Evolution of c-f hybridization in valence transition compound $YbInCu_4$ observed by ARPES

R. Kamimori[a], Y. Tanimoto[b], H. Sato[c], M. Arita[c], S. Kumar[c], K. Shimada[c], K. T. Matsumoto[d], K. Hiraoka[d]

[a]*Graduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[b]*Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[c]*Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima 739-0046, Japan*
[d]*Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan*

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Yb compounds shows rich variety of interesting phenomena originated from the hybridization between the delocalized conduction electrons and localized Yb 4*f* electrons (*c* - *f* hybridization). The Yb valence in the compounds often fluctuates between divalent state (Yb^{2+}:$4f^{14}$) and trivalent state (Yb^{3+}:$4f^{13}$) and has a non-integer value averaged over the compounds. $YbInCu_4$ shows a first order valence transition at T_v = 42 K. The mean Yb valences were estimated to be ~2.90 in the high temperature phase and ~ 2.74 in the low temperature phase by means of the hard x-ray photoemission spectroscopy for the Yb 3*d* core states [1]. The magnetic susceptibility changes sharply from the Curie-Weiss behavior above T_v to Pauli paramagnetic behavior below T_v. The Kondo temperature also varies from T_K ~ 25 to ~ 400 K, which indicates that a degree of *c* - *f* hybridization is enhanced in the low temperature phase. A number of studies of electronic structure of $YbInCu_4$ by means of angle-integrated photoemission spectroscopy have been reported [1-3]. We successfully observed the increase of the *c* - *f* hybridization strength below T_v by means of the low-energy excited photoemission spectroscopy at $h\nu$ = 7 eV [3]. On the other hand, angle-resolved photoemission spectroscopy (ARPES) study for $YbInCu_4$ has been limited because it is difficult to prepare a clean and flat surface to obtain the clear ARPES spectra by the usual fracturing method. Only two ARPES results have been reported so far, where the signature of the *c* - *f* hybridization is reported [4, 5]. To observe the evolution of the *c* - *f* hybridization in the low temperature phase of $YbInCu_4$ by ARPES, the preparation of the clean and flat surface is indispensable.

In this study, we prepared the clean and flat $YbInCu_4$(001) surface suitable for ARPES measurements as follows. First, the $YbInCu_4$ single crystal was polished *ex situ* until a mirror-like (001) surface plane was obtained. Then, the polished surface was *in situ* cleaned by repeating Ar ion sputtering and heating at about 400 °C. The cleanliness and flatness of the prepared surface are confirmed by means of the Auger electron spectroscopy and low-energy electron diffraction. Single crystals of $YbInCu_4$ were synthesized by the flux-method. The ARPES experiments on $YbInCu_4$(001) were performed at undulator beamlines BL-1 and BL-9A of Hiroshima Synchrotron Radiation Center (HSRC).

First, we measured incident photon energy dependence of the ARPES spectra of $YbInCu_4$(001) between $h\nu$ = 30 and 172 eV taken at 23 K along [100] direction to observe the k_z dispersion. Figures 1(a) and 1(b) show ARPES intensity plots at $h\nu$ = 64 and 96 eV, respectively. A vertical axis represents binding energy (E_B) relative to the Fermi energy (E_F). The dispersive Cu 3*d* bands are clearly observed around E_B ~ 3 eV. The flat bands due to the bulk-derived Yb^{2+} $4f_{7/2}$ and $4f_{5/2}$ states are found near E_F and 1.35 eV, respectively. From the periodicity of the $h\nu$ dependent ARPES spectra, the inner potential is determined to be about 13 eV. The ARPES spectra at $h\nu$ = 64 and 96 eV (Figs. 1 (a) and 1 (b)) are those along *X* - *U* and *Γ* - *K* directions, respectively.

Figures 2 (a) and (b) present the ARPES spectra measured along [110] direction at 120 K (high temperature phase) and 10 K (low temperature phase), respectively. The excitation energy is $h\nu$ = 14 eV and the ARPES spectra are measured along the *X* - *W* direction. The flat band due to the Yb^{2+} $4f_{7/2}$ states

are observed at $E_B \sim 0.03$ eV and two dispersive upward bands due to the conduction electrons are also detected (*c* and *c'* in Figs. 2(a) and 2(b)). The two conduction electron bands are well reproduced by the band-structure calculation for $LuInCu_4$ using the WIEN2k code [6]. It is noted that the inner conduction electron band (*c*) bents downward just below the Yb^{2+} $4f_{7/2}$ band, indicating the gap formation originated from the *c* - *f* hybridization. The splitting between the two bands is increased at 10 K as shown with "Δ" in Figs. 2(a) and 2(b) for a guide, which indicates that the *c* - *f* hybridization is enhanced in the low temperature phase. The enhanced splitting is clearly seen in the ARPES spectra at $k = 0.17$ Å^{-1} in Fig. 2(c).

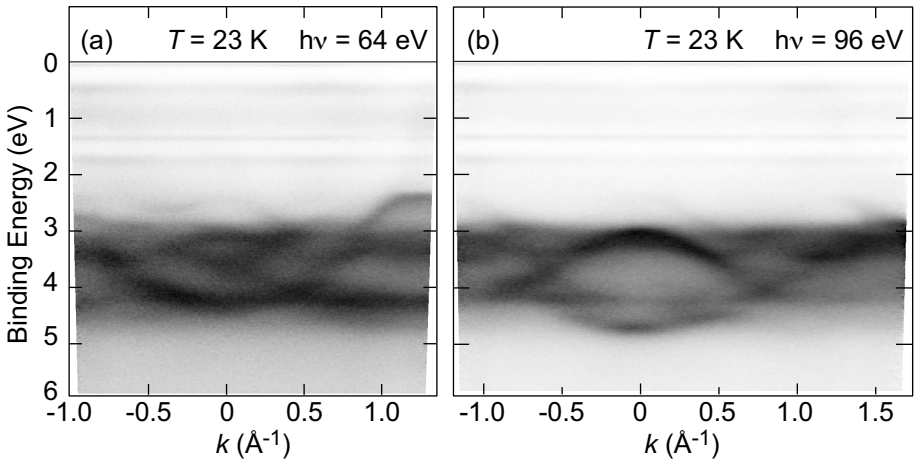

FIGURE 1. ARPES intensity plots of $YbInCu_4$(001) along [100] direction measured at 23 K with (a) $h\nu = 64$ eV and (b) $h\nu = 96$ eV.

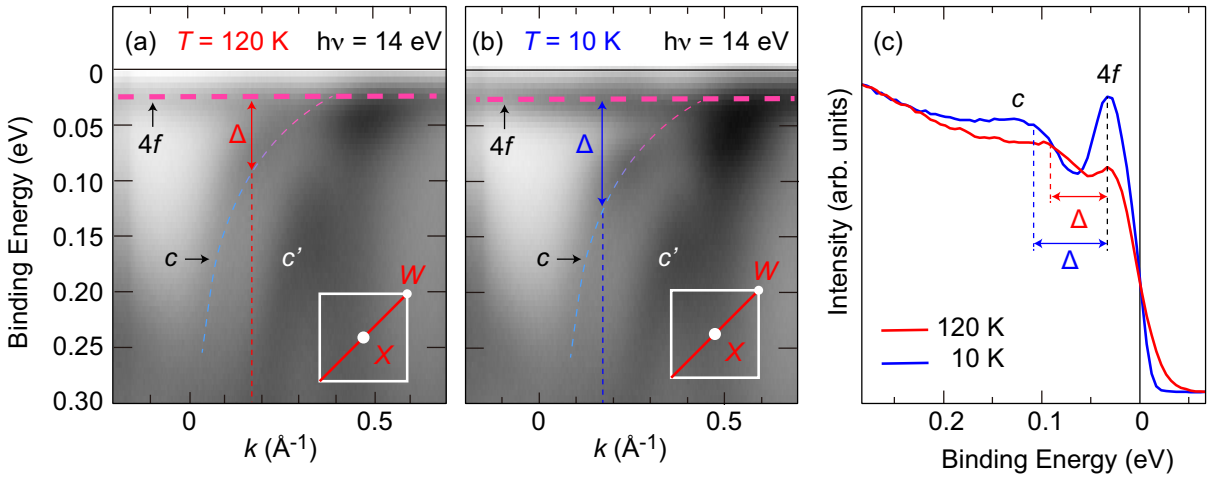

FIGURE 2. ARPES intensity plots of $YbInCu_4$(001) along *X* - *W* directions measured between 120 and 10 K with $h\nu = 14$ eV.

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