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Low-energy excited photoemission study of the valence transition of $YbInCu_4$

Kunta Yoshikawa,[1,*] Hitoshi Sato,[2] Masashi Arita,[2] Yukiharu Takeda,[2,†] Koichi Hiraoka,[3] Kenichi Kojima,[4] Kenichiro Tsuji,[1]
Hirofumi Namatame,[2] and Masaki Taniguchi[1,2]
[1]*Graduate School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526, Japan*
[2]*Hiroshima Synchrotron Radiation Center, Hiroshima University, Kagamiyama 2-313, Higashi-Hiroshima 739-8526, Japan*
[3]*Faculty of Engineering, Ehime University, Bunkyo-cho 3, Matsuyama 790-8577, Japan*
[4]*Faculty of Integrated Arts and Sciences, Hiroshima University, Kagamiyama 1-7-1, Higashi-Hiroshima 739-8521, Japan*
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Low-energy excited photoemission spectra of $YbInCu_4$ with isostructural first-order valence transition at $T_V=42$ K have been measured with high-energy resolution. In the spectra measured at $h\nu=7$ eV in the low-temperature phase, the hybridization between the conduction-band (CB) and Yb $4f$ states is successfully observed as a structure at ~ 47 meV below the Fermi level. This structure abruptly shows up below T_V, indicating that a degree of the CB—Yb $4f$ hybridization increases in the low-temperature phase. Temperature dependence of the spectra at $h\nu=14$ eV suggests that the valence transition takes place at higher temperatures than $T_V=42$ K in some phases near the surface.

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I. INTRODUCTION

$YbInCu_4$ is a valence fluctuating compound with an isostructural first-order valence transition at $T_V=42$ K.[1–3] The magnetic susceptibility in the high-temperature phase exhibits the Curie-Weiss behavior and the effective magnetic moment is estimated to be $p=4.64\mu_B$,[4] showing that the Yb valence is close to $z\sim 3.0$. From the abrupt increase of the lattice constant of about 0.5% at T_V, the decrease of the valence below T_V is evaluated to be $\Delta z\sim 0.1$ taking into account the ionic radii of the Yb^{2+} and Yb^{3+} ions.[2]

Photoemission spectroscopy (PES) is a powerful tool to observe the electronic states of solids. A great number of high-energy resolution PES experiments have been carried out for $YbInCu_4$, mainly focused on the Yb $4f$ states to detect the valence transition directly.[5–12] The Yb valence, derived from the valence-band PES spectra measured between $h\nu=43$ and 800 eV, is smaller than those from thermodynamic measurements of the magnetic susceptibility and lattice constant,[5,7,12] and the change around T_V is rather gradual in contrast to the sharp change observed in the other physical properties.[13] Reinert *et al.* pointed out that the inconsistencies of the Yb valence and its temperature dependence between PES and thermodynamic data are due to the surface sensitivity of PES with the small probing depth λ and that there exists the subsurface region with different properties from the bulk.[5]

Recently, we have carried out the hard x-ray PES at $h\nu=5.95$ keV in order to detect the valence transition in the bulk.[14] The sharp valence transition is successfully observed in the Yb $3d$ and the valence-band hard x-ray PES spectra. The analysis of the $3d$ spectra clearly provides the Yb valence close to the thermodynamic results in comparison with PES using ultraviolet and soft x-ray regions.[5–12]

On the other hand, in the valence transition of $YbInCu_4$, the Kondo temperature (T_K), which is a measure of hybridization between the conduction-band (CB) and Yb $4f$ states (c-f hybridization), also changes from $T_{K+}\sim 25$ K in the high-temperature phase to $T_{K-}\sim 400$ K in the low-temperature phase.[15] The Yb^{2+} $4f_{7/2}$ peak of the Yb compounds, called the Kondo resonance peak, appears at k_BT_K below the Fermi level (E_F) according to the single-impurity Anderson model (SIAM).[16] Within SIAM, the change of the Kondo temperature ΔT_K should be observed as a discontinuous shift of the Kondo resonance peak by $k_B\Delta T_K\sim 32$ meV. However, the smaller shifts of only 5 (Ref. 10) and 3 meV (Ref. 11) have been reported, so far.

The increase of T_K suggests that the degree of the c-f hybridization increases at the valence transition from the high- to low-temperature phases. In order to investigate the change of the c-f hybridization and further reveal the mechanism of the valence transition, the experimental knowledge on the behavior of the CB states around T_V becomes essentially important.

In this study, we have carried out the low-energy excited PES experiments at $h\nu=7$ eV for the $YbInCu_4$ single crystal with high-energy resolution, in order to investigate the CB states through the valence transition in the bulk. Although it is difficult to estimate accurately the photoionization cross section of orbitals at this energy, because no information for the low-energy case is given in the widely referred-to tables by Yeh,[17] the Yb^{2+} $4f$ components clearly observed in the PES spectra of YbB_{12} measured at $h\nu=125$ eV become negligibly small at 21.2 eV.[18] Also for the PES spectrum of $YbSnCu_4$ at $h\nu=7$ eV, we find only an almost flat structure in the Yb^{2+} $4f$ peak region.[19] Thus the PES spectra at $h\nu=7$ eV are considered to provide information on the electronic structure of the CB states. As concerns the probing depth λ of the PES spectra, recently, Kiss *et al.* have demonstrated that the feature of the PES spectra of Nb using vacuum ultraviolet laser at $h\nu=6.994$ eV is essentially unchanged before and after the surface treatment, indicating that the spectrum is sensitive to the bulk.[20] The λ value depends strongly on materials and, in particular, shows different behaviors for the electron kinetic region less than 200 eV due to the different electron-loss functions.[21] Although we

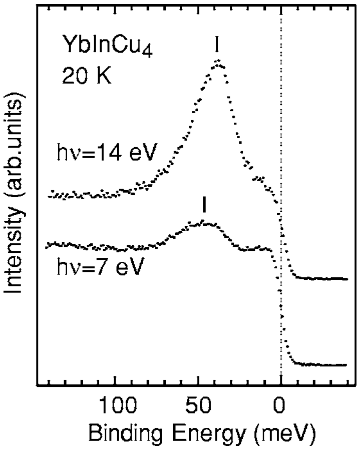

FIG. 1. PES spectra of $\mathrm{YbInCu_4}$ measured at 20 K with the excitation energies of $h\nu=7$ and 14 eV.

have no experimental data of λ for $\mathrm{YbInCu_4}$, the PES spectra at $h\nu=7$ eV also for $\mathrm{YbInCu_4}$ are assumed to be sensitive to the bulk, as shown by the results by Kiss *et al.*[20] (see Fig. 2).[22] We have also performed the PES experiments at $h\nu=14$ eV in order to discuss the *c*-*f* hybridization and λ dependence of the spectra.

II. EXPERIMENT

The low-energy excited PES experiments for $\mathrm{YbInCu_4}$ were carried out using a hemispherical analyzer (Gammadata-Scienta SES2002) on the beamline BL-9 of the synchrotron light source (HiSOR) at Hiroshima Synchrotron Radiation Center (HSRC). The beam from an undulator is monochromatized using an off-plane Eagle-type monochromator with a 600-lines/mm spherical grating.[23,24] The total energy resolution was set to 8 meV. Clean surfaces were obtained *in situ* by fracturing at 80 K in the analysis chamber with a working pressure of 3.0×10^{-10} Torr. After fracturing, the PES experiments were carried out only on the first cooling to 20 K through the valence transition,[7,8] in order to prevent a formation of defects in the sample by repetition passing through the transition temperature.[13] The binding energy of the PES spectra is defined with respect to E_F, determined from the Au spectra.

Single crystals of $\mathrm{YbInCu_4}$ were grown by the flux method similar to that described by Sarrao *et al.*[13] The constituent elements with stoichiometric ratios in InCu flux were put in an alumina crucible and sealed in an evacuated quartz ampoule. Then the sample was heated to 1100 °C and cooled slowly to 800 °C. After keeping at 800 °C for 20 h, the flux was removed. The crystal structure of the grown sample was confirmed to be the C15b type by x-ray powder-diffraction measurements. The temperature width of the valence transition at $T_V=42$ K was below 2 K, confirmed from the magnetic susceptibility measurements.

III. RESULTS AND DISCUSSION

Figure 1 shows the PES spectra of $\mathrm{YbInCu_4}$ near E_F measured at 20 K with the excitation energies of $h\nu=7$ and 14 eV. We find that the spectrum at $h\nu=14$ eV exhibits a prominent peak at 39 meV. A basic feature of the spectrum is similar to that of the PES spectra at $h\nu=21.2$ (Refs. 10 and 11), 43 (Ref. 5), and 60 eV (Ref. 7). In comparison with the previous works, this peak is assigned to the Yb^{+2} $4f_{7/2}$ states hybridized with the CB states. On the other hand, the spectrum at $h\nu=7$ eV shows a different feature from that at $h\nu=14$ eV. As mentioned in the section of introduction, the structure around 47 meV is considered to be due to almost pure CB states hybridized with the Yb 4*f* states. The CB-derived structure appears in almost the same binding-energy region of the main peak at $h\nu=14$ eV.

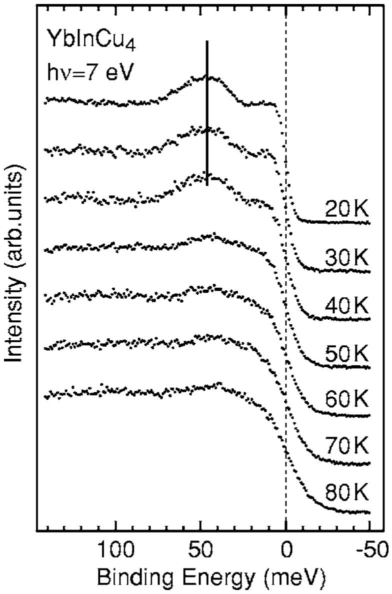

FIG. 2. Temperature dependence of PES spectra of $\mathrm{YbInCu_4}$ measured at $h\nu=7$ eV from 80 to 20 K. The structure around 47 meV suddenly increases through the valence transition from 50 to 40 K.

The temperature dependence of the PES spectra measured at $h\nu=7$ eV from 80 to 20 K is shown in Fig. 2. The spectra are normalized using the spectral intensities in the binding-energy region of 100–150 meV. Above 50 K, we find no peak structure and the substantially weak and broad structure is only observed over the top 70-meV region. With decreasing temperature through the valence transition from 50 to 40 K, the structure suddenly shows up at 47 meV (vertical bar). It should be noticed that the spectral feature is almost unchanged for the high-temperature phase and also for the low-temperature phase. The remarkable change takes place sharply between 50 and 40 K. Such a sharp change of the PES spectra is not observed[25] in the previous PES spectra measured below $h\nu=800$ eV.[5,6,9–12] This experimental result clearly shows that the spectra at $h\nu=7$ eV are actually sensitive to the bulk and the CB states abruptly changes due to the valence transition. From the energy position of 47 meV, roughly corresponding to $k_BT_K(T_{K-}\sim400$ K),[15] the structure observed below T_V would be related to the Kondo resonance state from the viewpoint of the CB states. In addition, the temperature dependence of the PES spectra at $h\nu=7$ eV indicates that a degree of the *c*-*f* hybridization increases in the

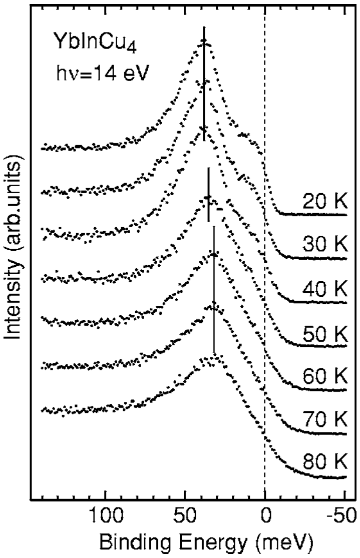

FIG. 3. Temperature dependence of PES spectra of $\mathrm{YbInCu_4}$ measured at $h\nu=14$ eV from 80 to 20 K. The peak energy shifts toward the deeper binding-energy with decreasing temperature.

low-temperature phase, in qualitatively agreement with the increase of T_K.

We present the temperature dependence of the PES spectra measured at $h\nu=14$ eV from 80 to 20 K in Fig. 3. The spectra are normalized using the spectral intensities in the binding-energy region of 100–150 meV. The prominent structures, originating from the Yb^{2+} $4f_{7/2}$ states hybridized with the CB states, appear at 33 meV for the spectra at 80, 70, and 60 K, and 35 meV for 50 K above T_V, while 39 meV for 40, 30, and 20 K below T_V. The energy shift toward the deeper binding-energy side with decreasing temperature is consistent with the increase of T_K. An amount of the shift of $\Delta E\sim 6$ meV between 80 and 20 K is substantially small in comparison with the amount of $k_B\Delta T_K\sim 32$ meV expected from SIAM, which has previously been pointed out from the PES experiments at $h\nu=21.2$ eV.[10,11] The peak intensity increases with decreasing temperature, in particular, between 50 and 40 K reflecting the valence transition, although the increase of the intensity is still observed from 80 K (see Fig. 4). The similar temperature dependence of the peak intensity is also observed in the PES spectra at $h\nu=800$ eV.[12]

We plot the intensity changes of the main structures in the PES spectra at $h\nu=7$ and 14 eV as a function of temperature in Fig. 4. Here, the change between maximum and minimum intensities is normalized to 100% after subtracting the constant background from the raw spectra. One notices the intensity begins to gradually increase already from 80 K for $h\nu=14$ eV as mentioned above. On the other hand, the sharp change is observed for $h\nu=7$ eV around the transition temperature, in comparison with the change for $h\nu=14$ eV. These experimental results are assumed to come from the fact that the PES spectra at $h\nu=7$ eV is much sensitive to the bulk and the gradual increase observed in the spectra at $h\nu=14$ eV is due to the contribution from the region near the surface, i.e., subsurface region pointed out by Reinert *et al.*[5] One also notices the slight increase in intensity at 50 K for the spectrum measured at $h\nu=7$ eV, which is directly observed in the raw spectra. This means that the contribution of the subsurface region to the spectra is not completely negligible still in the PES spectra at $h\nu=7$ eV.

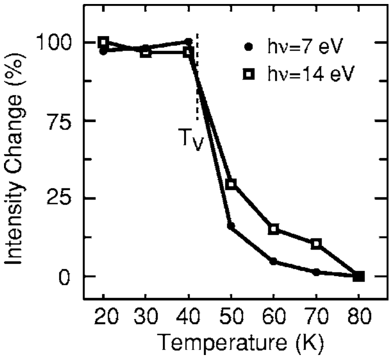

FIG. 4. Intensity change of the main structures in the PES spectra measured at $h\nu=7$ and 14 eV as a function of temperature. The change between maximum and minimum is normalized to 100%. We notice the sharp change for $h\nu=7$ eV and rather gradual change for $h\nu=14$ eV.

From Fig. 3, the Yb^{2+} $4f_{7/2}$ peak energy in the high-temperature phase is deeper than $k_BT_{K+}(T_{K+}\sim 25$ K) and is rather close to $k_BT_{K-}(T_{K-}\sim 400$ K), although that in the low-temperature phase nearly reflects $T_{K-}\sim 400$ K. From these experimental results, we assume that the transition temperatures in the subsurface region are substantially higher than $T_V=42$ K of the bulk. The Yb^{2+} $4f_{7/2}$ peaks observed around 33–35 meV at 80–50 K in Fig. 3 would be signals almost from the subsurface region, where some phases already undergo the valence transition even above $T_V=42$ K. This assumption also interprets that the Yb valence estimated from the PES experiments at $h\nu=43$ (Ref. 5) and 800 eV (Ref. 12) decreases in advance of the valence transition.

The higher transition temperature is qualitatively understood taking into account that the Yb valence of an outer most layer is divalent, while nearly trivalent in the bulk. Since the ionic radius of the Yb^{2+} ion is about 10% larger than that of the Yb^{3+} ion, the lattice constant in the subsurface region should be larger than that in the bulk. With the larger space around the Yb ion, the transition to the divalent states is easy to take place.

Now, we shall be concerned with the CB states hybridized with the Yb^{2+} $4f_{7/2}$ states in $\mathrm{YbInCu_4}$. The Cu $3d$, $4sp$, Yb $5d$, $6s$, and In $5sp$ states compose the CB states of $\mathrm{YbInCu_4}$. In order to experimentally specify the main orbitals hybridized with the Yb^{2+} $4f_{7/2}$ states in the low-temperature phase, we have carried out the same experiments for the $\mathrm{YbCdCu_4}$ single crystal[26,27] with the same C15b-type crystal structure as $\mathrm{YbInCu_4}$. $\mathrm{YbCdCu_4}$ does not show the valence transition and T_K of $\mathrm{YbCdCu_4}$ is estimated to be $\sim$220 K.[28] The valence electrons of the Cd and In atoms are nominally $(5s)^2$ and $(5s)^2(5p)$, respectively.

Figure 5 exhibits the low-energy excited PES spectra of $\mathrm{YbCdCu_4}$ measured at 20 K.[29] In the spectra at $h\nu=14$ eV, we notice a peak at $\sim$20 meV due to the Yb^{2+} $4f_{7/2}$ states hybridized with the CB states. The energy position quantitatively corresponds to k_BT_K ($T_K\sim 220$ K).[28] Also in the spectra at $h\nu=7$ eV, a broad structure due to the CB states is

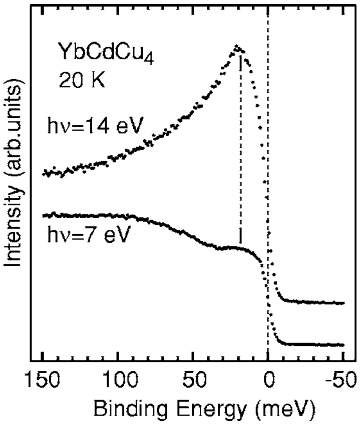

FIG. 5. PES spectra of $YbCdCu_4$ measured at 20 K with the excitation energies of $h\nu=7$ and 14 eV.

slightly observed at ~20 meV. We consider that this structure would be related to the Kondo resonance state of $YbCdCu_4$ from the viewpoint of the CB states.[30] However, the intensity is negligibly weak in comparison with that of main structure at 47 meV for $YbInCu_4$ in the low-temperature phase (Fig. 1).

The different experimental results between the spectra of $YbInCu_4$ and $YbCdCu_4$ measured at $h\nu=7$ eV indicate that the main structure at 47 meV for $YbInCu_4$ is not related to the Yb and Cu-derived CB states. Under assumptions of the nearly equal photoionization cross sections of the In $5s$ and Cd $5s$ states, we are clearly led to the conclusion that the In $5p$ states mainly contribute to the main structure at 47 meV for $YbInCu_4$. Although the photoionization cross sections are not given for the low-energy case, only that of the In $5p$ states rapidly increases with decreasing $h\nu$ from 16.7 to 10 eV.[17] The present result shows that the hybridization between the In $5p$ and Yb^{2+} $4f_{7/2}$ states suddenly changes followed by the valence transition. According to the band-structure calculation of $YbInCu_4$,[31] the In $5p$ states more contribute near E_F than the In $5s$ states. Thus it is expected that the In $5p$-Yb^{2+} $4f_{7/2}$ hybridization plays the most important role for the valence transition of $YbInCu_4$ among the c-f hybridization.

IV. CONCLUSION

The low-energy excited PES measurements with the high-energy resolution have been carried out from 80 to 20 K for the $YbInCu_4$ single crystal and the CB electronic structure near E_F in the bulk has been investigated. The CB-derived structure in the PES spectra at $h\nu=7$ eV suddenly grows in intensity through the valence transition from the high- to low-temperature phases. In comparison with the PES spectra of $YbCdCu_4$, this structure is mainly attributed to the In $5p$ states hybridized with the Yb^{2+} $4f_{7/2}$ states, and the In $5p$ states are expected to contribute largely to the valence transition of $YbInCu_4$. The energy position of the Yb^{2+} $4f_{7/2}$ peak in the PES spectra at $h\nu=14$ eV supports the existence of the subsurface region[5] with the higher transition temperature.[12]

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*Electronic address: kunta@hiroshima-u.ac.jp
†Also at Synchrotron Radiation Research Center, JAERI/SPring-8, Koto 1-1-1, Mikazuki-cho, Sayo-gun, Hyogo 679-5148, Japan.

[1] I. Felner and I. Nowik, Phys. Rev. B **33**, 617 (1986).
[2] I. Felner, I. Nowik, D. Vaknin, U. Potzel, J. Moser, G. M. Kalvius, G. Wortmann, G. Schmiester, G. Hilscher, E. Gratz, C. Schmitzer, N. Pillmayr, K. G. Prasad, H. de Waard, and H. Pinto, Phys. Rev. B **35**, 6956 (1987).
[3] K. Kojima, H. Hayashi, A. Minami, Y. Kasamatsu, and T. Hihara, J. Magn. Magn. Mater. **81**, 267 (1989).
[4] B. Kindler, D. Finsterbusch, R. Graf, F. Ritter, W. Assmus, and B. Luthi, Phys. Rev. B **50**, 704 (1994).
[5] F. Reinert, R. Claessen, G. Nicolay, D. Ehm, S. Hüfner, W. P. Ellis, G.-H. Gweon, J. W. Allen, B. Kindler, and W. Asmus, Phys. Rev. B **58**, 12808 (1998).
[6] J. J. Joyce, A. J. Arko, J. L. Sarrao, K. S. Graham, Z. Fisk, and P. S. Riseborough, Philos. Mag., Suppl. **9**, 1 (1999).
[7] D. P. Moore, J. J. Joyce, A. J. Arko, J. L. Sarrao, L. Morales, H. Höchst, and Y. D. Chuang, Phys. Rev. B **62**, 16492 (2000).
[8] J. J. Joyce, A. J. Arko, L. Morales, J. L. Sarrao, and H. Höchst, Phys. Rev. B **63**, 197101 (2001).
[9] F. Reinert, R. Claessen, G. Nicolay, D. Ehm, S. Hüfner, W. P. Ellis, G.-H. Gweon, J. W. Allen, B. Kindler, and W. Asmus, Phys. Rev. B **63**, 197102 (2001).
[10] T. Susaki, A. Fujimori, M. Okusawa, J. L. Sarrao, and Z. Fisk, Solid State Commun. **118**, 413 (2001).
[11] H. Sato, K. Hiraoka, M. Taniguchi, Y. Nishikawa, F. Nagasaki, H. Fujino, Y. Takeda, M. Arita, K. Shimada, H. Namatame, A. Kimura, and K. Kojima, J. Phys.: Condens. Matter **14**, 4445 (2002).
[12] H. Sato, K. Yoshikawa, K. Hiraoka, M. Arita, K. Fujimoto, K. Kojima, T. Muro, Y. Saitoh, A. Sekiyama, S. Suga, and M. Taniguchi, Phys. Rev. B **69**, 165101 (2004).
[13] J. L. Sarrao, C. D. Immer, C. L. Benton, Z. Fisk, J. M. Lawrence, D. Mandrus, and J. D. Thompson, Phys. Rev. B **54**, 12207 (1996).
[14] H. Sato, K. Shimada, M. Arita, K. Hiraoka, K. Kojima, Y. Takeda, K. Yoshikawa, M. Sawada, M. Nakatake, H. Namatame, M. Taniguchi, Y. Takata, E. Ikenaga, S. Shin, K. Kobayashi, K. Tamasaku, Y. Nishino, D. Miwa, M. Yabashi, and T. Ishikawa, Phys. Rev. Lett. **93**, 246404 (2004).
[15] J. M. Lawrence, S. M. Shapiro, J. L. Sarrao, and Z. Fisk, Phys. Rev. B **55**, 14467 (1997).
[16] R. I. R. Blyth, J. J. Joyce, A. J. Arko, P. C. Canfield, A. B.

Andrews, Z. Fisk, J. D. Thompson, R. J. Bartlett, P. Riseborough, J. Tang, and J. M. Lawrence, Phys. Rev. B **48**, 9497 (1993).

[17] J. J. Yeh, *Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters* (Gordon and Breach Science Publishers, Langhorne, PA, 1993).

[18] T. Susaki, A. Sekiyama, K. Kobayashi, T. Mizokawa, A. Fujimori, M. Tsunekawa, T. Muro, T. Matsushita, S. Suga, H. Ishii, T. Hanyu, A. Kimura, H. Namatame, M. Taniguchi, T. Miyahara, F. Iga, M. Kasaya, and H. Harima, Phys. Rev. Lett. **77**, 4269 (1996).

[19] Unpublished data.

[20] T. Kiss, T. Shimojima, F. Kanetaka, K. Kanai, T. Yokoya, S. Shin, Y. Onuki, T. Togashi, C. Q. Zhang, C. T. Chen, and S. Watanabe, J. Electron Spectrosc. Relat. Phenom. **144–147**, 953 (2005).

[21] C. J. Powell, A. Jablonski, I. S. Tilinin, S. Tanuma, and D. R. Penn, J. Electron Spectrosc. Relat. Phenom. **98–99**, 1 (1999).

[22] For the materials with the unusual low-energy excitations, λ may show the anomalous behavior possibly, but unlikely.

[23] T. Matsui, H. Sato, K. Shimada, M. Arita, S. Senba, H. Yoshida, K. Shirasawa, M. Morita, A. Hiraya, H. Namatame, and M. Taniguchi, Nucl. Instrum. Methods Phys. Res. A **467–468**, 537 (2001).

[24] M. Arita, K. Shimada, H. Namatame, and M. Taniguchi, Surf. Rev. Lett. **9**, 535 (2002).

[25] The drastic change around the valence transition has been observed in the valence-band and Yb 3*d* PES spectra measured with hard x ray of $h\nu=5.95$ keV (Ref. 14).

[26] K. Hiraoka, K. Kojima, T. Hihara, and T. Shinohara, J. Magn. Magn. Mater. **140–144**, 1243 (1995).

[27] K. Hiraoka, K. Murakami, S. Tomiyoshi, T. Hihara, T. Shinohara, and K. Kojima, Physica B **281–282**, 173 (2000).

[28] J. L. Sarrao, C. D. Immer, Z. Fisk, C. H. Booth, E. Figueroa, J. M. Lawrence, R. Modler, A. L. Cornelius, M. F. Hundley, G. H. Kwei, J. D. Thompson, and F. Bridges, Phys. Rev. B **59**, 6855 (1998).

[29] For $YbCdCu_4$, the electronic structure in the subsurface region is assumed not to be so different from that in the bulk, since the valence transition does not take place and the ionic radii of the Yb ions are similar between the subsurface region and bulk.

[30] In order to investigate whether the broad structure at ~20 meV is related to the Kondo resonance state of $YbCdCu_4$, the temperature-dependent PES experiments at $h\nu=7$ eV is in progress.

[31] V. N. Antonov, M. Galli, F. Marabelli, A. N. Yaresko, A. Ya. Perlov, and E. Bauer, Phys. Rev. B **62**, 1742 (2000).