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Yb 4f states of YbXCu4 (X = Cd, Mg, Zn and Sn) investigated by high-resolution soft X-ray photoemission spectroscopy

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Abstract

Yb 4f electronic structure of $YbXCu_4$ (X = Cd, Mg, Zn and Sn) has been investigated by means of high-resolution soft X-ray photoemission spectroscopy (SX-PES) with the excitation energy of $h\nu = 800$ eV, in comparison with the results of the valence transition compound $YbInCu_4$. The SX-PES spectra of $YbCdCu_4$ exhibit the temperature dependence similar to $YbInCu_4$, while those of the other $YbXCu_4$ compounds almost no temperature dependence. The X-dependence of the Yb 4f states suggests that the low In 5p density of states is important for the valence transition of $YbInCu_4$.

Keywords: Electronic states; Photoelectron spectroscopies; Synchrotron radiation

Among the C15b-type compounds $YbXCu_4$ [1], $YbInCu_4$ has the most extensively been studied so far, because of a first-order valence transition at $T_V = 42$ K [2–4]. The Curie–Weiss magnetic susceptibility with the nearly trivalent Yb ions above T_V, changes sharply to the temperature-independent Pauli paramagnetism below T_V. From the expansion of the lattice constant, the Yb valence below T_V is estimated to be ∼2.9. Recently, we have investigated the Yb 4f states of $YbInCu_4$ by means of high-resolution soft X-ray photoemission spectroscopy (SX-PES) with the excitation energy of $h\nu = 800$ eV and successfully observed the change of the Yb 4f states in accordance of the valence transition at T_V: (i) the intensity of the Yb^{2+} 4f peaks remarkably increases while that of the Yb^{3+} 4f multiplet structures decreases from high to low temperature phases and (ii) the Yb^{3+} 4f structures shift toward the deeper binding-energy side by ∼50 meV below T_V [5].

The electronic structure of the other $YbXCu_4$ compounds has relatively less been studied, so far. The experimental knowledge on the X-dependence of the electronic structure is expected to become important for understanding the mechanism of the valence transition of $YbInCu_4$. The purpose of the present study is to investigate the X-dependence of the electronic structure of $YbXCu_4$ (X = Cd, Mg, Zn and Sn) by means of the soft X-ray photoemission spectroscopy, in comparison with the results of $YbInCu_4$.

Valence-band SX-PES spectra of $YbXCu_4$ excited with $h\nu = 800$ eV were measured on beamline BL-25SU at SPring-8 [6]. Synchrotron radiation from the twin helical undulator was monochromatized using a varied-line-spacing plane grating monochromator (VLSPGM) and a hemispherical photoelectron analyzer (Gammadata-Scienta SES200) was used to measure the angle-integrated spectra. The total energy resolution was around 100 meV. Clean surfaces were in situ obtained by fracturing under the ultrahigh vacuum below 3×10^{-10} Torr for all samples. After fracturing, the SX-PES experiments were carried out with decreasing temperature. Binding energy is relative to the Fermi level (E_F).

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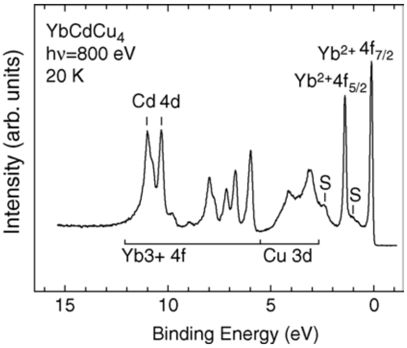

Fig. 1. SX-PES spectrum of $YbCdCu_4$ measured at 20 K with $h\nu = 800$ eV.

Single crystals of $YbCdCu_4$ were grown by the flux method [7,8] and polycrystals of $YbMgCu_4$ and $YbZnCu_4$ by melting an appropriate amount of the constituent elements in an arc-furnace. As for $YbSnCu_4$, recently, Hiraoka et al. have, for the first time, succeeded in the growth of the single crystal by the Bridgman method [9]. The crystal structure of the grown samples was confirmed to be the C15b-type by X-ray powder diffraction measurements.

Fig. 1 shows the SX-PES spectrum of $YbCdCu_4$ measured at 20 K with $h\nu = 800$ eV. The basic feature of the spectrum is similar to that of $YbInCu_4$ [5]. The spectrum almost reflects the Yb 4f states except for the Cu 3d states at 2.5–5 eV and the Cd 4d states at 10–12 eV taking into account the photoionization cross-sections of photoelectrons [10]. 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 1.4 eV. The surface contributions are observed as weak structures on the shallower binding-energy sides of the Yb^{2+} $4f_{5/2}$ and Cu 3d structures as indicated by vertical lines with “S”. The Yb^{3+} 4f states are found at 5.5–12 eV as multiplet structures due to the Coulomb interaction between the two Yb 4f holes.

The temperature dependence of the Yb^{2+} and Yb^{3+} 4f-derived SX-PES spectra of $YbCdCu_4$ are shown in Fig. 2(a and b), respectively. Since the temperature dependence of the Yb^{3+} 4f spectra is substantially weak in comparison with that of the Yb^{2+} 4f spectra, the Yb^{3+} 4f spectrum measured at 150 K is also depicted just on the spectrum at 20 K by a thin solid curve in Fig. 2(b). One notices that with decreasing temperature from 150 to 20 K, the Yb^{2+} 4f peaks gradually increase in intensity, while the Yb^{3+} 4f multiplet structures decrease, indicating that the Yb valence decreases to be divalent. In addition, the Yb^{3+} 4f structures slightly shift toward deeper binding-energy side with decreasing temperature. These temperature dependences of the Yb^{2+} and Yb^{3+} 4f spectra are observed in the higher temperature phase of $YbInCu_4$ [5], suggesting that the electronic structure of $YbCdCu_4$ is close to that of $YbInCu_4$.

The Yb valences derived from the SX-PES spectra by the fitting procedure described in Ref. [5], are estimated to be ∼2.78 at 150 K and ∼2.75 at 20 K. Here, it should be noticed that with decreasing the Yb valence, the Yb^{3+} 4f structures shift toward the deeper binding-energy side. This relation is clearly observed just at the valence transition of $YbInCu_4$ [5]. The energy position of the Yb^{3+} 4f shallowest peak around 6 eV, furthermore, almost linearly depends on the Yb valence both for $YbInCu_4$ and $YbCdCu_4$. This means that an amount of $\varepsilon_f + U$ [5] is closely related to the Yb valence, where ε_f and U represent the energy to add the bare 4f hole and the Coulomb interaction energy between the 4f holes, respectively. Similar energy shift is also detected for the valence transition compound $EuPd_2Si_2$ [11].

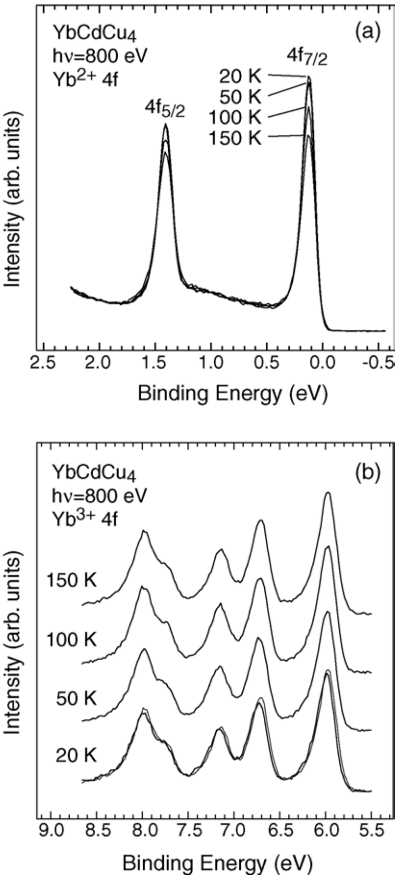

Fig. 2. Temperature dependences of (a) Yb^{2+} and (b) Yb^{3+} 4f-derived SX-PES spectra of $YbCdCu_4$. A thin solid curve on the Yb^{3+} 4f spectrum at 20 K shows that at 150 K for comparison.

Fig. 3 shows the SX-PES spectra of $YbSnCu_4$, $YbMgCu_4$ and $YbZnCu_4$ measured at 20 K with $h\nu = 800$ eV. In contrast to $YbInCu_4$ and $YbCdCu_4$, the temperature dependence is not detected for the three compounds. Only for $YbSnCu_4$, the intensity of the Yb^{3+} 4f multiplet structures is substantially weak and the Yb valence is close to divalent. The Yb^{3+} 4f shallowest peak at 6.3 eV is the deepest among $YbXCu_4$, which follows the relation between its energy position and the Yb valence.

As mentioned above, the electronic structure of $YbCdCu_4$ is considered to be close to that of $YbInCu_4$. In addition, from the similar temperature dependence of the Yb^{2+} $4f_{7/2}$ peak observed in the photoemission spectra of $YbAgCu_4$ [12] and $YbInCu_4$ [13] measured at $h\nu = 21.2$ eV, $YbAgCu_4$ is also expected to have the electronic structure similar to

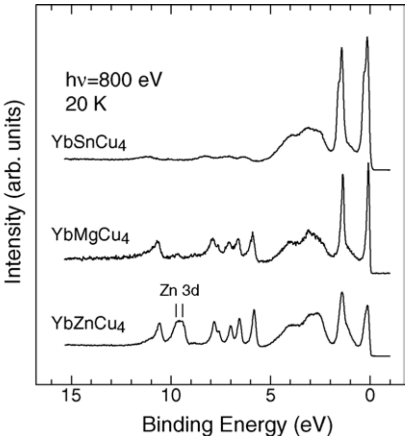

Fig. 3. SX-PES spectra of $YbSnCu_4$, $YbMgCu_4$ and $YbZnCu_4$ measured at 20 K with $h\nu = 800$ eV.

$YbInCu_4$. It is noted that the Ag, Cd, In and Sn atoms locate in this order in the periodic table. Their nominal valence electron configurations are $(5s)^1$, $(5s)^2$, $(5s)^2(5p)^1$ and $(5s)^2(5p)^2$, respectively. The experimental results suggest that the hybridization between the Yb 4f states and 5sp-derived conduction-band states and, in particular, the low 5p density of states is important for the valence transition of $YbInCu_4$. Actually, the structure which would originate from the Yb 4f–In 5p hybridization bands, is observed in the low-energy excited photoemission spectra of $YbInCu_4$ below T_V [14]. For $YbSnCu_4$, the excessive 5p electrons are considered to fill the Yb 4f hole and the Yb valence is close to be divalent. On the other hand, nominal valence electron configurations of the Mg and Zn atoms are $(3s)^2$ and $(4s)^2$, respectively. Due to their similar valence electrons to the Cd atom, the Yb ions are mixed divalent and trivalent states in $YbMgCu_4$ and $YbZnCu_4$ as $YbCdCu_4$. In contrast to $YbCdCu_4$, however, almost no temperature dependence of the spectra is observed. The energy position and density of states of the 3sp- and 4sp-derived conduction-band states should be different from those of the 5sp bands and the Yb 4f level in the 5sp bands is considered to be important for the valence transition of $YbInCu_4$.

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