

## Valence Transition of YbInCu<sub>4</sub> Observed in Hard X-Ray Photoemission Spectra

Hitoshi Sato,<sup>1,\*</sup> Kenya Shimada,<sup>1</sup> Masashi Arita,<sup>1</sup> Koichi Hiraoka,<sup>2</sup> Kenichi Kojima,<sup>3</sup> Yukiharu Takeda,<sup>1,†</sup> Kunta Yoshikawa,<sup>4</sup> Masahiro Sawada,<sup>1</sup> Masashi Nakatake,<sup>1</sup> Hirofumi Namatame,<sup>1</sup> Masaki Taniguchi,<sup>1,4</sup> Yasutaka Takata,<sup>5</sup> Eiji Ikenaga,<sup>6</sup> Shik Shin,<sup>5,7</sup> Keisuke Kobayashi,<sup>6</sup> Kenji Tamasaku,<sup>8</sup> Yoshinori Nishino,<sup>8</sup> Daigo Miwa,<sup>8</sup> Makina Yabashi,<sup>6</sup> and Tetsuya Ishikawa<sup>8</sup>

<sup>1</sup>Hiroshima Synchrotron Radiation Center, Hiroshima University, Kagamiyama 2-313, Higashi-Hiroshima 739-8526, Japan

<sup>2</sup>Faculty of Engineering, Ehime University, Bunkyo-cho 3, Matsuyama 790-8577, Japan

<sup>3</sup>Faculty of Integrated Arts and Sciences, Hiroshima University, Kagamiyama 1-7-1, Higashi-Hiroshima 739-8521, Japan

<sup>4</sup>Graduate School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526, Japan

<sup>5</sup>Soft X-Ray Spectroscopy Laboratory, RIKEN/SPring-8, Koto 1-1-1, Mikazuki-cho, Sayo-gun, Hyogo 679-5148, Japan

<sup>6</sup>JASRI/SPring-8, Koto 1-1-1, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan

<sup>7</sup>Institute for Solid State Physics (ISSP), The University of Tokyo, Kashiwa, Chiba 277-8581, Japan

<sup>8</sup>Coherent X-Ray Optics Laboratory, RIKEN/SPring-8, Koto 1-1-1, Mikazuki-cho, Sayo-gun, Hyogo 679-5148, Japan

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Yb 3*d* and valence-band photoemission spectra of the first-order valence-transition compound YbInCu<sub>4</sub> have been measured with hard x ray at an excitation energy of 5.95 keV. Abrupt changes are clearly observed in both spectra around the transition temperature  $T_V = 42$  K, in comparison with ultraviolet and soft x-ray photoemission (VUV-PES and SX-PES) spectra. From the Yb 3*d* spectra, the Yb valence has been estimated to be  $\sim 2.90$  from 220 down to 50 K and  $\sim 2.74$  at 30–10 K. We propose that Yb 3*d* hard x-ray photoemission spectroscopy is a very powerful method to estimate the valence of Yb with high accuracy. On the other hand, the Yb<sup>2+</sup> 4*f*-derived peaks in the valence-band spectra exhibit a remarkable enhancement below  $T_V$ . The shape of the valence-band spectra is different from those of the VUV-PES and SX-PES spectra above  $T_V$ , reflecting the In 5*s* and 5*p* contributions.

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YbInCu<sub>4</sub> has attracted great interest because of the first-order valence transition at  $T_V = 42$  K [1–3]. In accordance with the valence transition, abrupt changes in the lattice volume, electrical resistivity, magnetic susceptibility, and other physical properties are observed with no change of the crystal structure. In the high-temperature phase, the Yb valence ( $z$ ) is generally believed to be  $z \sim 3$  from the Curie-Weiss susceptibility, and the valence change at  $T_V$  is estimated to be  $\Delta z \sim 0.1$ , that is,  $z \sim 2.9$  in the low-temperature phase from the lattice expansion taking into account the ionic radii of Yb<sup>2+</sup> and Yb<sup>3+</sup> [2].

In order to observe the valence transition of YbInCu<sub>4</sub> directly, high energy resolution photoemission spectroscopy (PES) experiments have been extensively carried out, so far [4–11]. It is known that the PES experiments yield a smaller Yb valence than that expected from the thermodynamic measurements. Reinert *et al.*, for the first time, performed the detailed temperature-dependent vacuum-ultraviolet PES (VUV-PES) measurements at  $h\nu = 43$  eV [4]. The Yb valence, estimated from the intensity ratio of the Yb<sup>2+</sup> and Yb<sup>3+</sup> 4*f*-derived structures in the valence bands, changes from  $z \sim 2.85$  at 220 K to  $z \sim 2.56$  at 20 K rather continuously even passing through the valence transition. Based on the small probing depth  $\lambda \sim 5\text{Å}$  of VUV-PES at  $h\nu = 43$  eV [12], they proposed the existence of a subsurface region with different physical properties from the bulk.

In our previous soft x-ray PES (SX-PES) experiments at  $h\nu = 800$  eV, the estimated Yb valence is  $z \sim 2.81$  at 100 K, decreases gradually to 50 K, and changes sharply to  $z \sim 2.68$  at 40 K [11]. We find, however, some discrepancies between the SX-PES and thermodynamic results; (i) the Yb valence begins to decrease from a temperature higher than  $T_V = 42$  K with lowering temperature, (ii) the Yb valence is still smaller than that expected from the thermodynamic data.

Recently, hard x-ray PES (HX-PES) has been successfully realized [13,14]. Since the escape depth of photoelectrons with a kinetic energy between 5 and 10 keV ranges from around 50 to over 100 Å [14], HX-PES can probe a much deeper region from the surface than VUV-PES and SX-PES. In this Letter, we present the Yb 3*d* and valence-band HX-PES spectra of YbInCu<sub>4</sub> with the drastic change around the valence transition, and demonstrate that the Yb 3*d* HX-PES spectra are strikingly powerful for the valence estimation.

The HX-PES experiments were performed on beam line BL29XU of SPring-8 [15]. Synchrotron radiation from the undulator was monochromatized to 5.95 keV with a Si(111) double crystal and Si(333) channel-cut monochromators. A hemispherical photoelectron analyzer (Gammadata-Scienta SES2002) modified to accommodate photoelectron kinetic energies up to 6 keV, was used to measure the Yb 3*d* and valence-band HX-PES spectra [14]. The total energy resolution was set to 270 meV.

YbInCu<sub>4</sub> single crystals were grown by a flux method similar to that described by Sarrao *et al.* [16]. By means of magnetic susceptibility measurements, we confirmed that the transition temperature of the present sample was  $T_V = 42$  K with a width of 2 K. Clean surfaces were obtained by fracturing at room temperature under  $5 \times 10^{-9}$  Torr in the preparation chamber, and the samples were immediately transferred into the analysis chamber below  $3 \times 10^{-10}$  Torr. The HX-PES experiments were carried out only on the first cooling through the valence transition in order to prevent the defect formation in the sample by repetition passing through the transition [16]. Binding energy is referred to the Fermi level ( $E_F$ ) estimated from Au spectra.

Figure 1 shows the temperature dependence of the Yb  $3d$  HX-PES spectra of YbInCu<sub>4</sub> measured between 220 and 10 K. The Yb  $3d$  spectra are split into the  $3d_{5/2}$  region at 1515–1540 eV and  $3d_{3/2}$  region at 1560–1585 eV due to the spin-orbit interaction. In comparison with  $3d_{5/2}$  spectra of the Yb metal and Yb<sub>2</sub>O<sub>3</sub> [17], where the Yb ions are purely divalent and trivalent, respectively, a single peak at 1519.5 eV is attributed to the Yb<sup>2+</sup>  $3d_{5/2}$  states and multiplet structures at 1524–1536 eV to the Yb<sup>3+</sup>  $3d_{5/2}$  states. Similarly, a single peak at 1567 eV and multiplet structures at 1572–1584 eV are assigned to the Yb<sup>2+</sup>  $3d_{3/2}$  and Yb<sup>3+</sup>  $3d_{3/2}$  states, respectively. Broad structures at 1543 and 1591 eV are due to plasmon excitations. It should be noticed that the drastic change in intensity is clearly observed from 50 to 30 K through the valence transition.

In order to estimate the Yb valence from the intensity ratio of the Yb<sup>2+</sup>- and Yb<sup>3+</sup>-derived structures [18], we have carried out the curve fitting of the Yb  $3d$  spectra. For simplicity, Gaussian functions were assumed for the plas-

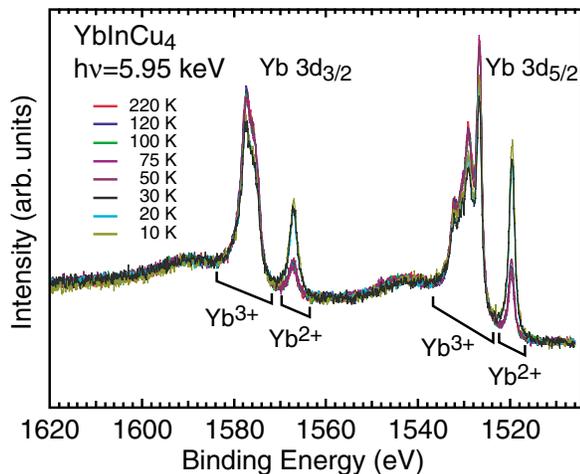


FIG. 1 (color). Temperature-dependent Yb  $3d$  HX-PES spectra of YbInCu<sub>4</sub> from 220 to 10 K. Spectra are classified into the  $3d_{5/2}$  and  $3d_{3/2}$  regions and both parts clearly separate further into the Yb<sup>2+</sup> and Yb<sup>3+</sup> components. Between 50 and 30 K, a remarkable change is observed, reflecting the valence transition at  $T_V = 42$  K.

mon curves. On the other hand, line spectra convoluted with the Lorentzian function for lifetime broadening and the Gaussian function for the instrumental resolution of 270 meV were assumed to stand for the Yb  $3d$  structures. The Yb<sup>3+</sup>  $3d$  structures were fitted using the slightly modified results of the atomic multiplet calculation. As a typical example, the fitting result of the experimental spectrum at 10 K is drawn in Fig. 2. The Yb<sup>2+</sup>  $3d$  lines and Yb<sup>3+</sup>  $3d$  multiplets are also shown as vertical lines. The background contribution due to secondary electrons was estimated by Shirley's method [20]. The fitting curve reproduces well the experimental spectrum with respect to the relative intensity and spectral width.

The estimated Yb valences from the fitting procedure are shown by circles in Fig. 3, in comparison with the results of the VUV-PES by diamonds [4,21] and SX-PES by squares [11]. Here,  $\lambda$  for the VUV-PES, SX-PES, and HX-PES are expected to be 5, 15, and 75 Å, respectively [12]. The Yb valence at 220 K is  $z \sim 2.90$ , almost constant down to 50 K, and then sharply drops to  $z \sim 2.74$  from 50 to 30 K through the valence transition. It should be noticed that the results for the Yb valence are the closest to the thermodynamic results (see Fig. 3), and the change through the valence transition is the sharpest among the three PES measurements.

The Yb valences derived from the VUV-PES [4] and also SX-PES [11] spectra gradually decrease with lowering

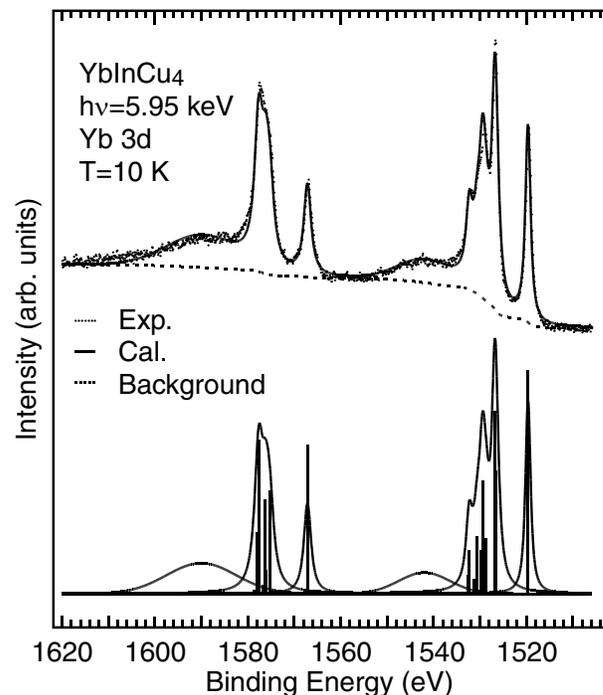


FIG. 2. Curve fitting of the Yb  $3d$  HX-PES spectrum of YbInCu<sub>4</sub> measured at 10 K. Line spectra convoluted with the Lorentzian function for a lifetime broadening and Gaussian function for an instrumental resolution are used. Plasmon-derived structures are represented by Gaussian functions.

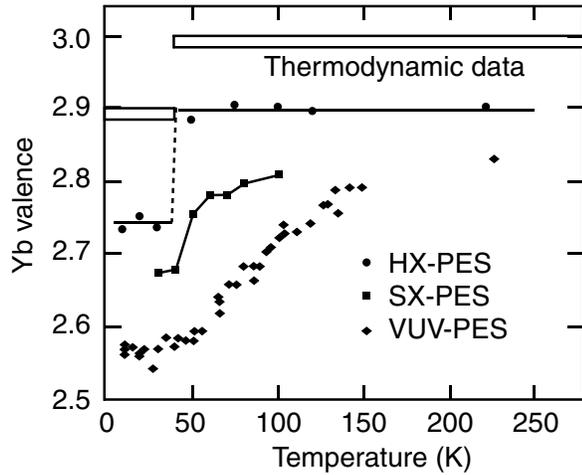


FIG. 3. Temperature-dependent Yb valence derived from the Yb 3d HX-PES spectra, in comparison with the VUV-PES [4] and SX-PES [11] results. Thermodynamic results are also shown.

temperature in advance of the valence transition at  $T_V = 42$  K. On the other hand, the Yb valence evaluated from the Yb 3d HX-PES above  $T_V$  is almost constant and the change at  $T_V$  is very sharp. These results indicate that the Yb 3d HX-PES spectra with large  $\lambda$  are almost free from contribution of the subsurface region [4] with a transition temperature higher than  $T_V = 42$  K in the bulk, probably due to a change of the stoichiometry or lattice distortion near the surface [11]. From the VUV-PES results with the continuous change [4] and SX-PES results with the discontinuous change at  $T_V$  [11], the thickness of the subsurface region is expected to be 5–15 Å.

While the thermodynamic measurements provide indirect information on the Yb valence, x-ray spectroscopies can observe the  $\text{Yb}^{2+}$  and  $\text{Yb}^{3+}$  components directly. Just after the discovery of  $\text{YbInCu}_4$ , Yb  $L_{\text{III}}$ -edge x-ray absorption spectroscopy (XAS) experiments were carried out to evaluate the Yb valence [2]. In case of the Yb  $L_{\text{III}}$  XAS, however,  $\text{Yb}^{2+}$ - and  $\text{Yb}^{3+}$ -derived spectra fairly overlap each other and there are some ambiguities in the separation of the spectrum into the two components. In addition, the Lu  $L_{\text{III}}$  XAS spectrum of  $\text{LuInCu}_4$  is substituted for the  $\text{Yb}^{2+}$ - and  $\text{Yb}^{3+}$ -derived XAS spectra for deconvolution [22]. The accuracy of the analysis is, thus, rather limited. Recently, on the other hand, Dallera *et al.* reported that bulk-sensitive Yb  $L_{\alpha 1}$  resonant inelastic x-ray scattering (RIXS) experiments can detect the sharp valence transition of  $\text{YbInCu}_4$  [23]. Because of the resonance enhancement, however, the relative intensity between the  $\text{Yb}^{2+}$  and  $\text{Yb}^{3+}$  components, which also overlap in the RIXS spectrum, does not provide the Yb valence directly and one has to rely on the XAS spectrum as a reference of the Yb valence.

One can recognize that Yb 3d HX-PES spectra are very suitable to overcome the difficulties for the Yb valence estimation described above. No other core states from the

In and Cu ions, and no other Auger electrons disturb the Yb 3d spectra. Furthermore, the  $\text{Yb}^{2+}$ - and  $\text{Yb}^{3+}$ -derived structures are well separated. In addition, the hybridization effect is negligible for the Yb valence estimation, in contrast to the valence-band PES spectra, where conduction-band (CB) states hybridized with Yb 4f states also contribute to the intensity just in the same region of the  $\text{Yb}^{2+}$  4f peak. The analysis of Yb 3d spectra is obvious and the Yb valence can solely be derived. Yb 3d HX-PES can thus be regarded as the straightforward method for the quantitative estimation of the Yb valence with high accuracy in comparison to Yb  $L_{\text{III}}$  XAS, Yb  $L_{\alpha 1}$  RIXS and valence-band PES.

Here, we comment on the deviation of the present Yb valences from the thermodynamic results. As for the high-temperature phase, according to recent magnetic susceptibility measurements, the effective magnetic moment derived from the Curie constant is  $\mu_{\text{eff}} = 4.09\text{--}4.15 \mu_B/\text{Yb}$  [24], smaller than  $\mu_{\text{eff}} = 4.54 \mu_B/\text{Yb}$  for the free  $\text{Yb}^{3+}$  ion. The authors mention that the Yb ion in the high-temperature phase should be trivalent and the reduction of  $\mu_{\text{eff}}$  is caused by the Kondo interaction in terms of the Kondo impurity model. The small  $\mu_{\text{eff}}$  value, however, also suggests an existence of the  $\text{Yb}^{2+}$  ions. In fact, the  $\text{Yb}^{2+}$  component is clearly observed also in the  $L_{\alpha 1}$  RIXS spectra at 50 K [23]. Accordingly, we conclude that some divalent Yb ions actually exist in the bulk even for the high-temperature phase and believe that the Yb valence evaluated from the thermodynamic data with the small  $\mu_{\text{eff}}$  value should be smaller than  $z = 3$ . Also for the valence change at  $T_V$ , the valence estimation using Yb 3d HX-PES is direct, in comparison with that using the lattice expansion [2], which depends on the adopted radii of the  $\text{Yb}^{2+}$  and  $\text{Yb}^{3+}$  ions.

Finally, in Fig. 4, we demonstrate the drastic change due to the valence transition in the valence-band HX-PES spectra measured at 220, 50, and 20 K. Two peaks derived from the  $\text{Yb}^{2+}$  4f<sub>7/2</sub> states at 0.1 eV and  $\text{Yb}^{2+}$  4f<sub>5/2</sub> states at 1.45 eV are significantly enhanced in the spectrum at 20 K compared with those at 50 and 220 K, while the  $\text{Yb}^{3+}$  4f multiplet structures at 5.5–12 eV reduce their intensity. The amount of the enhancement for the  $\text{Yb}^{2+}$  4f peaks is quite remarkable in comparison with the VUV-PES [4] and SX-PES [11] experiments, again indicating that the present spectra are almost free from contribution from the subsurface region due to large  $\lambda$ .

Since CB states such as In 5sp, as well as Yb 4f states, contribute to the valence-band HX-PES spectra [25], its feature is different from those of VUV-PES [4] and SX-PES [11] spectra. In particular, in the top 2 eV region, the spectra at 220 and 50 K basically exhibit the non-4f density of states with two peaks at 0.4 and 1.4 eV. Based on the band-structure calculation of  $\text{YbInCu}_4$  [26] and the photoionization cross sections [25], we tentatively attribute this structure to the In 5p states. The In 5sp and In 5s

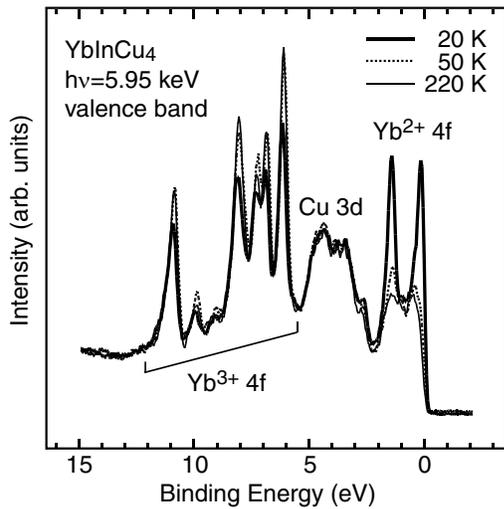


FIG. 4. Temperature-dependent valence-band HX-PES spectra of  $\text{YbInCu}_4$  measured at 220, 50, and 20 K. From 50 to 20 K, the feature of the spectra exhibits a remarkable change, reflecting the valence transition at  $T_V = 42$  K.

contributions are also observed in the  $\text{Cu } 3d$  and  $\text{Yb}^{3+} 4f$  multiplet regions, respectively.

Further improvement of HX-PES with respect to the energy resolution enables us to discuss the change of the  $\text{Yb } 4f$  and CB states around the valence transition simultaneously. The detailed studies of the high energy resolution valence-band HX-PES spectra near  $E_F$ , is expected to reveal which orbitals mainly hybridize with the  $\text{Yb } 4f$  states and play an important role for the valence transition of  $\text{YbInCu}_4$ .

In summary, by means of HX-PES, we have successfully observed the sharp valence transition of  $\text{YbInCu}_4$  in both the  $\text{Yb } 3d$  and valence-band spectra. The  $\text{Yb}$  valence is estimated to be  $\sim 2.90$  and  $\sim 2.74$  in the high-temperature and low-temperature phases, respectively. The change of the valence-band HX-PES spectra through the valence transition is quite drastic in comparison with the VUV-PES [4] and SX-PES [11] results.

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\*Electronic address: jinjin@hiroshima-u.ac.jp

†Present address: Synchrotron Radiation Research Center, JAERI/SPring-8, Koto 1-1-1, Mikazuki-cho, Sayo-gun, Hyogo 679-5148, Japan

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