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Permalink
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Journal
SOLID STATE COMMUNICATIONS, 118(8)

ISSN
0038-1098

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Publication Date
2001

DOI
10.1016/S0038-1098(01)00118-1

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High-resolution photoemission study of the valence transition in YbInCu₄

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Received 22 February 2001; accepted 6 March 2001 by H. Akai

Abstract

We have performed a photoemission study of YbInCu₄, which undergoes a first-order phase transition at T_c = 40 K between the low-temperature intermediate-valence state and the high-temperature local-moment state. The Yb 4f photoemission peak (Kondo peak) just below the Fermi level, which probably originates from the subsurface region of the YbInCu₄ samples but tracks the valence transition in the bulk YbInCu₄, has been studied above and below T_c. It has been found that the 4f photoemission peak is shifted from ~ - 35 meV at 75 K to ~40 meV at 7 K. By analyzing the 4f peak position and the Yb valence in the two phases using the Anderson impurity model, we find that the bare 4f level, which is located close to the Fermi level, is shifted downward and the hybridization strength decreases in going from the high-temperature to low-temperature phases. © 2001 Published by Elsevier Science Ltd.

PACS: 79.60.-i; 75.30.Mb; 71.28.+d

Keywords: D. Heavy fermions; D. Phase transitions; E. Photoelectron spectroscopies

The isostructural first-order transition in YbInCu₄, which was first found by Felner and Nowik in 1986 [1], has attracted much attention due to sudden changes in the transport and thermodynamic properties within a very narrow temperature range around T_c = 40–70 K [1–4]. A collection of Yb²⁺ local moments in the high–temperature phase is transformed to a Pauli–paramagnetic state with an intermediate Yb valence in the low–temperature phase. The Curie–Weiss magnetic susceptibility above T_c changes sharply to the temperature-independent Pauli paramagnetism and the electrical resistivity is reduced by about one order of magnitude. While Felner et al. [2] reported the first-order transition in Yb₀.₄In₉.₆Cu₄ with the disordered C15 Laves-phase structure (Fd3m), subsequent studies have confirmed that the sharp transition occurs in YbInCu₄, which has the ordered C15B structure (F43m) both above and below T_c [5]. Since the ionic radius of Yb²⁺ is larger than that of Yb³⁺, the lattice constant increases by 0.15% on cooling across T_c. From the change in the lattice constant the decrease in the Yb valence through the transition has been estimated to be ~ 0.1 [2]. Yb L_III-edge X-ray absorption studies [2,6] have shown that the Yb valence decreases from ~ 2.9 to ~ 2.8 on cooling. A neutron powder diffraction study [5] confirmed the lattice expansion below T_c and detected no change in the crystal symmetry between the two phases.

Photoemission spectroscopy (PES) is a direct probe of occupied electronic states and is expected to give clear information especially for Yb compounds, where the 4f level is mostly occupied and signals from the outermost atomic layer are energetically well separated from bulk signals [12]. So far, several groups [7–11] have performed photoemission studies of YbInCu₄ and have found the decrease of the Yb valence on cooling. However, the absolute value of the valence of ‘bulk’ Yb deduced from the photoemission spectra is much smaller than that deduced from the magnetic susceptibility and the lattice constant.

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0038-1098/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0038-1098(01)00118-1
According to Reinert et al. [9], the valence deduced from PES changes continuously across $T_c$, i.e. from 2.56 at 20 K to 2.85 at 220 K. In order to explain the difference in the Yb ‘bulk’ valence between PES and the other more bulk-sensitive experiments, it has been proposed that apart from the outermost layer, the subsurface region within the photo-electron escape depth may also be different from the bulk [7,9]. Although not completely bulk sensitive, PES studies of YbInCu$_4$ may give useful information about the valence transition in bulk YbInCu$_4$ because the valence change across $T_c$ in the subsurface region of YbInCu$_4$ reflects the valence transition in the bulk. Indeed, Moore et al. [11] found a sudden change in the $4f$ photoemission intensity at $T_c$. So far, except for the reported small Yb valence compared to the bulk [7,9–11] little is known about the subsurface electronic structure of YbInCu$_4$.

In the present work, we have focused on the $4f$ peak position just below the Fermi level ($E_F$), i.e. the Kondo peak. Sarrao et al. [4] estimated the Kondo temperature in YbInCu$_4$ to be $T_K = 20$ K above $T_c$ and 430 K below $T_c$ by fitting the $J = 7/2$ Coqblin–Schrieffer model to the measured magnetic susceptibility. Lawrence et al. [13] analyzed the inelastic neutron spectrum of YbInCu$_4$ using the Anderson impurity model (AIM) and deduced $T_K$ to be 25 K above $T_c$ and 405 K below it. According to AIM, the Kondo peak appears at $-k_B T_K$ in the photoemission spectrum and thus an energy shift of the peak as large as $\sim 35$ meV would be expected through $T_c$ in YbInCu$_4$ if one could measure bulk-sensitive PES spectra. Although the previous PES measurements have revealed a strong temperature dependence in the spectral weight of the Kondo peak [8–10] such an energy shift has not been reported yet. The increase in the $4f$ electron number below $T_c$ should be accompanied by a decrease in the number of conduction electrons, which would lower the Fermi level. Such a shift may change possibly the bare $4f$-level position ($e_f^0$) measured from $E_F$ and the DOS at $E_F$, $\rho(E_F)$, both of which determine the $4f$ electronic states.

Single crystals of YbInCu$_4$ were grown from high-purity constituent materials with InCu flux [4]. The prepared samples showed a sharp jump in the magnetic susceptibility and the electrical resistivity at $T_c = 42$ K with a narrow temperature range of 2 K. Photoemission measurements were performed using an Omicron EA 125 HR analyzer and a VG He discharge lamp. Samples with a cleavage post were transferred from a preparation chamber into the analyzer chamber in the $10^{-11}$ Torr range and were cleaved in situ. The acceptance angle of the electron analyzer was set to $\pm 8^\circ$, which corresponds to one third of the Brillouin zone area of YbInCu$_4$ for the He I radiation ($h\nu = 21.2 \text{ eV}$), and the cleaved surfaces were irregular, probably making the measured spectra angle integrated ones. Photoemission spectra between $-19 \text{ eV}$ and $E_F$ were almost reproducible between different cleaving as reported by Reinert et al. [9]. The measurements were made at 75 and 7 K, bracketing

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1 We have chosen cleaving for the surface preparation in the present study rather than scraping because photoemission spectra of YbInCu$_4$ from scraped surfaces showed an extrinsic broad peak at $-0.25 \text{ eV}$ [8,9], which would have originated from the disordered surface layers. In addition, we note that scraping below $T_c$ might raise the temperature at the sample surface repeatedly across $T_c$. The possibility of the build-up of the strain in such a thermal cycle has been pointed out by Sarrao et al. [4].
Fig. 3. Calculated 4f photoemission spectra: (a) $\epsilon_B^0 = 0.120$ eV and $\Delta = 0.042$ eV, (b) $\epsilon_B^0 = 0.067$ eV and $\Delta = 0.030$ eV, and (c) $\epsilon_B^0 = 1.0$ eV and $\Delta = 0.37$ eV.

$T_c = 42$ K. Since the cleavage at 7 K requires cooling of the sample with the post across $T_c$, at which the sample shows the lattice expansion, all the samples were cleaved at 75 K. We evaporated Au onto each sample to determine the $E_F$ position and the energy resolution. The energy resolution thus deduced was 20–22 meV for the He I spectra and ~60 meV for the He II ($h\nu = 40.8$ eV) spectra. As Reinert et al. discussed in detail [9], the 4f peak intensity just below $E_F$ decreased with time after the cleavage. Thus we took the 4f spectra near $E_F$ while changing the temperature as 75 K – 7 K – 75 K – 7 K for each in situ cleaved sample to extract intrinsic time dependence. Those spectra were measured within ~5 h after the cleavage. Fig. 1 shows an He II wide energy-range scan of the valence band of YbInCu$_4$ taken just after cleavage. The sharp signals just below $E_F$ and at −1.3 eV correspond to the $4f^{14} \rightarrow 4f^{13}_{5/2}$ and $4f^{14} \rightarrow 4f^{13}_{7/2}$ transition, respectively. The broad peak around −1 eV, on the other hand, corresponds to the $4f^{14} \rightarrow 4f^{13}_{5/2}$ transition at the Yb atoms in the outermost layer. The other outmost Yb$^{2+}$ signal of the $4f^{14} \rightarrow 4f^{13}_{5/2}$ transition is overlapped by the Cu 3d band, which extends from −2 to −5 eV. Between −5 and −13 eV appears the multiplet structure of the $4f^{13} \rightarrow 4f^{12}$ transition. The In 4d core level is observed around −17 eV.

Fig. 2 shows the He I photoemission spectra near $E_F$ taken with higher energy resolution. We have normalized the spectra to the average intensity between −0.25 and −0.20 eV. The spectra consist of the 4f peak just below $E_F$, which corresponds to the 4f Kondo peak, and the conduction band with a flat density of states (DOS). Such a flat conduction-band DOS near $E_F$ has been observed in the non-f reference compound LuInCu$_4$ [7,10]. The inset shows a series of spectra taken in a sequence after a cleavage. They show that the Yb 4f spectral weight decreases with time, but the intensity change between the two phases was reproducible and the peak position in each phase did not change.

On cooling from 75 to 7 K across $T_c$, the Kondo peak becomes remarkably stronger in accordance with the decrease in the Yb 4f valence. At the same time, the intensity maximum of $\sim 35$ meV at 75 K is shifted by about 5 meV away from $E_F$. This value is much smaller than what the bulk magnetic measurements predict according to AIM. Note that the Fermi–Dirac (FD) function at 75 K is 0.99 at $\sim 35$ meV and therefore does not affect the peak position appreciably. Such a shift was not observed in the previous work [8–11], probably due to insufficient energy resolution. Joyce et al. [10] measured a shift of the spin-orbit replica of the Kondo peak (4f$^{13} \rightarrow 4f^{13}_{5/2}$ signal) at $\sim 1.3$ eV across $T_c$ but found no shift in their spectra taken with the energy resolution of $\sim 45$ meV. We note that the spin-orbit replica is further broadened due to the shorter life time of the photolevel in comparison with the Kondo peak just below $E_F$.

In order to interpret the above temperature dependence of the photoemission spectra in the subsurface region, we have calculated the 4f photoemission spectra using AIM to the second order in $1/N_f$, where $N_f$ is the degeneracy of the $J = 7/2$ 4f level. The model consists of the degenerate $J = 7/2$ 4f level of $N_f = 8$ at $\epsilon_f^0$ and the continuum extending from $-B = -0.15$ eV to $+B = 0.15$ eV with the $J = 5/2$ level being neglected. We have calculated both $I(4f^{14} \rightarrow 4f^{13})$ and $I(4f^{13} \rightarrow 4f^{12})$, where $I(4f^{13} \rightarrow 4f^{12})$ is the 4f$^{13} \rightarrow 4f^{12}$ photoemission intensity, using a finite Coulomb repulsion $U = 7$ eV to compare $n_{4f} = I(4f^{13} \rightarrow 4f^{12})[I(4f^{13} \rightarrow 4f^{12}) + 7/8I(4f^{14} \rightarrow 4f^{13})]$ and the ground-state 4f-hole occupancy $n_{4f}$. Basis states in the calculation are lowest-order $f^{14}$, $f^{13}$, and $f^{12}$ states and second-order $f^{14}$ state [16,18] for the initial ground state and lowest-order $f^{13}$, $f^{12}$, and $f^{11}$ states and second-order $f^{14}$ and $f^{13}$ states for the final states. Here, the second-order states include one electron-hole pair in the continuum. We define the 4f hole occupancy in the ground state as $n_{4f}$ as $l(c(13))^2 + 2c(12)^2$, where the ground state $|\psi_0\rangle$ is expressed as $|\psi_0\rangle = c(14)|4f^{14}\rangle + c(13)|4f^{13}\rangle + c(12)|4f^{12}\rangle$. Since the 4f peak appeared in the energy region where the FD function is almost unity at the measurement temperatures, we did not take into account the effect of the FD function.

We have reproduced the photoemission peak position observed in the present experiment and $n_{4f}$ deduced by

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2 Instrumental energy resolution might shift the intensity maximum to a slightly higher binding energy due to the asymmetry of the peak.

3 In the case of $n_f \sim 0.5$, different 4f configurations are strongly mixed with each other and $n_{4f}$ underestimates the $n_f$ (and hence underestimates the Yb valence) [17].
Reinert et al. [9] as shown by curves (a) and (b) in Fig. 3. We note that recent PES study by Moore et al. [11] has given similar values of $n_{ij}$. We have convoluted all the calculated spectra with a Gaussian of 22 meV FWHM. From the experimentally determined peak position and $n_{ij}$, $\epsilon_f^0$ and the $4f$-conduction band hybridization strength $\Delta = \pi n_B \rho(\epsilon)(V)^2 d\epsilon$ in the AIM [17], where $V(\epsilon)$ is the hybridization matrix element and $\rho(\epsilon)$ is the conduction-band DOS, are uniquely determined. We obtained $\epsilon_f^0 = 0.120$ eV and $\Delta = 0.042$ eV to reproduce the 75 K spectrum (a) and $\epsilon_f^0 = 0.067$ eV and $\Delta = 0.030$ eV to reproduce the peak position of the 7 K spectrum (b). Here, we have adjusted only these two parameters to reproduce both the peak position and $n_{ij}$. Owing to the weak hybridization strength $\Delta$, the discrepancy between $n_{ij}$ and $n_{ij}$ is negligibly small: $n_{ij}(n_{ij}) = 0.67 (0.66)$ at 75 K and 0.58 (0.57) at 7 K. This confirms that the Yb valence in the subsurface region is indeed smaller than that in the bulk in YbInCu$_4$. (If $\epsilon_f^0 = 1.0$ eV [10] and $\Delta = 3.18$ eV, $n_{ij} = 0.57$ and $n_{ij} = 0.77$ are quite different.)

Since the Hall coefficient $R_H$ at 7 K is smaller than that at 75 K by one order of magnitude in YbInCu$_4$ [6], the DOS around $E_F$ would be higher below $T_c$ than that above it, which would increase $\Delta$ in the low-temperature phase. On the other hand, the expansion of the lattice below $T_c$ would reduce $V(\epsilon)$ and hence $\Delta$ below $T_c$. The present result of the decrease in $\Delta$ below $T_c$ indicates that the effect of the reduction of $V(\epsilon)$ exceeds the effect of the increase in the carrier number. We note that $\epsilon_f^0 = 0.067-0.120$ eV is very small in comparison with typical values of $\epsilon_f^0 = 0.3-1.0$ obtained or assumed in the previous photoemission studies of Yb compounds [10,14–16]. We have calculated photoemission spectra with $\epsilon_f^0 = 1.0$ eV [10] by varying $\Delta$ to reproduce the peak position of $-40$ meV as shown by curve (c) in Fig. 3. We have found that $n_{ij} = 0.86 (n_{ij} = 0.90)$, which is much larger than the experimentally observed value, as pointed out by Joyce et al. [10]. Therefore, the proximity of the bare $4f$ level to $E_F$ and the smallness of $\Delta$ is responsible for the small $4f$ hole occupancy ($n_{ij} \ll 1$) with the $4f$ peak position relatively close to $E_F$, which is characteristic of the photoemission spectra of YbInCu$_4$. The small value of $\epsilon_f^0$ may be the origin of the $4f$ instability because a small change in $\epsilon_f^0$ or $\Delta$, which is negligible in the case of large $\epsilon_f^0$ and $\Delta$, may vary $n_{ij}$ dramatically. Presumably the present PES results for the subsurface region would therefore be qualitatively correct in the bulk and would be useful to understand the valence instability in bulk YbInCu$_4$.

In summary, we have studied the photoemission spectra of YbInCu$_4$ with high energy resolution. We have observed that the divalent $4f$ peak is shifted away from $E_F$ on cooling across $T_c$. The $4f$ peak position and the Yb valence were analyzed using AIM with a finite $U$. We have shown that the proximity of $\epsilon_f^0$ to $E_F$ and the smallness of $\Delta$ are characteristic of YbInCu$_4$ and are responsible for the valence instability because $n_{ij}$ changes sensitively for a small change in $\epsilon_f^0$ or $\Delta$. We have also shown that the discrepancy between $n_{ij}$ and $n_{ij}$ is small for YbInCu$_4$ owing to the weak hybridization strength $\Delta$.

Acknowledgements

We would like to thank Professor V. Zlatić for fruitful discussion. T.S. acknowledges support from the JSPS Research Fellowship for Young Scientists.

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4 According to Moore et al. [11], $n_{ij}$ is 0.72 in the high-temperature phase and 0.60 in the low-temperature phase. Their $n_{ij}$ values and the $4f$ peak position observed in the present measurement are given by $\epsilon_f^0 = 0.195$ eV and $\Delta = 0.065$ eV for the high-temperature phase and by $\epsilon_f^0 = 0.082$ eV and $\Delta = 0.034$ eV for the low-temperature phase. These different values of $\epsilon_f^0$ and $\Delta$ do not change the discussion here.
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