Photoemission study on YbZn$_{1-x}$Sn$_x$Cu$_4$

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Abstract. We have investigated the electronic structure of YbZn$_{1-x}$Sn$_x$Cu$_4$ with $x = 0.5$ by means of hard x-ray photoemission spectroscopy (HAXPES) with $\hbar \nu = 5.95$ keV and low photon energy photoemission spectroscopy (LEPES) with $\hbar \nu = 14$ eV. The Yb valence derived from the Yb 3$d$ HAXPES spectrum remarkably decreases between 100 and 20 K; 2.90 at 300 K and 2.78 at 20 K. The LEPES spectra exhibit a prominent peak near the Fermi level which is attributed to the Kondo resonance peak. The Kondo temperature is estimated to be $T_K \sim 210$ K from an energy position of the peak extrapolated to zero temperature.

1. Introduction

A family of YbXCu$_4$ ($X = \text{In, Cd, Ag, Au, Cu, Zn etc.}$) with the cubic AuBe$_5$-type structure exhibits a wide variety of physical properties [1]. Among them, YbInCu$_4$ undergoes the first-order valence transition at $T_V = 42$ K [2]. The Yb valences are estimated to be 2.90 and 2.74 in the high- and low-temperature phases, respectively, from hard x-ray photoemission spectroscopy (HAXPES) with $\hbar \nu = 5.95$ keV for the Yb 3$d$ core states [3]. The magnetic susceptibility is the Curie-Weiss type above $T_V$ and the Pauli paramagnetic type below $T_V$. The Kondo temperature $T_K$ also changes from $T_{K+} \sim 25$ K to $T_{K-} \sim 400$ K [4]. Reflecting the high $T_{K-}$, the Kondo resonance peak suddenly appears below $T_V$ in the low photon energy photoemission spectra (LEPES spectra) with $\hbar \nu = 7$ eV at binding energy of $E_B = 47$ meV relative to the Fermi level ($E_F$) [5].

Among YbXCu$_4$, only YbInCu$_4$ exhibits the valence transition. The transition is expected to be controlled by the conduction-band electronic structure depending on X. Considering the nominal valence electrons of Zn (4$s^2$4$p^0$), In (5$s^2$5$p^1$) and Sn (5$s^2$5$p^2$), the conduction-band electronic structure of the solid solution YbZn$_{1-x}$Sn$_x$Cu$_4$ with $x = 0.5$ is considered to be similar to that of YbInCu$_4$ and the valence transition is expected. In this paper, we report the HAXPES ($\hbar \nu = 5.95$ keV) and LEPES ($\hbar \nu = 14$ eV) results on YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$. A remarkable decrease of the Yb valence was found below 100 K, though the sharp valence transition was not...
reported in the several transport experiments [6]. The Yb valences above 100 K were almost unchanged with $\sim 2.90$ and decreased to 2.78 at 20 K. These values are close to those of YbInCu$_4$ in the high- and low-temperature phases, respectively [3]. In the LEPES spectra, the Kondo resonance peak was clearly observed near $E_F$. The energy position of the peak extrapolated to zero temperature indicated $T_K \sim 210$ K, consistent with the characteristic temperature $T_0$ derived from the magnetic susceptibility and specific heat measurements [6].

2. Experimental

We carried out the HAXPES and LEPES experiments at the undulator beamlines BL15XU [7] of SPring-8 and BL-9A [8] of Hiroshima Synchrotron Radiation Center (HSRC), respectively. Both spectra were measured using the hemispherical analyzer (VG SCIENTA R4000). Total energy resolutions were set to 240 meV for the HAXPES spectra and 10 meV for the LEPES spectra. $E_B$ of the spectra are relative to $E_F$ calibrated using the Fermi edge of Au spectra.

The polycrystalline samples of YbZn$_{1-x}$Sn$_x$Cu$_4$ with $x = 0.5$ used for the present experiments were prepared by the procedure described elsewhere [6]. The $x$-value is nominal one derived from a mixture ratio of starting materials. According to the electron probe micro analysis and wavelength dispersion spectroscopy, the main phase has the chemical composition of Yb$_{0.97}$Zn$_{0.45}$Sn$_{0.44}$Cu$_{1.14}$ [6]. Clean surfaces were obtained by fracturing in situ.

3. Results and discussion

Figure 1 shows the HAXPES spectra for the Yb 3d core level of YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$ measured between 300 and 20 K. The Yb 3d spectrum is split into the 3d$_{5/2}$ region lower than $E_B = 1560$ eV and 3d$_{3/2}$ region higher than $E_B = 1560$ eV due to the spin-orbit interaction. In each region, the Yb$^{2+}$ and Yb$^{3+}$ components are clearly resolved. Prominent peaks at 1520 and 1567 eV are attributed to the Yb$^{2+}$ 3d$_{5/2}$ and Yb$^{2+}$ 3d$_{3/2}$ states, respectively. Multiplet structures originating from the Yb$^{3+}$ 3d$_{5/2}$ (1524 – 1535 eV) and Yb$^{3+}$ 3d$_{3/2}$ (1572 – 1580 eV) states are caused by the 3d$^9$4f$^{13}$ photoemission final states. Broad structures around 1544 and 1590 eV are ascribed to the plasmon excitation associated with the Yb$^{3+}$ 3d photoemission.

Both the Yb$^{2+}$ and Yb$^{3+}$ components are observed in the spectra for all temperature range, which clearly indicates that the valence of the Yb ions in YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$ fluctuates. Although the temperature dependence is small between 300 and 100 K, the spectra exhibit a remarkable change below 100 K. With decreasing temperature, the Yb$^{2+}$ peaks are enhanced, while the
Yb$^{3+}$ peaks are reduced, which indicates that the Yb valence remarkably gets closer to Yb$^{2+}$ below 100 K.

It is known that quantitative lineshape analyses of the Yb 3$d$ HAXPES spectra provide the Yb valence with high accuracy [3, 9]. In order to obtain the Yb valence, we fitted the Yb 3$d$ spectra. The fit of the spectrum taken at 20 K is shown in Fig. 2 (a) as an example. We used the single line spectrum for the Yb$^{2+}$ component. As regards the Yb$^{3+}$ component, we used the slightly modified line spectra obtained by the atomic multiplet calculation. These line spectra were convoluted with the Lorentzian function taking into account the lifetime broadening. The plasmon features were assumed to be represented by the Gaussian function. All components were broadened with the Gaussian function for the instrumental resolution. After that, the background contribution due to the secondary electrons was added according to the Shirley’s method [10].

The Yb valence can simply be evaluated from $v = 2 + [I_2/(I_2 + I_3)]$, where $I_2$ and $I_3$ are integrated intensities of the Yb$^{2+}$ and Yb$^{3+}$ components. The valences using $I_2$ and $I_3$ obtained from the fits are plotted as a function of temperature in Fig. 2 (b). As we see also from the Yb 3$d$ spectra in Fig. 1, the Yb valence is almost unchanged between 300 and 100 K and is evaluated to be $v = 2.90$. Below 100 K the valence rapidly decreases on cooling and reaches $v = 2.78$ at 20 K.

The remarkable decrease of the Yb valence below 100 K evokes the valence transition of YbInCu$_4$, where the valence changes sharply across $T_V = 42$ K from $v = 2.90$ in the high-temperature phase to $v = 2.74$ in the low-temperature phase [3]. These values are very close to those of YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$ at 300 – 100 and 20 K, respectively. The temperature dependence of the valences in Fig. 2 (b) is similar to that of YbInCu$_4$ including the absolute values except for the sharpness of the valence change. We assume that the conduction-band electronic structure of YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$ is similar to that of YbInCu$_4$, which is responsible for the large valence change below 100 K. It should be noted, however, YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$ is indicated to be a typical Kondo lattice system with Fermi liquid ground state from the transport experiments [6].

In order to confirm the relation between the large valence change and similarity of the conduction-band electronic structure, the experiments for YbZn$_{1-x}$Sn$_x$Cu$_4$ with changing $x$ precisely around $x = 0.5$ are required. In addition, the experiments for YbCd$_{1-x}$Sn$_x$Cu$_4$ are also important. The Cd atom is located at just right side of In in the periodic table. Its nominal valence electron is

![Figure 2](image_url)

**Figure 2.** (a) Fit of the Yb 3$d$ HAXPES spectrum of YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$ measured at 20 K. (b) Yb valences of YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$ derived from the Yb 3$d$ HAXPES spectra as a function of temperature.
5s25p0 and the conduction-band electronic structure of YbCd0.5Sn0.5Cu4 is expected to be more similar to that of YbInCu4 compared to YbZn0.5Sn0.5Cu4.

Figure 3 (a) shows the LEPES spectra of YbZn0.5Sn0.5Cu4 in the vicinity of EF measured between 300 and 10 K. At low temperatures, one can see a prominent and asymmetric peak near EF. With decreasing temperature, the energy position of the peak becomes closer to EF and the intensity becomes higher. The peak with similar temperature dependence has also been observed in YbCdCu4 [11] and YbNi3Ga9 [12]. Based on these results, the peak near EF is ascribed to the Kondo resonance peak. The temperature dependence is well described within a framework of the single impurity Anderson model (SIAM) [13]. The Kondo peak can be discernible even at 300 K, indicating the strong hybridization between the Yb 4f and conduction electrons in YbZn0.5Sn0.5Cu4.

According to SIAM, the Kondo peak at zero temperature appears at kBT K with kB of the Boltzmann constant [14]. In order to estimate the energy position of the Kondo peak, we fitted the LEPES spectra assuming a single Doniach-Sunjic function for the Kondo peak and the Fermi-Dirac distribution functions for the conduction-band density of states [11, 15]. The back ground contribution was taken into account with the same procedure as the fits of the Yb 3d HAXPES spectra. The peak energies derived from the fits (not shown here) are plotted as a function of temperature in Fig. 3 (b). The peak energy of E_B = 66 meV at 300 K continuously decreases to E_B = 20 meV at 10 K. No remarkable change is observed, in particular, around 100 K. The energy positions are tentatively fitted with a quadratic function as shown by a dotted line in Fig. 3 (b). The peak energy extrapolated to zero temperature is estimated to be E_B ∼18.3 meV, which corresponds to TK ∼ 210 K.

Tsujii estimated the characteristic temperature for the Kondo effect (T0) of YbZn0.5Sn0.5Cu4 from the magnetic susceptibility and specific heat measurements [6]. The magnetic susceptibility χ exhibits a broad maximum around 70 K with the Curie-Weiss behavior around room temperature, which is a characteristic behavior for a Kondo-lattice system with nonmagnetic ground state. The temperature dependence of χ is well described with the Bethe ansatz solution of the Coqblin-Schrieffer model [16] for J = 7/2 with T0 = 255K. T0 is also estimated to be 203 K from the electronic specific heat coefficient γ of 150 mJ/molK2 using γ = πRJ/3T0 with R of the gas constant. TK derived from our LEPES spectra is in good agreement with these values.

Figure 3. (a) LEPES spectra of YbZn0.5Sn0.5Cu4 in the vicinity of EF measured between 300 and 10 K. (b) Energy positions of the Kondo resonance peak in (a) as a function of temperature.
4. Conclusions
We have carried out the HAXPES and LEPES on YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$. The Yb valence deduced from the Yb 3d HAXPES spectra is unchanged at $v \sim 2.90$ between 300 and 100 K, while the valence remarkably decreases to $v = 2.78$ at 20 K. The temperature dependence of the valence is similar to that of YbInCu$_4$ including the absolute values except for its sharpness. We found remarkable similarities of the valence changes between YbZn$_{0.5}$Sn$_{0.5}$Cu$_4$ and YbInCu$_4$, which is possibly related to the similarities of the conduction-band electronic structures. The Kondo resonance peak is observed in the LEPES spectra and its peak energy extrapolated at zero temperature indicates $T_K \sim 210$ K, which is consistent with $T_0$ derived from the magnetic susceptibility and specific heat measurements [6].

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