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

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(Received July 10, 2002)

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 $3d \to 4f$ 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.

PACS numbers: 79.60.–i, 71.20.Eh, 71.27.+a, 71.20.–b

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

* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

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 $3d \to 4f$ 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 $3d \to 4f$ 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 $3d \to 4f$ RPE is qualitatively different from that obtained from the surface-sensitive $4d \to 4f$ RPE result [13].

Furthermore, we measured Pr $3d \to 4f$ 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

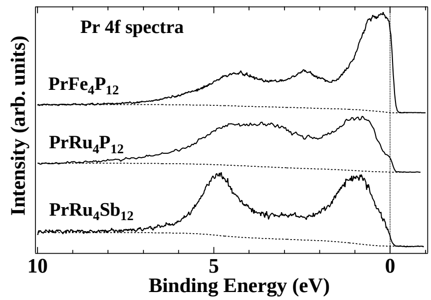

Fig. 1. Pr $4f$ spectra for $PrFe_4P_{12}$, $PrRu_4P_{12}$, and $PrRu_4Sb_{12}$ at 20K. All the spectra are normalized to the same area after subtracting the background contribution. The backgrounds shown by the broken lines are obtained by the *Shirley procedure* [14].

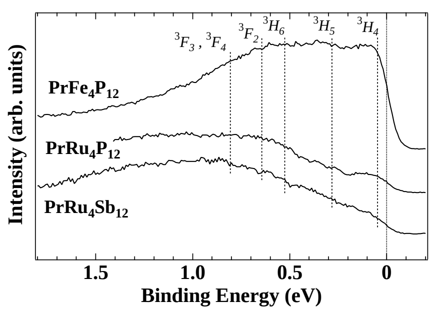

Fig. 2. High-resolution Pr $3d \rightarrow 4f$ on-resonance PE spectra near E_F at 20K.

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.

We are grateful to Dr. T. Muro, and Dr. Y. Saitoh for their experimental assistance. The research was performed at SPring-8 under the support of a Giant-in-Aid for COE Research (10CE2004) of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

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