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Soft-x-ray high-resolution photoemission study on the valence transitions in $YbInCu_4$

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Valence-band electronic structure of $YbInCu_4$ has been investigated by means of high-resolution photoemission spectroscopy with an excitation energy of $h\nu = 800$ eV. With decreasing temperature from 50 to 40 K, the intensity of the Yb^{2+} $4f$ peak increases remarkably, while that of the Yb^{3+} $4f$ multiplet structures decreases due to the valence transition at 42 K. The Yb valence directly derived from the photoemission spectra is $z \sim 2.81$ at 100 K, decreases continuously to 50 K and changes sharply to $z \sim 2.68$ at 40 K. The larger valence compared with the other photoemission experiments with smaller probing depth suggests that there is a subsurface region in $YbInCu_4$. We have also found that the Yb^{3+} $4f$ multiplet structures shift toward the deeper binding-energy side by ~50 meV with decreasing temperature from 50 to 40 K. This energy shift is assumed to reflect that the energy to add the bare Yb $4f$ hole increases for the low-temperature region in accordance with the valence transition.

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I. INTRODUCTION

$YbInCu_4$ with a C15b-type structure has attracted great interests 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 the other physical properties are observed with no change of the crystal structure. Thermodynamic data have shown that the Yb valence changes from $z \sim 3$ to $z \sim 2.9$ with decreasing temperature,[2] while the Yb L_{III}-edge x-ray absorption spectroscopy (XAS) experiments have shown a change from $z \sim 2.9$ to $z \sim 2.8$.[2,4] The Kondo temperature is also reported to change from $T_{K+} \sim 25$ K to $T_{K-} \sim 400$ K.[5]

For direct investigation of electronic structure of $YbInCu_4$, a great number of photoemission spectroscopy (PES) experiments have been performed so far.[6–14] The Yb valence estimated from the PES experiments was smaller than that from the thermodynamic and Yb L_{III} XAS measurements. Reinert *et al.*, for the first time, carried out the temperature-dependent PES experiments in detail with an excitation energy of $h\nu = 43$ eV and the energy resolution of 80 meV.[7] Growth of the Yb^{2+} $4f_{7/2}$ peak near the Fermi level (E_F) in the PES spectra, was rather continuous through the valence transition, in contrast to the abrupt change of the thermodynamic data. The Yb valence estimated from the intensity ratio of the Yb^{2+} and Yb^{3+} $4f$-derived structures, gradually decreased from $z \sim 2.85$ at 220 K to $z \sim 2.56$ at 20 K. From the experimental results, they proposed an existence of a subsurface region, physical properties of which are different from the bulk, in $YbInCu_4$ within a probing depth of the PES spectra. Reinert *et al.* also performed x-ray photoemission experiments with a monochromatized Al $K\alpha$ line ($h\nu = 1486.6$ eV) and reported the sharp change of the Yb valence compared with the PES measurements at $h\nu = 43$ eV, after expanding the total change to an absolute scale from 0 to 100% over the investigated temperature range.[11] Because of a difficulty for a distinction between bulk and surface contributions to the PES spectra due to the energy resolution of about 300 meV, the authors estimated $z \sim 2.67 \pm 0.15$ only in the low-temperature phase, which is slightly larger than $z \sim 2.56$ obtained from the PES measurements at $h\nu = 43$ eV.[7] Their results indicate that the high-energy resolution PES experiments with the larger probing depth is important.

On the other hand, Moore *et al.* reported the sudden increase in the intensity of the Yb^{2+} $4f_{7/2}$ and $4f_{5/2}$ peaks of the PES spectra at $h\nu = 60$ eV,[9] where the probing depth is not so large, and the authors insisted that there is no subsurface region. They also measured the PES spectrum at 20 K excited with $h\nu = 500$ eV and estimated the Yb valence to be $z \sim 2.60$ at 20 K. Furthermore, by comparing the Yb^{2+} $4f_{5/2}$ peak intensities in the spectra at $h\nu = 60$ eV between above and below T_V (70 and 12 K), they derived $z \sim 2.72$ at 70 K.

In the present study, we have carried out high-energy resolution PES measurements on the $YbInCu_4$ single crystal excited with $h\nu = 800$ eV (Ref. 15) and investigated how the valence-band electronic structure changes near the valence transition. Contribution from the other orbitals to the spectra in the energy range of the Yb^{2+} $4f$-derived structures at $h\nu = 800$ eV is negligible, since the spectra reflect almost only the Yb $4f$ states except for the Cu $3d$ states; the cross section of the Cu $3d$ states relative to that of the Yb $4f$ states is ~0.3 and those of the other orbitals composing the va-

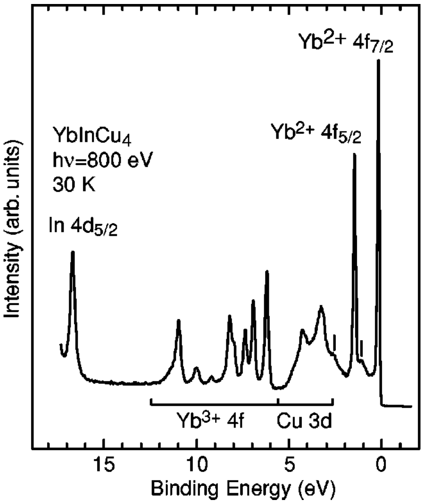

FIG. 1. PES spectrum of $YbInCu_4$ measured at 30 K with $h\nu=800$ eV. The Yb^{2+} $4f_{7/2}$ and $4f_{5/2}$ states are observed near E_F and at 1.45 eV, respectively, together with surface contributions (vertical lines). Structures between 2.5 and 5 eV, between 5 and 12 eV and at ~16.7 eV are ascribed to the Cu $3d$, Yb^{3+} $4f$ and In $4d_{5/2}$ states, respectively.

lence bands are extremely small.[9,16] We can, thus, estimate directly the temperature-dependent Yb valence only from the intensity ratio of the Yb^{2+} and Yb^{3+} $4f$-derived structures in the PES spectra at $h\nu=800$ eV.[17]

Only temperature dependence of the Yb^{2+} $4f$ states has mainly been discussed in the previous PES measurements on $YbInCu_4$.[6–13] The Yb^{3+} $4f$-derived structures also include information on the Yb $4f$ states since those are clearly observed in the PES spectra at $h\nu=800$ eV as multiplet structures due to the Coulomb interaction between two Yb $4f$ holes in the $4f$ (Ref. 12) final states of the PES process. In the present study, we also focus on the temperature dependence of the Yb^{3+} $4f$ multiplet structures through the valence transition. Preliminary PES data at $h\nu=800$ eV for the scraped $YbInCu_4$ surfaces have been presented in Ref. 14.

II. EXPERIMENTAL

Valence-band PES spectra of $YbInCu_4$ excited with $h\nu=800$ eV, where the probing depth is estimated to be ~15 Å, were measured at BL-25SU beam line of SPring-8.[18] Synchrotron radiation from the twin helical undulator was monochromatized by using a varied-line-spacing plane grating monochromator (VLSPGM) with a line density of 600 lines/mm and a hemispherical photoelectron analyzer (Gammadata-Scienta SES200) was used to measure the angle-integrated PES spectra. A detection angle was set to normal to the surface. The total energy resolution of the spectra was around 100 meV. The In $4d_{5/2}$ core spectra of $YbInCu_4$ at $h\nu=30.7$ eV were also collected at undulator beamline BL9 of HiSOR, Hiroshima synchrotron radiation center (HSRC). An off-plane Eagle monochromator[19,20] with a 1200 lines/mm spherical grating and the SES2002 analyzer were used to measure the PES spectra. The total-energy resolution was set to 8 meV at 20 K. Clean surfaces were *in situ* obtained by fracturing at 100 K under the ultrahigh vacuum below 3×10^{-10} Torr. After the fracturing, the PES experiments were carried out only on the first cooling through the valence transition,[9,10] in order to prevent a formation of defects in the sample by repetition passing through the transition.[21] A full set of the temperature-dependent PES spectra was measured within 2 h for the valence bands and 4 h for the In $4d_{5/2}$ states. Binding energy is defined with respect to E_F, which are determined from the spectra of the Au film.

Samples used for the present experiments were $YbInCu_4$ single crystals grown by the flux growth method similar to that described by Sarrao *et al.*[21] The constituent elements with stoichiometric ratios in InCu flux were put in an alumina crucible and sealed in an evacuated quartz ampoule. The sample was then heated to 1100 °C and cooled slowly down to 800 °C. After keeping at 800 °C for 20 h, the flux was removed. The crystal structure was confirmed by means of x-ray powder diffraction measurements. The temperature width of the valence transition at $T_V=42$ K was within 2 K from the measurements of the magnetic susceptibility.

III. RESULTS AND DISCUSSION

Figure 1 shows the PES spectrum of $YbInCu_4$ measured at 30 K with $h\nu=800$ eV. The basic feature of the spectrum is similar to that at 20 K with $h\nu=500$ eV.[9,10] The spectrum almost reflects the Yb $4f$ states except for the Cu $3d$ states.[22] The Cu $3d$ contribution to the spectrum in the binding-energy region from 2.5 to 5 eV is substantially weak in comparison with those measured in the ultraviolet region[7,9,12,13] because of the energy-dependent cross sections of photoelectrons.[16] One notices the Yb^{2+} $4f_{7/2}$ states as a prominent peak near E_F with a spin-orbit partner of the $4f_{5/2}$ peak at 1.45 eV, which are believed to come from the bulk. In spite of the larger escape depth of photoelectrons compared with the PES experiments in the ultraviolet region, the surface contributions are still observed as weak structures on the shallower binding-energy sides of the Yb^{2+} $4f_{5/2}$ and Cu $3d$-derived structures as indicated by vertical lines. The Yb^{3+} $4f$ states, on the other hand, are found at 5.5–12 eV as multiplet structures due to the Coulomb interaction between the two Yb $4f$ holes. A prominent peak at 16.7 eV is ascribed to the In $4d_{5/2}$ states.

Figures 2 and 3 present temperature dependence of the Yb^{2+} and Yb^{3+} $4f$ photoemission regions of the PES spectra as Fig. 1, respectively. Here the spectra have been normalized to the total area intensity in the binding-energy region between -1.5 and 17.5 eV. The intensities of the normalized spectra coincide over the binding-energy region of 13–17.5 eV including the In $4d_{5/2}$ peak and the Cu $3d$ states at all temperatures (see Fig. 1). The temperature dependence is found only in the Yb^{2+} and Yb^{3+} $4f$ regions.

Both the Yb^{2+} $4f_{7/2}$ and $4f_{5/2}$ peaks in Fig. 2 exhibit a similar behavior with changing temperature. The surface contribution to the spectra is almost independent of temperature. With decreasing temperature from 100 to 50 K, the intensity of the $4f$ peaks continuously increases. Between 50 and 40 K, we notice a remarkable enhancement of the $4f$

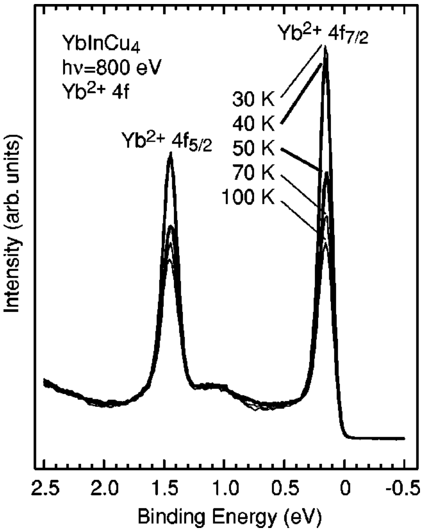

FIG. 2. Temperature dependence of PES spectra in the Yb^{2+} $4f$ region of YbInCu_4. Almost only Yb^{2+} $4f_{7/2}$ and $4f_{5/2}$ peaks exhibit an enhancement with decreasing temperature and the enhancement is the most remarkable between 50 and 40 K.

peaks, reflecting that the number of the Yb^{2+} ions suddenly increases due to the valence transition. The $4f$ peak intensity is almost unchanged between 40 and 30 K. The continuous increase of the $4f$ peak intensity in the high-temperature phase has also been observed in the PES spectra at $h\nu = 21.22$ eV[13] and those at $h\nu = 43$ eV.[7]

As shown in Fig. 3, on the other hand, with decreasing temperature the intensity of the Yb^{3+} $4f$ multiplet structures decreases, corresponding to the increase of the Yb^{2+} $4f$ peaks. In particular, the reduction of the intensity is remarkable between 50 and 40 K. Since the total area intensity of the Yb^{2+} and Yb^{3+} $4f$ structures is conserved within $\pm 2.5\%$ at all temperatures, it is reasonably assumed that the spectral weight transfers from the Yb^{3+} to Yb^{2+} $4f$ regions. Furthermore, it should be noticed that the multiplet structures simultaneously shift toward the deeper binding-energy side by 50 meV with almost no change of the feature with respect to the relative energies and intensities. In addition, the width of the spectra becomes narrower at 40 K.

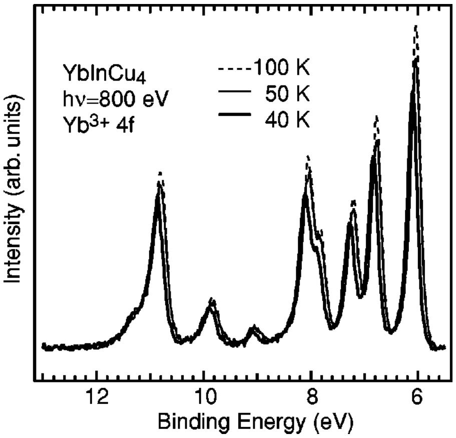

FIG. 3. Temperature dependence of PES spectra in the Yb^{3+} $4f$ region of YbInCu_4. The intensity is reduced with decreasing temperature and the multiplet structures suddenly shift toward the deeper binding-energy side between 50 and 40 K.

The Yb valence can directly be evaluated from the intensity ratio of the Yb^{2+} and Yb^{3+} $4f$-derived structures. However, the surface components also contribute to the PES spectra. In order to extract the bulk components from the Yb^{2+} $4f$ spectra, we have carried out the curve fitting of the PES spectra in the Yb^{2+} $4f$ photoemission region. For simplicity, we use the Gaussian functions for the structures coming from the bulk and surface. First, we attempt to fit the spectra using four Gaussian functions, B(7/2), B(5/2), S(7/2), and S(5/2). Here B(7/2) and B(5/2) curves represent the bulk-originated Yb^{2+} $4f_{7/2}$, and $4f_{5/2}$ peaks, respectively, and a symbol of S means the surface contributions as indicated by vertical lines in Fig. 1. The fitted results, however, do not reproduce the experimental PES spectra and some weak contributions are found just below the bulk-originated $4f_{7/2}$ and $4f_{5/2}$ peaks. If the asymmetric Doniach-Sunjuc line shapes are used for B curves, the tail of the $4f_{7/2}$ peak cannot be reproduced. Therefore, we add two Gaussian functions of SS(7/2) and SS(5/2) curves for these components, assuming to be additional surface contributions probably coming from the second layer.[23] These structures are clearly observed in the PES spectra for the scraped surfaces as well as the surface-originated structures (S) compared with those for the fractured surfaces and their intensities are independent of temperature.[14] The same temperature-independent structures also appear in the PES spectra for the scraped YbAl_3 surfaces measured at $h\nu = 102$ eV, although the authors attribute the structures to the YbAl_2 impurity phase.[24]

To decrease the number of adjustable parameters, the relative intensity between $X(7/2)$ and $X(5/2)$ ($X = \mathrm{B,S,SS}$) is fixed to 4:3 and the energy separation between them is also fixed to 1.292 eV. The same full width at half maximum (FWHM) is assumed for each X curves. The peak energy and FWHM of S curves are assumed to be independent of temperature. The same assumptions are adopted for SS curves. As for B curves, only peak energies are fixed.

The Yb^{3+} $4f$ spectra have also been fitted by using the multiplet structures calculated by Gerken.[25] The line spectra multiplied by a factor of 1.1 for the energy scale, which was pointed out by the author, convoluted with the Lorenzian function for a lifetime and the Gaussian function for an instrumental resolution, qualitatively reproduces well the experimental PES spectra. In the present study, the energies and intensities of 13 line spectra are more or less modified from those by Gerken to reproduce better the spectra. The relative energies and intensities of the modified line spectra, and FWHM's of the Lorenzian and Gaussian functions for convolution are fixed for all temperature.[26] Only the energy and intensity of a set of 13 lines are used as parameters. As an example, the fitted result for the PES spectrum at 30 K is presented in Fig. 4. The modified line spectra for the Yb^{3+} $4f$ multiplet structures are also shown as vertical lines. In spite of the simple assumption, the spectrum derived from the fitting procedure reproduces well the experimental spectrum with respect to the relative intensity and spectral width.

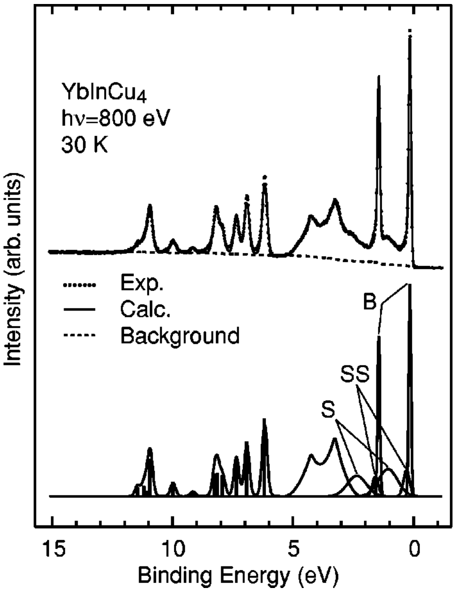

FIG. 4. Curve fitting for the PES spectrum of YbInCu$_4$ measured at 30 K. Six Gaussian functions are assumed for the Yb^{2+} $4f$ region and modified line spectra by Gerken[25] convoluted with the Lorenzian function for a lifetime and Gaussian function for an instrumental resolution are used for the Yb^{3+} $4f$ region. See text in detail.

Here background contribution due to secondary electrons is calculated by the Shirley's method.[27]

The Yb valence derived from the curve-fitting procedure mentioned above is shown as a function of temperature in Fig. 5. The Yb valence is $z \sim 2.81$ at 100 K and continuously decreases to $z \sim 2.75$ at 50 K. And then, between 50 and 40 K, the valence abruptly decreases to $z \sim 2.68$ reflecting the valence transition at $T_V = 42$ K. Below 40 K, the valence exhibits no remarkable change. This behavior can also be supposed from the temperature dependence of the Yb^{2+} $4f$ raw spectra in Fig. 2. The change of the valence through the valence transition is $\Delta z \sim 0.1$. Although the estimated valence is smaller than those from the thermodynamic data[2] and Yb L_{III} XAS spectra,[2,4] our result is larger by ~0.1 than those from the PES spectra at $h\nu = 43$ eV[7] and $h\nu = 60$ and 500 eV.[9,28]

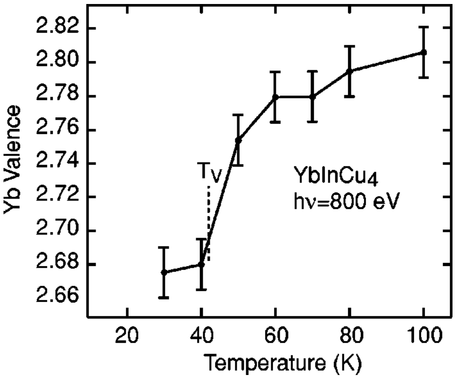

FIG. 5. The Yb valence of YbInCu$_4$ derived from the curve fitting as a function of temperature. The valence continuously decreases from 100 to 50 K and changes abruptly between 50 and 40 K.

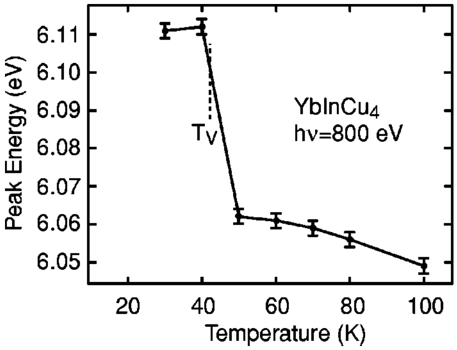

FIG. 6. The energy shift of the Yb^{3+} $4f$ multiplet structure of YbInCu$_4$. The binding energy of the shallower line spectrum derived from the curve fitting is plotted as a function of temperature.

The probing depth of the present PES spectra at $h\nu = 800$ eV is larger than that of the PES spectra at $h\nu = 43$, 60, and 500 eV. Also as seen from Fig. 8 of Ref. 9, the more bulk-sensitive measurements lead the Yb valence closer to 3+ in the high-temperature phase. Accordingly, our experimental results support the existence of the subsurface region pointed out by Reinert *et al.*,[7] where the Yb ions are close to the divalent state in comparison with those in the bulk. In spite of the existence of the subsurface region, however, the clear change can be observed in the PES spectra, showing that the valence transition takes place even in the surface within the probing depth of the PES spectra at $h\nu = 800$ eV (~15 Å).

We might assume that the gradual decrease of the Yb valence in advance of the valence transition at $T_V = 42$ K suggests the higher transition temperature near the surface than the bulk. Recently, Moriyoshi *et al.* performed x-ray crystal structure analyses of YbInCu$_4$ single crystals grown by the flux and Bridgman methods.[29] According to their results, in case of the sample with $T_V = 63$ K grown by the Bridgman method, the In sites are occupied by excessive Cu ions. On the other hand, the samples with $T_V = 42$ K grown by both methods are stoichiometric. The site substitution, distortion, and so on would be found near the fractured surface and would raise the transition temperature. The experimental result that the width of the Yb^{3+} multiplet structures is slightly broader above $T_V = 42$ K than below $T_V = 42$ K, supports that many states in the surroundings of the Yb ions exist in the high-temperature region.

From the curve-fitting procedure, the energy shift of the Yb^{3+} multiplet structure is derived as a function of temperature. The binding energy of the shallower line spectrum at ~6.1 eV is plotted in Fig. 6. It should be noticed that the binding energy shifts suddenly toward the deeper binding-energy side with decreasing temperature through the valence transition. An amount of the energy shift is 50 meV. On the other hand, the Yb^{2+} $4f$ peaks do not shift so much through the valence transition.[30] The similar energy shift with an amount of 0.2 eV has been observed for the Eu^{3+} $4f$-derived structure in the PES spectra of EuPd$_2$Si$_2$.[31] This compound shows a gradual valence transition from $z \sim 2.3$ above 180 K

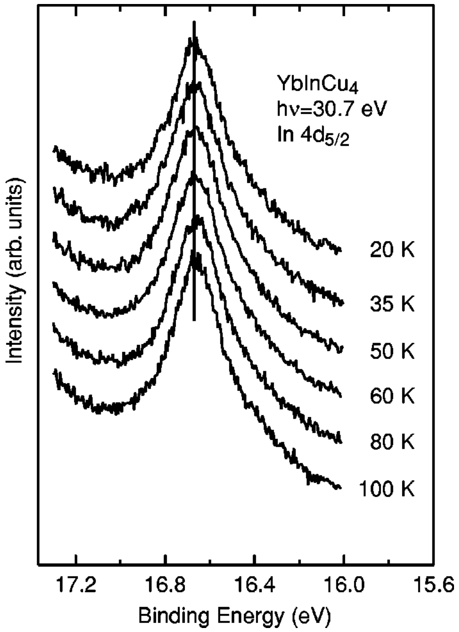

FIG. 7. Temperature dependence of PES spectra in the In $4d_{5/2}$ region of $YbInCu_4$. No energy shift is observed within the present experimental accuracy.

to $z \sim 2.8$ below 130 K and the energy shift occurs to the shallower binding-energy side with decreasing temperature through the transition.

On the other hand, almost no energy shift is observed in the In $4d_{5/2}$ core spectra. In order to confirm whether a slight energy shift takes place in the In $4d_{5/2}$ state in accordance with the valence transition, we have carried out PES experiments at $h\nu = 30.7$ eV with higher-energy resolution. The experimental results are presented in Fig. 7. We notice no energy shift in the In $4d_{5/2}$ spectra within the experimental accuracy. In addition, the energy shift of the Cu $3d$ structure is also not observed in the temperature dependence of the PES spectra in Fig. 1. The energy shift, thus, takes place only in the Yb^{3+} $4f$ multiplet structures.

The sudden energy shift of the Yb^{3+} $4f$ multiplet structures indicates that the electronic structure with respect to the Yb $4f$ states changes drastically near the valence transition. An energy separation between the Yb^{2+} and Yb^{3+} $4f$ PES spectra roughly gives an amount of $\epsilon_f + U$, where ϵ_f and U represent the energy to add the bare $4f$ hole and the averaged Coulomb interaction energy between the $4f$ holes, respectively. Accordingly, the energy shift of the Yb^{3+} $4f$ multiplet structures is assumed to originate from the increase of $\epsilon_f + U$.

Since U has an atomiclike character, the U value is considered to be almost unchanged through the valence transition and the ϵ_f value rather changes by ~ 50 meV suddenly. Theoretical analysis of the Yb^{2+} $4f_{7/2}$ PES spectra of $YbInCu_4$ measured at $h\nu = 21.22$ eV based on the single impurity Anderson model (SIAM), leads to the result that the ϵ_f value changes from -0.120 eV in the high-temperature phase to -0.067 eV in the low-temperature phase, that is, 53 meV shift.[12,32] Susaki investigated how the energy position of the Yb^{3+} $4f$ PES spectra depends on ϵ_f for the Yb compounds based on SIAM.[33] With increasing ϵ_f, the energy shifts to the deeper binding-energy side, and the amount of the shift is dominated by ϵ_f. On the other hand, the energy of the Yb^{2+} $4f$ peak is almost independent on ϵ_f. The energy shift is, thus, interpreted by the change of the ϵ_f value between high- and low-temperature phases.

For the high-temperature phase, with decreasing temperature from 100 to 50 K, the Yb^{3+} $4f$ multiplet structures gradually shift toward the deeper binding-energy side by ~ 10 meV. Before undergoing the valence transition, the ϵ_f value is plausibly considered to be unchanged. Based on calculations by SIAM,[33] the gradual energy shift would be explained by an increase of the degree of the hybridization between the Yb $4f$ and conduction-band states due to the reduction of the lattice constant with decreasing temperature. This is supported by the experimental result that similar behavior is observed also for $YbCdCu_4$ with no valence transition.[34]

IV. CONCLUSION

The PES spectra of the $YbInCu_4$ single crystal have been measured at $h\nu = 800$ eV from 100 to 30 K. With decreasing temperature from 100 to 50 K, the Yb^{2+} $4f$ peaks gradually grow in intensity, while the Yb^{3+} $4f$ multiplet structures are reduced. Between 50 and 40 K, the remarkable enhancement of the Yb^{2+} $4f$ peaks is observed and the Yb^{3+} $4f$ multiplet structures exhibit the sudden energy shift toward the deeper binding-energy side by 50 meV together with the reduction of the intensity. There is little difference in the PES spectra between 40 and 30 K.

The Yb valence derived from the PES spectra shows the sharp change between 50 and 40 K, in contrast to the results at $h\nu = 43$ eV by Reinert *et al.*[7] The derived valence is smaller than those from the thermodynamic data[2] and the Yb L_{III} XAS spectra,[2,4] while larger than those from the PES experiments by Reinert *et al.* ($h\nu = 43$ eV) (Ref. 7) and Moore *et al.* ($h\nu = 60$ and 500 eV).[9] These results suggest the existence of the subsurface region, where the Yb valence is smaller than the bulk. As for this point, the PES experiments using the hard x ray as an excitation source ($h\nu = 6$ keV) is in progress. The energy shift of the Yb^{3+} multiplet structures observed clearly near the valence transition would be explained by the increase of the ϵ_f value, while the gradual shift for the high-temperature phase by the hybridization between the Yb $4f$ and conduction-band states.

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