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Photoemission spectroscopy of Ce-filled skutterudites

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Ce-based compounds CeT_4P$_{12}$ (T = Fe, Ru and Os) show semiconducting properties and have smaller lattice constants than those expected from trivalent lanthanide contraction. This fact may indicate that Ce 4f states in CeT_4P$_{12}$ have strong hybridization with conduction (c) electron states and have an intermediate valence. Therefore, the energy gap in CeT_4P$_{12}$ can be regarded as a c-f hybridization gap[1].

In order to gain an experimental evidence for strong hybridization in CeT_4P$_{12}$, we have performed the photoemission spectroscopy on CeFe$_4$P$_{12}$ using hard x-ray (5.94 keV) at SPring-8. Since the escape depth of photoelectrons becomes longer with increasing photon energy for excitation, a hard x-ray photoemission spectroscopy is very important to investigate the bulk electronic structure. Recently, this method has been applied to the f electron system including valence transition compounds EuNi$_2$(Si$_{0.2}$Ge$_{0.8}$)$_2$[2] and YbInCu$_4$[3]. These results were confirmed the consistency with their bulk properties.

Ce 3d core level photoemission spectra of CeFe$_4$P$_{12}$ show typical three peak structures attributed to f^0, f^1 and f^2 final state. With increasing excitation energy from soft to hard x-ray, a significant enhancement of f^2 peak intensity is observed. Since f^2 final state is caused by charge transfer screening of the core hole from the valence band to 4f states, f^2 peak intensity is considered as an indication of c-f hybridization. Therefore, this result indicates that the c-f hybridization of CeFe$_4$P$_{12}$ is intrinsically strong, in accord with the prediction by band calculation[1].

References

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