Evolution of electronic states in the Kondo alloy system Yb$_{1-x}$Lu$_x$B$_{12}$

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We have studied the effect of Lu substitution on the Kondo insulator YbB$_{12}$ by high-resolution photoemission. Comparison of the spectra of YbB$_{12}$, Yb$_{0.5}$Lu$_{0.5}$B$_{12}$, and LuB$_{12}$ reveals that the density of states (DOS) of the B $sp$-derived conduction band near the Fermi level is reduced in YbB$_{12}$ over a rather wide ($\sim$40 meV) energy region. Lu substitution (i) recovers the reduced B $sp$ DOS, (ii) shifts the Yb 4f-derived Kondo peak towards higher binding energy, and (iii) decreases the Yb valence. These results are consistently analyzed using the Anderson-impurity model, and imply interaction between the Yb 4f ions mediated by the Yb 4f-B $sp$ hybridization in YbB$_{12}$. [S0163-1829(97)03846-0]

Kondo insulators have attracted many researchers’ attention due to their unique ground states and unusual low-energy excited properties. In a preceding work, we have pursued this issue from the photoemission spectroscopic point of view for YbB$_{12}$, which is the only Yb-based Kondo insulator. We have found that the observed position of the Kondo peak persists up to $T \gtrsim 60$ K in the Yb-rich region while it saturates to a constant value in the Lu-rich region. It shows a broad maximum at about 75 K and follows a Curie-Weiss law above $\sim 150$ K. Magnetic contributions to the low-temperature specific heat of Yb$_{1-x}$Lu$_x$B$_{12}$ show a $T$-linear behavior in Lu-rich ($x \approx 0.5$) samples while in $x \approx 0.25$ samples they show a clear Schottky-type behavior similar to pure YbB$_{12}$ with its maximum at $\sim 40$ K, again showing that the gap disappears only for a large amount of Lu substitution. The Lu 4f level forms the closed-shell 4$f^{14}$ configuration and is located well below $E_F$. Thus in the first approximation, the extra electrons added by Lu substitution are trapped in the Lu 4f level and do not contribute to the transport properties. Nevertheless the Lu substitution leads to the doping of a small number of conduction electrons because the valence of Lu (3+) is somewhat larger than that of Yb ($\sim 2.86^+)$.

Polycrystalline samples of Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ and LuB$_{12}$ were prepared by reducing Yb$_2$O$_3$ and Lu$_2$O$_3$ at 2200 °C. The LuB$_{12}$ samples contained a trace amount of Lu$_2$O$_3$. PES measurements were performed using He resonance lines (He I: $h\nu = 21.2$ eV; He II: 40.8 eV) and synchrotron radiation ($h\nu = 125$ eV). The latter measurements were made at beam line BL-3B of the Photon Factory, National Laboratory for High Energy Physics. The Fermi edge of Au film evaporated on the sample surface after each series of measurements was used to determine the Fermi level ($E_F$) position and the instrumental resolution. The resolution was $21 \pm 2$, $28 \pm 2$, and $55 \pm 2$ meV for He I, He II, and $h\nu = 125$ eV, respectively. All the measurements were done at $T \approx 30$ K. The base pressure of the spectrometer was $5 \times 10^{-11}$ Torr for the He I and He II measurements and $3.5 \times 10^{-10}$ Torr for the synchrotron radiation measurements. The sample surfaces were repeatedly scraped in situ with a diamond file.
Yb 0.5 Lu 0.5 B 12 is shifted toward higher binding energy by Lu 4f. For the photon energy of 125 eV used here, the Yb and Lu f cross sections are dominant. 13 Signals from Yb consist of two structures characteristic of valence fluctuating Yb compounds: divalent (4f14→4f13) and trivalent (4f13→4f12) parts. The divalent part is further decomposed into surface and bulk components, as shown in the figure. For Yb0.5Lu0.5B12, signals from the Lu 4f14→4f13 transition overlap the trivalent Yb signal. Prior to subtraction, the two spectra were normalized to the trivalent Yb valence so that no Yb trivalent signal appeared in the difference spectrum. In the difference spectrum, in addition to the prominent doublets from the bulk and surface Lu atoms, one can see residual divalent signals of bulk and surface Yb atoms near Ef, indicating that the Lu substitution causes a decrease of the Yb valence. Since the bulk residual signal amounts to ~30% of the bulk divalent signal in YbB12, the Yb valence in Yb0.5Lu0.5B12 is estimated to be ~2.82 compared with Yb valence ~2.86 in YbB12. 4

The hν=125 eV spectra in the upper panel of Fig. 2 (dots) show the Kondo peak corresponding to the j=7/2 final state of the 4f14→4f13 doublet. One notices distinct differences between the two spectra: (i) the peak for Yb0.5Lu0.5B12 is shifted toward higher binding energy by about 10 meV, and (ii) is broadened compared to that for YbB12. In order to discuss the Yb 4f signal with better resolution (~28 meV for Yb0.5Lu0.5B12 and ~42 meV for YbB12), we subtracted the He I spectra from the He II spectra so that the subtracted spectra, broadened with the resolution difference, agreed with the 125 eV spectra. Note that although there is a Yb 4f contribution in the He II spectra, the B 2p contribution is dominant in both the He I and He II spectra. 13 For hν=125 eV the B 2s contribution, which is relatively small for He I, is not negligible and thus we have allowed a small discrepancy between broadened He II – He I difference spectra and the 125 eV spectra on the higher binding energy side of the Kondo peak as shown in the upper panel of Fig. 2. As we fitted the difference spectra using Mahan’s asymmetric line shape convoluted with a Gaussian, the Gaussian width corresponding to the instrumental resolution was sufficient to fit the spectrum of YbB12 while larger Gaussian broadening was needed for Yb0.5Lu0.5B12. The fits show that the peak position is ~23 meV below Ef for YbB12 and ~31 meV for Yb0.5Lu0.5B12.

We compare the He I spectra of YbB12, Yb0.5Lu0.5B12, and LuB12 in the upper panel of Fig. 3. The figure reveals a gradual recovery of the missing spectral weight in the B 2p density of states (DOS) around Ef as Lu is substituted for Yb. Note that the spectral change occurs in a rather wide energy range of ~40 meV, in comparison with the transport activation energy of YbB12 (~6 meV). The spectrum of LuB12 could be fitted to a linearly varying DOS multiplied by the Fermi distribution function of 30 K as shown in the lower panel of Fig. 3; the solid curves in the upper panel are convolutions of the DOS curves in the lower panel with the instrumental resolution. The DOS curves employed to fit the spectra of Yb0.5Lu0.5B12 and YbB12 have a dip or pseudogap (produced by subtracting Gaussians from the linear DOS) around Ef. The spectral intensity at Ef for YbB12 thus turned out to be depressed by ~25% compared to

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**Figure 1** shows the entire valence-band spectra of Yb0.5Lu0.5B12 and YbB12 (Ref. 4) and their difference spectrum. For the photon energy of 125 eV used here, the Yb and Lu 4f photoionization cross sections are dominant. 13 Signals from Yb consist of two structures characteristic of valence fluctuating Yb compounds: divalent (4f14→4f13) and trivalent (4f13→4f12) parts. The trivalent part is further decomposed into surface and bulk components, 4,14,15 as shown in the figure. For Yb0.5Lu0.5B12, signals from the Lu 4f14→4f13 transition overlap the trivalent Yb signal. Prior to subtraction, the two spectra were normalized to the trivalent Yb signal intensity so that no Yb trivalent signal appeared in the difference spectrum. In the difference spectrum, in addition to the prominent doublets from the bulk and surface Lu atoms, one can see residual divalent signals of bulk and surface Yb atoms near Ef, indicating that the Lu substitution causes a decrease of the Yb valence. Since the bulk residual signal amounts to ~30% of the bulk divalent signal in YbB12, the Yb valence in Yb0.5Lu0.5B12 is estimated to be ~2.82 compared with Yb valence ~2.86 in YbB12. 4

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**Figure 2**. Photoemission spectra of Yb0.5Lu0.5B12 and YbB12 near Ef. Upper panel: Spectra taken with hν=125 eV (dots) and broadened He II – He I difference spectra (solid curves). Middle panel: He II – He I difference spectra (dots) and fits using Mahan’s line shape (solid curves). Lower panel: Calculated spectra using the AIM convoluted with a Gaussian of FWHM 40 meV.
LuB\textsubscript{12}. An attempt to fit the spectra with a small (a few meV) but fully opened gap at \( E_F \) has been unsuccessful.

The relationship between the “pseudogap” of the \( \sim 40 \) meV width and the \( \sim 6 \) meV transport gap is not clear at present. A recent electron tunneling study of SmB\textsubscript{6}, which is another Kondo insulator with a transport activation energy of \( \sim 4 \) meV,\textsuperscript{18} has revealed a broad dip of \( \sim 40 \) meV width around \( E_F \).\textsuperscript{19} Such a dip or pseudogap might be a characteristic feature of the Kondo insulators.

In the framework of the Anderson-impurity model (AIM), the properties of an Yb ion in the Kondo singlet ground state are described by\textsuperscript{7}

\[
\delta = B \exp \left( - \frac{\pi \epsilon_f^0}{N_f \Delta} \right), \quad \frac{\Delta}{\Delta + \pi \delta / N_f},
\]

to lowest order in \( 1/N_f \) with \( U_{ff} = \infty \), where \( \delta = k_B T_K \) is the Kondo peak position in the PES spectra, \( B \) is the conduction-band width above \( E_F \), \( \epsilon_f^0 \) is the bare \( f \) \((13 \rightarrow 14) \) level measured from \( E_F \) \((\epsilon_f^0 > 0)\), \( N_f = 8 \) is the degeneracy of the 4\textsubscript{f1/2} level, and \( n_f \) denotes the \( f \)-hole occupancy. We define the hybridization strength by \( \Delta = (\pi B f_0^2 \rho(\epsilon) V(\epsilon)^2 d\epsilon \), where \( \rho(\epsilon) \) is the conduction-band DOS and \( V(\epsilon) \) is the hybridization matrix element between the \( f \) and conduction electrons.\textsuperscript{20} In Yb\textsubscript{1−\textit{x}}Lu\textsubscript{\textit{x}}B\textsubscript{12}. Lu substitution may change two parameters of the model: (i) electron doping raises the Fermi level and thus reduces \( \rho(\epsilon) \); (ii) the recovery of the B \( sp \) band DOS \( \rho(\epsilon) \) around \( E_F \) increases \( \Delta \). With these changes in \( \rho(\epsilon) \) and \( \Delta \), \( \delta \) increases and hence \( n_f \) decreases according to Eq. (1), in qualitative agreement with the PES results. However, the calculations to lowest order in \( 1/N_f \) deal with only the unoccupied side of the conduction band for Yb compounds and are not influenced by the change in the conduction-band DOS below \( E_F \) as observed in the He I spectra. Also, the line shape of the Kondo peak cannot be analyzed with lowest-order calculations, which necessarily give a single and hence symmetric peak below \( E_F \).

In order to consider the effect of changes in the B \( sp \) band near \( E_F \) on the \( f \)-electron spectra, we have calculated the 4\textsubscript{f} photoemission spectra at \( T = 0 \) K to second order in 1/\( N_f \).\textsuperscript{21} A flat DOS of 0.3 eV width is considered for the conduction band with \( E_F \) in the middle.\textsuperscript{22} We have included lowest order \( f^{14}, f^{13} \), and \( f^{12} \) states and second order \( f^{14} \) state for the calculation of the initial state\textsuperscript{21} and lowest order \( f^{13}, f^{12} \), and \( f^{11} \) states and second order \( f^{14} \) and \( f^{13} \) states for the photoemission final states. Here, the lowest order \( f^{14} \) state stands for the state with \( n \) (\( n-1 \)) electrons in the conduction band for the initial (final) state. An electron-hole pair is added in the second-order states. Using this model, we have reproduced both the intensity ratio \( I(4f^{13} \rightarrow 4f^{12})/I(4f^{14} \rightarrow 4f^{13}) \), corrected for the difference in \( N_f \) \((=8 \text{ and } 14) \), and the Kondo peak position in the YbB\textsubscript{12} spectrum with \( \Delta = 0.21 \) eV, \( \rho_f^0 = 0.7 \) eV, and \( U_{ff} = 7 \) eV.\textsuperscript{23} The AIM calculations have thus given an asymmetric Kondo peak as shown in the lower panel of Fig. 2 although they cannot fully reproduce the experimentally observed asymmetry.\textsuperscript{24,25}

As already clear in Eq. (1), both decreasing \( \Delta \) and increasing \( \rho_f^0 \) cause qualitatively similar changes in the Kondo peak: the weight of the Kondo peak becomes smaller with its position approaching \( E_F \) and the weight of the 4\textsubscript{f13}−4\textsubscript{f12} transition increases; the \( f \)-hole occupancy \( n_f \) approaches unity. As \( \rho_f^0 \) changes, the position of the 4\textsubscript{f13}−4\textsubscript{f12} structure at the binding energy of about \( -\epsilon_f^0 + U_{ff} \) should be shifted by the same amount. Since the shift of the 4\textsubscript{f13}−4\textsubscript{f12} signal is much less than 0.1 eV (Fig. 1), we conclude that the change of \( \Delta \) rather than that of \( \rho_f^0 \) dominates the spectral change caused by the Lu substitution. In order to reproduce the changes in both the intensity ratio \( I(4f^{13} \rightarrow 4f^{12})/I(4f^{14} \rightarrow 4f^{13}) \) and the Kondo peak position in going from YbB\textsubscript{12} to Yb\textsubscript{0.5}Lu\textsubscript{0.5}B\textsubscript{12}, \( \Delta \) is varied from 0.21 eV to 0.28 eV as shown in the lower panel of Fig. 2 with other parameters fixed. The increase in \( \Delta \) with Lu substitution deduced from the AIM analysis is consistent with the recovery of the B \( sp \) DOS near \( E_F \) in the wide energy range observed in the He I spectra. The consistent changes of the Yb 4\textit{f} spectra and the B \( sp \) DOS mean that the presence of the 4\textit{f}-derived spectral weight near \( E_F \) affects the B \( sp \) DOS, which in turn affects the 4\textit{f} states on neighboring Yb atoms. That is, the 4\textit{f} states at different Yb sites are interacting with each other through the hybridization, indicating that the Kondo singlet in YbB\textsubscript{12} is not completely localized.

We have also studied the effect of gap opening in the conduction band using the AIM. We opened a narrow \((\sim 10 \) meV\) square-well-shaped gap locating the Fermi level at the middle of the gap, and found that the Kondo peak became narrower with its weight (and hence \( n_f \)) conserved and that the high-energy 4\textsubscript{f13}−4\textsubscript{f12} structure did not change at all. Experimentally we have indeed observed the narrowing of the Kondo peak in going from Yb\textsubscript{0.5}Lu\textsubscript{0.5}B\textsubscript{12} to YbB\textsubscript{12} but a substantial change in \( n_f \). Therefore the changes in the 4\textit{f} spectral line shape with Lu substitution do not necessarily imply the opening of a narrow gap in the B \( sp \) DOS. The absence of the narrow gap in the PES spectra in spite of the semiconducting behavior may indicate that the states near \( E_F \)
are localized due to disorder or that the Fermi level is located near the bottom of the band gap.

According to the AIM, the shift of the Kondo peak with Lu substitution should be accompanied by an increase of the Kondo temperature. Indeed the temperature where the magnetic susceptibilities reach the maximum\textsuperscript{11} increases by 10–20 K but to a lesser extent than the shift of the Kondo peak position. The maximum in the magnetic susceptibility near the bottom of the band gap.

In summary, we have studied how Lu substitution into YbB\textsubscript{12} changes the low-energy electronic structure. In going from YbB\textsubscript{12} to LuB\textsubscript{12}, the broad dip in the B sp-derived DOS is gradually filled and the simple Fermi edge is recovered; the Kondo peak is shifted towards higher binding energy. According to the AIM analysis, the change in the 4f spectral line shape is caused by the recovery of the conduction-band DOS around E\textsubscript{F}. Since the recovery of the conduction-band DOS is certainly caused by the disappearance of the Yb 4f spectral weight near E\textsubscript{F}, the present results reveal that interaction between the Yb ions is mediated by the 4f-conduction-band hybridization and therefore that there is finite interaction between the Kondo singlets in YbB\textsubscript{12}.

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\textsuperscript{22} The conduction band has been replaced by discrete levels \(\varepsilon_k (1 \leq k \leq N)\) with 0.01 eV interval; see, A. Kotani, T. Jo, and J. C. Parlebas, Adv. Phys. \textbf{37}, 37 (1988).
\textsuperscript{23} In our calculation, the equation \(I(4f^{13}\rightarrow4f^{12})/I(4f^{14}\rightarrow4f^{13})=[(N_f-1)\bar{n}_f]/[N_f(1-\bar{n}_f)]\) underestimates \(\bar{n}_f\) by 5% owing to the Yb 4f–B sp hybridization. The same discrepancy has been discussed in Ref. 7 in the case of Ce compounds.
\textsuperscript{24} P. Weibel \textit{et al.} [Z. Phys. B \textbf{91}, 337 (1993)] have reported that the Kondo peak is asymmetric and broader than the single-impurity calculation for YbAgCu\(_4\).
\textsuperscript{25} We calculated the spectra by changing the conduction-band width from 0.3 eV to 3 eV, and found that the calculated Kondo peak was most asymmetric for 0.3 eV although the total B sp band width is as large as several eV. The effectively narrow band width would be a consequence of the renormalization of those effects which do not enter the AIM explicitly. Within a single impurity model, O. Gunnarsson and K. Schönhammer [Phys. Rev. B \textbf{40}, 4160 (1989)] have reported that for low-energy excitations of order \(k_BT\), Coulomb interaction between the 4f and conduction electrons renormalizes the hopping integral so that it has a maximum at \(E_F\). Interaction between different Yb sites mediated by the Yb 4f–B sp hybridization might be another cause of the renormalization.