Strongly correlated electronic states of Yb$_{1-x}$Lu$_x$B$_{12}$ and Sm$_{1-y}$Eu$_y$B$_6$ studied by highly bulk-sensitive photoelectron spectroscopy

J Yamaguchi$^1$, A Sekiyama$^1$, S Imada$^2$, A Higashiya$^3$, K Tamasaku$^3$, M Yabashi$^{3,4}$, T Ishikawa$^{3,4}$, T Ito$^5$, S Kimura$^5$, F Iga$^6$, T Takabatake$^6$, S Yeo$^7$, S -I Lee$^8$, H -D Kim$^9$ and S Suga$^1$

1 Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
2 College of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan
3 RIKEN/SPRing-8, Sayo, Hyogo 679-5148, Japan
4 JASRI/SPRing-8, Sayo, Hyogo 679-5198, Japan
5 UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan
6 Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8526, Japan
7 Korea Atomic Energy Research Institute, Daejeon 305-600, Korea
8 Department of Physics, Sogang University, Seoul 121-742, Korea
9 Pohang Accelerator Laboratory, Pohang 790-784, Korea

E-mail: yamaguchi@decima.mp.es.osaka-u.ac.jp

Abstract. Impurity-substituted Kondo semiconductors Yb$_{1-x}$Lu$_x$B$_{12}$ and Sm$_{1-y}$Eu$_y$B$_6$ have been studied by the highly bulk-sensitive hard x-ray ($h\nu \sim 8$ keV) photoelectron spectroscopy. The valence-band spectra for Yb$_{1-x}$Lu$_x$B$_{12}$ have been analyzed by the single-impurity Anderson model (SIAM). The temperature dependence of the bulk Yb 4$f$ peak positions for $x = 0$ cannot be interpreted within the SIAM, whereas that for $x = 1/8$ could be understood by the SIAM. This suggests that the Kondo lattice coherence, which is essential for pure YbB$_{12}$, collapses due to the substitution of $x = 1/8$. For Sm$_{1-y}$Eu$_y$B$_6$, the $y$ dependence of the Sm and Eu 3$d$ core-level spectra has been systematically examined. We have found that the Sm valence increases with $y$ due to the reduction of the hybridization between the Sm 4$f$ and valence-bands.

1. Introduction

YbB$_{12}$ and SmB$_6$ have been well known as valence fluctuating (VF) Kondo semiconductors and intensively studied because of their physical properties [1, 2]. The Kondo semiconductors behave as metals with localized $f$ magnetic moments at high temperatures, whereas they develop a narrow energy gap (the order of 10 meV) at the Fermi level ($E_F$) at low temperatures. It is generally thought that the gap formation originates from the hybridization of the narrow $f$ band with broad itinerant valence-bands. Despite many experimental and theoretical approaches, the mechanism of the gap is still controversial. The main problem is the origin of the VF ground state, which seems to be directly related to the gap formation.

To examine the evolution of the narrow gap for YbB$_{12}$, electronic properties of the Lu substituted system Yb$_{1-x}$Lu$_x$B$_{12}$ have been studied. The optical absorption study [3] has indicated that the gap formation for YbB$_{12}$ is dominated by the Kondo lattice coherence while

© 2010 IOP Publishing Ltd
the inelastic neutron scattering (INS) study [4] has suggested that the Yb single-site effects are essential for the gap formation. Thus, detailed investigations of the bulk electronic states of Yb$_{1-x}$Lu$_x$B$_{12}$ are required to settle these controversies between optical and INS studies.

As for SmB$_6$, to investigate the origin of the Sm VF behavior, the x-ray absorption spectroscopy (XAS) measurements at the Sm $L_{III}$-edge have been performed on the impurity-substituted systems [5]. However, the Sm valence estimated from the $L_{III}$-edge XAS has some ambiguities because the Sm$^{2+}$ and Sm$^{3+}$ components strongly overlap in the XAS spectra. More accurate estimation of the bulk Sm valence is required to clarify the VF behavior for SmB$_6$.

In this paper, we report on the studies of the highly bulk-sensitive hard x-ray photoelectron spectroscopy (HAXPES) for the impurity-substituted Kondo semiconductors Yb$_{1-x}$Lu$_x$B$_{12}$ and Sm$_{1-y}$Eu$_y$B$_6$. For Yb$_{1-x}$Lu$_x$B$_{12}$, the temperature ($T$) dependence of the bulk Yb $4f$ spectra is analyzed by the non-crossing approximation (NCA) based on the single-impurity Anderson model (SIAM). For Sm$_{1-y}$Eu$_y$B$_6$, the $y$ dependence of the bulk Sm valence at 20 K is estimated from the Sm 3$d$ core-level spectra.

2. Experimental

The single crystals of Yb$_{1-x}$Lu$_x$B$_{12}$ ($x = 0$ and 1/8) and Sm$_{1-y}$Eu$_y$B$_6$ ($y = 0.15, 0.5, 0.8,$ and 0.95) were grown by the floating-zone method [6]. HAXPES measurements were performed with synchrotron radiation ($h\nu \sim 8$ keV) at the BL19LXU of SPring-8, by using the MBS A1-HE electron analyzer. The samples were fractured in situ with a base pressure of better than $5 \times 10^{-8}$ Pa. The energy calibration was performed by the Au Fermi edge at each measuring temperature. The total energy resolution was set to 65 meV for Yb$^{2+}$ $4f_{7/2}$ spectra near $E_F$. 120 meV for valence-band spectra in the wide energy region from $-1$ to 13.5 eV, and 450 meV for Sm and Eu 3$d$ core-level spectra.

3. Results and discussion

Figure 1(a) shows the valence-band HAXPES spectra of Yb$_{1-x}$Lu$_x$B$_{12}$ ($x = 0$ and 1/8) at 20 K. In both systems the Yb$^{3+}$ $4f$ multiplet structures [10] and Yb$^{2+}$ $4f$ doublet ($J = 7/2$ and 5/2) peaks are observed due to the VF behaviors. The broad surface-peaks in 1–2 eV, which were observed in low-$h\nu$ PES for $x = 0$ [7], are well suppressed in the present HAXPES spectra owing to the high bulk sensitivity. Considering the band-structure calculations [8] and the photoionization cross sections [9], the structures in 2–6 eV are derived from the B 2$sp$ states.

To evaluate the $T$ dependence of the bulk Yb $4f$ peak positions for $x = 0$ and 1/8, we have carried out the spectral fitting with the Lorentzian and Gaussian functions. The fitting results compared with the experimental data of the first peak ($3^2H_6$) in the Yb$^{3+}$ $4f$ multiplet structures and the Yb$^{2+}$ $4f_{7/2}$ peak are shown in Figs. 1(b)–1(e). The $T$ dependence of the peak positions is summarized in Fig. 2. The shift of the Yb$^{2+}$ $4f_{7/2}$ peak for $x = 0$ is $\sim$20 meV toward lower binding energies ($E_B$) with decreasing $T$ from 200 to 20 K (see $\bullet$ in the upper panel of Fig. 2). On the other hand, the shift of the center of gravity (COG) of the Yb$^{3+}$ $4f$ multiplet structures for $x = 0$ is at most $\sim$10 meV toward higher $E_B$ (see the lower panel of Fig. 2). In contrast, for $x = 1/8$, the shift of the Yb$^{2+}$ $4f_{7/2}$ peak is at most $\sim$10 meV toward lower $E_B$ while the shift of COG of the Yb$^{3+}$ $4f$ multiplet structures is $\sim$30 meV toward higher $E_B$ with decreasing $T$ (see $\square$ in Fig. 2). For the quantitative discussions on the $T$ dependence of the bulk Yb $4f$ peak positions in Yb$_{1-x}$Lu$_x$B$_{12}$, we have carried out the NCA calculation based on SIAM with considering the crystalline electric field (CEF) effects [11]. The NCA calculation result on the $T$ dependence is also shown in Fig. 2. As shown in Fig. 2, the NCA result is in agreement with the $T$ dependence of the Yb$^{2+}$ and Yb$^{3+}$ $4f$ peak positions for $x = 1/8$ (see $\square$ in comparison with $\square$). However, the $T$ dependence for $x = 0$ cannot be reproduced by the SIAM, even if the CEF splittings of the $4f_{7/2}$ initial-state are properly taken into account. The $T$ dependence of the bulk Yb $4f$ peak positions for $x = 1/8$ could be explained within the SIAM with ignoring
the influence of the 4f lattice periodicity. However, this treatment is found to be not applicable to $x = 0$. Therefore, we conclude that the Kondo lattice coherence is important for the bulk electronic states for pure YbB$_{12}$ while it collapses due to the substitution of $x = 1/8$.

The Sm and Eu 3d core-level HAXPES spectra of Sm$_{1-y}$Eu$_y$B$_6$ ($y = 0.15, 0.5, 0.8$, and $0.95$) are given in Fig. 3. For all substituted systems, the structures observed from 1120 to 1160 eV are assigned to the Eu$^{2+}$ 3$d_{5/2}$ and 3$d_{3/2}$ multiplet states. The multiplet structures derived from the Sm 3$d_{5/2}$ and 3$d_{3/2}$ states are observed around 1080 and 1105 eV, respectively. As clearly seen in the spectra for $y \leq 0.5$, the Sm 3d multiplet structures consist of the Sm$^{2+}$ and Sm$^{3+}$ components. It should be noticed that the intensity ratio of the Sm$^{2+}$ to Sm$^{3+}$ components decreases with increasing $y$.

To estimate the $y$ dependence of the bulk Sm valence, we have calculated the Sm 3d spectra by the SIAM with considering the atomic multiplet effects [12]. The parameters of this calculation are the effective charge transfer energy $\Delta_{e\text{ff}}$, the core-hole potential $U_{d\text{f}}$, and the effective hybridization strength $V_{e\text{ff}}$. In all substituted systems the Sm 3d spectra have been reproduced by changing only the value of $V_{e\text{ff}}$. On the other hand, $\Delta_{e\text{ff}}$ and $U_{d\text{f}}$ have been regarded as constant values for all concentration $y$ ($\Delta_{e\text{ff}} = 10$ meV and $U_{d\text{f}} = 10.2$ eV). The estimated Sm valence and $V_{e\text{ff}}$ are shown as functions of $y$ in the inset of Fig. 3. With increasing $y$ the Sm valence increases while the value of $V_{e\text{ff}}$ decreases. The Sm 4f states are hybridized with the rare-earth 5$d$ and B 2$sp$ states around $E_F$. The Eu substitution for Sm could induce the shift of the rare-earth 5$d$ and B 2$sp$ bands toward the unoccupied state side, which causes a decrease
of the valence-band density of state near $E_F$ and consequently the reduction of $V_{\text{eff}}$. Such rigid-band shifts have been observed in the valence-band HAXPES spectra for Sm$_{1-y}$Eu$_y$B$_6$ (data not shown), which is consistent with the reduction of $V_{\text{eff}}$ with increasing $y$.

4. Summary
We have carried out the HAXPES measurements for Yb$_{1-x}$Lu$_x$B$_{12}$ and Sm$_{1-y}$Eu$_y$B$_6$. For Yb$_{1-x}$Lu$_x$B$_{12}$, from the NCA analyses, we have found that the $T$ dependence of the Yb$^{2+}$ and Yb$^{3+}$ 4$f$ peaks for $x = 1/8$ could be reproduced with the SIAM, whereas that for $x = 0$ deviates from the SIAM predictions. Therefore, the Kondo lattice coherence is important and plays an essential role in the narrow gap formation for pure YbB$_{12}$. For Sm$_{1-y}$Eu$_y$B$_6$, through spectral analyses based on the SIAM, we have found that the increase of the Sm valence with increasing $y$ is derived from the reduction of the hybridization between the Sm 4$f$ and valence-bands.

Acknowledgments
Financial support was provided by the Grant-in-Aid for Science Research (Contract Nos. 18104007, 18684015, and Innovative Areas “Heavy Electrons” No. 20102003) of MEXT, Japan and the Global COE program (G10) of JSPS, Japan.

References
[1] Kasaya M, Iga F, Negishi K, Nakai S and Kasuya T 1983 J. Magn. Magn. Mater. 31-34 437
[2] Menth A, Buehler E and Geballe T H 1969 Phys. Rev. Lett. 22 295
[3] Okamura H et al 2000 Phys. Rev. B 62 R13265
[4] Alekseev P A et al 2004 J. Phys.: Condens. Matter 16 2631
[5] Tarascon J M et al 1980 J. Phys. France 41 1135
[6] Iga F, Shimizu N and Takabatake T 1998 J. Magn. Magn. Mater. 177-181 337
[7] Saso T and Harima H 2003 J. Phys. Soc. Japan 72 1131
[8] Yeh J J and Lindau I 1985 At. Data Nucl. Data Tables 32 1
[9] Gerken F 1983 J. Phys. F: Met. Phys. 13 703
[10] Yamaguchi J et al 2009 Phys. Rev. B 79 125121
[11] Yamasaki A et al 2007 Phys. Rev. Lett. 98 156402