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High-resolution photoemission study of the valence transition in YbInCu_4

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Abstract

We have performed a photoemission study of YbInCu_4 , which undergoes a first-order phase transition at $T_v \approx 40$ 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 YbInCu_4 samples but tracks the valence transition in the bulk YbInCu_4 , has been studied above and below T_v . 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.

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The isostructural first-order transition in YbInCu_4 , 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 $T_v = 40\text{--}70$ K [1–4]. A collection of Yb^{3+} 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_v 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 $\text{Yb}_{0.4}\text{In}_{0.6}\text{Cu}_2$ with the disordered C15 Laves-phase structure ($Fd\bar{3}m$), subsequent studies have confirmed that the sharp transition occurs in YbInCu_4 , which has the ordered C15B structure ($F\bar{4}3m$) both above

and below T_v [5]. Since the ionic radius of Yb^{2+} is larger than that of Yb^{3+} , the lattice constant increases by 0.15% on cooling across T_v . 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_v 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 YbInCu_4 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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Fig. 1. Entire valence band of YbInCu₄ taken with $h\nu = 40.8$ eV. 'Surface' indicates the Yb $4f^{14} \rightarrow 4f_{7/2}^{13}$ transition in the outermost layer.

According to Reinert et al. [9], the valence deduced from PES changes continuously across T_v , 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 photoelectron escape depth may also be different from the bulk [7,9]. Although not completely bulk sensitive, PES studies of YbInCu₄ may give useful information about the valence transition in bulk YbInCu₄ because the valence change across T_v in the subsurface region of YbInCu₄ reflects the valence transition in the bulk. Indeed, Moore et al. [11] found a sudden change in the $4f$ photoemission intensity at T_v . 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 YbInCu₄.

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 YbInCu₄ to be $T_K \approx 20$ K above T_v and 430 K below T_v by fitting the $J = 7/2$ Coqblin–Schrieffer model to the measured magnetic susceptibility. Lawrence et al. [13] analyzed the inelastic neutron spectrum of YbInCu₄ using the Anderson impurity model (AIM) and deduced T_K to be 25 K above T_v 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 ~ 35 meV would be expected through T_v in YbInCu₄ 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_v should be accompanied by a decrease in the number of

Fig. 2. Yb $4f$ spectra near E_F corresponding to the $4f^{14} \rightarrow 4f_{7/2}^{13}$ transition. The solid and dashed curves represent the spectra taken at 75 and 7 K, respectively. The solid curve is the sum of the time-dependent raw spectra (1) and (3), which are shown in the inset, and the dashed curve is the sum of (2) and (4). The vertical bars in the figure are a guide to eyes.

conduction electrons, which would lower the Fermi level. Such a shift may change possibly the bare $4f$ -level position (ϵ_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 YbInCu₄ 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 $T_v = 42$ 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 YbInCu₄ for the He I radiation ($h\nu = 21.2$ eV), and the cleaved surfaces were irregular, probably making the measured spectra angle integrated ones. Photoemission spectra between -19 eV and E_F were almost reproducible between different cleaving as reported by Reinert et al. [9]¹. The measurements were made at 75 and 7 K, bracketing

¹ We have chosen cleaving for the surface preparation in the present study rather than scraping because photoemission spectra of YbInCu₄ from scraped surfaces showed an extrinsic broad peak at ~ 0.25 eV [8,9], which would have originated from the disordered surface layers. In addition, we note that scraping below T_v might raise the temperature at the sample surface repeatedly across T_v . 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) $\epsilon_f^0 = 0.120$ eV and $\Delta = 0.042$ eV, (b) $\epsilon_f^0 = 0.067$ eV and $\Delta = 0.030$ eV, and (c) $\epsilon_f^0 = 1.0$ eV and $\Delta = 0.37$ eV.

$T_v = 42$ K. Since the cleavage at 7 K requires cooling of the sample with the post across T_v , 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 $\rightarrow$ 7 K $\rightarrow$ 75 K $\rightarrow$ 7 K for each in situ cleaved sample to subtract extrinsic 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 YbInCu₄ taken just after cleavage. The sharp signals just below E_F and at -1.3 eV correspond to the $4f^{14} \rightarrow 4f_{7/2}^{13}$ and $4f^{14} \rightarrow 4f_{5/2}^{13}$ transition, respectively. The broad peak around -1 eV, on the other hand, corresponds to the $4f^{14} \rightarrow 4f_{7/2}^{13}$ transition at the Yb atoms in the outermost layer. The other outermost Yb²⁺ signal of the $4f^{14} \rightarrow 4f_{5/2}^{13}$ 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 $4f^{13} \rightarrow 4f_{7/2}^{12}$ 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 LuInCu₄ [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_v , the Kondo peak becomes remarkably stronger in accordance with the decrease in the Yb 4f valence. At the same time, the intensity maximum of ~ -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 -35 meV and therefore does not affect the peak position appreciably². 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 ($4f^{14} \rightarrow 4f_{5/2}^{13}$ signal) at ~ -1.3 eV across T_v but found no shift in their spectra taken with the energy resolution of ~ 45 meV. We note that the spin-orbit replica is further broadened due to the shorter life time of the photohole 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 ϵ_f^0 and the continuum extending from $-B \equiv -0.15$ eV to $+B \equiv 0.15$ 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 $I(4f^n \rightarrow 4f^{n-1})$ is the $4f^n \rightarrow 4f^{n-1}$ photoemission intensity, using a finite Coulomb repulsion $U = 7$ eV to compare $n_{f,l} \equiv I(4f^{13} \rightarrow 4f^{12})/[I(4f^{13} \rightarrow 4f^{12}) + 7/8 I(4f^{14} \rightarrow 4f^{13})]$ and the ground-state 4f-hole occupancy n_f^3 . 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 n_f as $|c(13)|^2 + 2|c(12)|^2$, where the ground state $|\psi\rangle$ is expressed as $|\psi\rangle = c(14)|4f^{14}\rangle + c(13)|4f^{13}\rangle + c(12)|4f^{12}\rangle$. 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 $n_{f,l}$ deduced by

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 $n_{f,l}$ 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 $n_{f,I}$. We have convoluted all the calculated spectra with a Gaussian of 22 meV FWHM. From the experimentally determined peak position and $n_{f,I}$, ϵ_f^0 and the 4f-conduction band hybridization strength $\Delta = \pi/2B \int_{-B}^B \rho(\epsilon)|V(\epsilon)|^2 d\epsilon$ 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)⁴. Here, we have adjusted only these two parameters to reproduce both the peak position and $n_{f,I}$. Owing to the weak hybridization strength Δ , the discrepancy between n_f and $n_{f,I}$ is negligibly small: n_f ($n_{f,I}$) is 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 YbInCu₄. (If $\epsilon_f^0 = 1.0$ eV [10] and $\Delta = 3.18$ eV, $n_{f,I} = 0.57$ and $n_f = 0.77$ 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 YbInCu₄ [6], the DOS around E_F would be higher below T_v than that above it, which would increase Δ in the low-temperature phase. On the other hand, the expansion of the lattice below T_v would reduce $V(\epsilon)$ and hence Δ below T_v . The present result of the decrease in Δ below T_v 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 Δ to reproduce the peak position of -40 meV as shown by curve (c) in Fig. 3. We have found that $n_{f,I} = 0.86$ ($n_f = 0.90$), 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 Δ is responsible for the small 4f hole occupancy ($n_{f,I} \ll 1$) with the 4f peak position relatively close to E_F , which is characteristic of the photoemission spectra of YbInCu₄. The small value of ϵ_f^0 may be the origin of the 4f instability because a small change in ϵ_f^0 or Δ , which is negligible in the case of large ϵ_f^0 and Δ , may vary n_f 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 YbInCu₄.

In summary, we have studied the photoemission spectra of YbInCu₄ with high energy resolution. We have observed that the divalent 4f peak is shifted away from E_F on cooling across T_v . The 4f peak position and the Yb valence were analyzed using AIM with a finite U . We have shown that the proximity of ϵ_f^0 to E_F and the smallness of Δ are characteristic of YbInCu₄ and are responsible for the valence instability because n_f changes sensitively for a small change in ϵ_f^0 or Δ . We have also shown that the discrepancy between $n_{f,I}$ and n_f is small for YbInCu₄ owing to the weak hybridization strength Δ .

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⁴ According to Moore et al. [11], $n_{f,I}$ is 0.72 in the high-temperature phase and 0.60 in the low-temperature phase. Their $n_{f,I}$ 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 ϵ_f^0 and Δ do not change the discussion here.

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