

Soft and hard X-ray photoemission of Pr and Sm filled skutterudites

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Electronic states of filled skutterudites have been investigated by bulk sensitive photoemission spectroscopy. The aim of this study is to clarify experimentally the $4f$ electronic state, whose deviation from integer valence is considered as one of the main origins of the anomalous quantum phenomena found in filled skutterudites. Considerable deviation has been found in $\text{PrFe}_4\text{P}_{12}$ and $\text{SmOs}_4\text{Sb}_{12}$, whose $4f$ characters have further turned out to be quite different from each other.

Pr $4f$ states in $\text{PrFe}_4\text{P}_{12}$, $\text{PrRu}_4\text{P}_{12}$, $\text{PrRu}_4\text{Sb}_{12}$ and $\text{PrOs}_4\text{Sb}_{12}$ were studied by means of resonant photoemission (RPES) induce by the Pr $3d \rightarrow 4f$ photoabsorption ($h\nu \sim 930$ eV). A very strong spectral intensity was observed just below the Fermi level (E_F) in the heavy-fermion system $\text{PrFe}_4\text{P}_{12}$ [1]. The increase of its intensity was observed as the temperature was lowered as $200 \rightarrow 100 \rightarrow 20$ K. We consider that this is the Kondo resonance of Pr, the origin of which is attributed to the strong hybridization between the Pr $4f$ and the conduction electrons. According to the $3d$ core-level spectroscopy ($3d$ XPS) with soft and hard x-rays up to 5.5 keV, the Pr $4f$ state in $\text{PrFe}_4\text{P}_{12}$ is composed of $4f^1$ (Pr^{4+}), $4f^2$ (Pr^{3+}) and $4f^3$ (Pr^{2+}) states with a ratio of 1 % : 91 % : 8 %. In the heavy fermion superconductor $\text{PrOs}_4\text{Sb}_{12}$ [2] also, finite $4f$ contribution was found near E_F although much smaller than $\text{PrFe}_4\text{P}_{12}$.

Sm $3d$ XPS with soft and hard x-rays up to 8 keV demonstrates that mixed valency is realized in the bulk of $\text{SmOs}_4\text{Sb}_{12}$ [3]. Furthermore, it was found that the Sm valence decreases below 100 K, namely, the ratio between $4f^5$ (Sm^{3+}) and $4f^6$ (Sm^{2+}) changes from 76 % : 24 % at 100 K to 73 % : 27 % at 18 K. This suggests that the Kondo coherence develops with approaching the proposed Kondo temperature ($T_K \sim 20$ K). In fact, RPES spectrum at 20 K is characterized by a finite contribution of the Sm $4f$ state at E_F . Theoretical analyses of Sm $3d$ XPS suggests that the energy difference between $4f^5$ and $4f^6$ is quite small whereas the hybridization between conduction band and the $4f$ state is weak. The origin of this characteristics is that the Sb cage around Sm is quite large, which lowers the energy of $4f^6$ state with larger ionic radius. In another heavy-fermion system $\text{SmFe}_4\text{P}_{12}$ [4], on the other hand, Sm is found to be much nearer to the $4f^5$ state and the Sm $4f$ contribution near E_F was found to be smaller.

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