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_4X_{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 $PrFe_4P_{12}$. 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_4X_{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 $PrRu_4P_{12}$ [3,5] and a superconducting transition at 1 K in $PrRu_4Sb_{12}$ [6]. $PrFe_4P_{12}$ 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 $4f$ state (c–f hybridization) must be appreciably strong. The aim of this paper is to investigate the Pr $4f$ electronic states by means of bulk-sensitive photoemission spectroscopy.

2. Experimental

The single crystals of $PrFe_4P_{12}$ and $PrRu_4Sb_{12}$ were grown by Sn-flux [2] and Sb-self-flux methods [6], respectively. The single-phase polycrystals of $PrRu_4P_{12}$ 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 BL25SU of SPring-8 [11]. The Pr $3d \rightarrow 4f$ 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 $4f$ 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 $3d \rightarrow 4f$ absorption maximum) PE spectrum. The Pr $4f$ spectra are dramatically different among Pr-based filled skutterudites and Pr metal [12]. The large variation of the Pr $4f$ spectrum clearly indicates the strong compound dependence of the valence band structure and of the hybridization between the Pr $4f$ and the valence electron states. We should note that the present Pr $4f$ spectrum of $PrFe_4P_{12}$ obtained from the bulk-sensitive Pr $3d \rightarrow 4f$ RPE is qualitatively different from that obtained from the surface-sensitive $4d \rightarrow 4f$ RPE result [13].

Furthermore, we measured Pr $3d \rightarrow 4f$ 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 $PrFe_4P_{12}$ at the binding energy of $E_B \simeq$ 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 $4f^2$ multiplet structures as shown by vertical broken lines [12]. The intensity ratio of

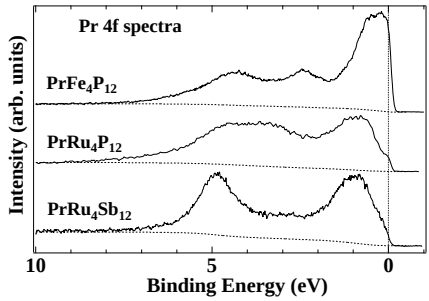

Fig. 1. Pr $4f$ spectra for $PrFe_4P_{12}$, $PrRu_4P_{12}$, and $PrRu_4Sb_{12}$ at 20K. All the spectra are normalized to the same area after subtracting the background contribution. The backgrounds shown by the broken lines are obtained by the *Shirley procedure* [14].

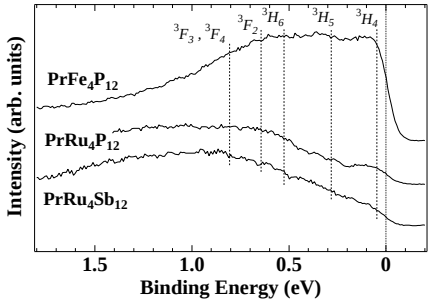

Fig. 2. High-resolution Pr $3d \rightarrow 4f$ on-resonance PE spectra near E_F at 20K.

the multiplet structures is quite similar between $PrRu_4P_{12}$ and $PrRu_4Sb_{12}$. In a strong contrast, the multiplet intensity for $PrFe_4P_{12}$ 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 $PrFe_4P_{12}$ is that the relative intensity of $^3H_4$ 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 $4f_{5/2}$ (Kondo resonance) to that of the $4f_{7/2}$ 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 $^3H_4$ multiplet, which is very strong in $PrFe_4P_{12}$, corresponds to the $4f_{5/2}$ component of Ce in a sense that they are both the multiplet structure nearest to E_F. Therefore, the prominent $^3H_4$ multiplet intensity in $PrFe_4P_{12}$ 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 $4f$ photoemission spectrum of $PrFe_4P_{12}$, whereas no Kondo resonance is seen in $PrRu_4P_{12}$ and $PrRu_4Sb_{12}$. The origin of the Kondo resonance in $PrFe_4P_{12}$ is considered to be due to the quadrupolar Kondo effect caused by the strong c–f hybridization between the Pr $4f$ and conduction electron states in the vicinity of E_F.

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