHAVIOR OF Pr 4f ELECTRONS IN FILLED SKUTTERUDITES STUDIED BY BULK-SENSITIVE PHOTOEMISSION*

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Pr 4f electronic structures in Pr-based filled skutterudites PrT\textsubscript{4}X\textsubscript{12} (T=Fe and Ru; X=P and Sb) have been studied by the high-resolution bulk-sensitive Pr 3d $\rightarrow$ 4f resonance photoemission spectroscopy. A very strong Pr 4f spectral intensity is observed just below the Fermi level in the heavy-Fermion PrFe\textsubscript{4}P\textsubscript{12}. This is the first observation of the Kondo resonance due to the quadrupolar Kondo effect, the origin of which is attributed to the strong hybridization between the Pr 4f and the conduction electrons.

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1. Introduction

Rare-earth filled skutterudite compounds RT\textsubscript{4}X\textsubscript{12} (R=rare earth; T=Fe, Ru, and Os; X=P, As, and Sb) are recently attracting much attention in view of the thermoelectric devices [1] and physics of strongly correlated

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systems [2–4]. Among them, Pr-based filled skutterudites exhibit various interesting properties such as a metal-insulator transition at around 64 K in PrRu$_4$P$_{12}$ [3, 5] and a superconducting transition at 1 K in PrRu$_4$Sb$_{12}$ [6]. PrFe$_4$P$_{12}$ is particularly interesting due to the phase transition at around 6.5 K and the Kondo-like behaviors [4]. In addition, the heavy electron mass has recently been found in the de Haas-van Alphen measurement [7]. In order for the heavy fermion behavior to be observed, the hybridization between the conduction band and the Pr 4$f$ state (4$f$ hybridization) must be appreciably strong. The aim of this paper is to investigate the Pr 4$f$ electronic states by means of bulk-sensitive photoemission spectroscopy.

2. Experimental

The single crystals of PrFe$_4$P$_{12}$ and PrRu$_4$Sb$_{12}$ were grown by Sn-flux [2] and Sb-self-flux methods [6], respectively. The single-phase polycrystals of PrRu$_4$P$_{12}$ were synthesized at high temperatures under high pressures using a wedge-type cubic-anvil high-pressure apparatus [3]. Photoemission (PE) measurements were carried out at the BL23SU of SPring-8 [11]. The Pr 3$d$ → 4$f$ resonance PE (RPE) spectra were measured with the best total energy resolution of ~80 meV in the full width at half maximum at around 900eV of the photon energy. The clean surfaces were obtained by fracturing the samples in situ in the ultrahigh vacuum.

3. Results and discussion

Figure 1 shows Pr 4$f$ spectra obtained by subtracting the off-resonance ($h\nu = 921.0$ eV) PE spectrum from the Pr on-resonance ($h\nu = 929.4$ eV corresponding to a slightly lower energy than Pr 3$d$ → 4$f$ absorption maximum) PE spectrum. The Pr 4$f$ spectra are dramatically different among Pr-based filled skutterudites and Pr metal [12]. The large variation of the Pr 4$f$ spectrum clearly indicates the strong compound dependence of the valence band structure and of the hybridization between the Pr 4$f$ and the valence electron states. We should note that the present Pr 4$f$ spectrum of PrFe$_4$P$_{12}$ obtained from the bulk-sensitive Pr 3$d$ → 4$f$ RPE is qualitatively different from that obtained from the surface-sensitive 4$d$ → 4$f$ RPE result [13].

Furthermore, we measured Pr 3$d$ → 4$f$ on-resonance PE spectra near Fermi level ($E_F$) with better resolution as shown in Fig. 2. The prominent feature is the strong peak of PrFe$_4$P$_{12}$ at the binding energy of $E_B \approx 100$ meV, the intensity of which is much stronger than other filled skutterudites. Structures between $E_F$ and $E_B = 1$ eV can be attributed to 4$f^2$ multiplet structures as shown by vertical broken lines [12]. The intensity ratio of
Fig. 1. Pr 4f spectra for PrFe₄P₁₂, PrRu₄P₁₂, and PrRu₄Sb₁₂ at 20K. All the spectra are normalized to the same area after subtracting the background contribution. The backgrounds shown by the broken lines are obtained by the Shirley procedure [14].

Fig. 2. High-resolution Pr 3d → 4f on-resonance PE spectra near E_F at 20K.

the multiplet structures is quite similar between PrRu₄P₁₂ and PrRu₄Sb₁₂. In a strong contrast, the multiplet intensity for PrFe₄P₁₂ increases from the larger E_B side and then stays almost constant as approaching E_F. The most outstanding point of the Pr 4f spectrum of PrFe₄P₁₂ is that the relative intensity of 3H₄ multiplet with respect to other multiplets is much larger than other filled skutterudites and Pr metal [12].

A Kondo Ce system can be characterized by the far larger intensity of the 4f₅/₂ (Kondo resonance) to that of the 4f₇/₂ component compared with a localized Ce system if they were measured at the same temperature [15]. When we compare the 4f spectra of Pr and Ce, the 3H₄ multiplet, which is very strong in PrFe₄P₁₂, corresponds to the 4f₅/₂ component of Ce in a sense that they are both the multiplet structure nearest to E_F. Therefore, the prominent 3H₄ multiplet intensity in PrFe₄P₁₂ can be interpreted as the
Kondo resonance due to the strong $c$-$f$ mixing. This is quite consistent with
the Kondo-like behavior in the resistivity and with the heavy electron mass
found in the de Haas-van Alphen measurement. In the high-temperature
phase, the ground state of Pr$^{3+}$ ion is considered as the non-Kramers doublet
[9,10]. Therefore, the Kondo resonance that we observed in PE spectrum
and all other Kondo-like behaviors [4,7] most probably originate from the
quadrupolar Kondo effect [8].

4. Conclusion

In conclusion, we have observed the Kondo resonance behavior in the
Pr 4$f$ photoemission spectrum of PrFe$_4$P$_{12}$, whereas no Kondo resonance
is seen in PrRu$_4$P$_{12}$ and PrRu$_4$Sb$_{12}$. The origin of the Kondo resonance in
PrFe$_4$P$_{12}$ is considered to be due to the quadrupolar Kondo effect caused
by the strong $c$-$f$ hybridization between the Pr 4$f$ and conduction electron
states in the vicinity of $E_F$.

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