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Evolution of electronic states in the Kondo alloy system $Yb_{1-x}Lu_xB_{12}$

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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 (~ 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.[1–3] In a preceding work,[4] we have pursued this issue from the photoemission spectroscopic point of view for YbB_{12}, which is the only Yb-based Kondo insulator.[5,6] We have found that the observed position of the Kondo peak agrees well with the Kondo temperature (T_K) deduced from the magnetic susceptibility in the framework of the single-impurity model. The highly asymmetric Kondo peak has been explained by a strongly energy-dependent self-energy correction to the one-electron band structure.[4,7–9] Since that work, some questions have remained unanswered. Firstly, there has not been a clear indication of gap opening at E_F in the spectra of YbB_{12}.[10] Secondly, the effects of hybridization between the Yb $4f$ state and B sp valence bands have not been clarified. By studying how the gap collapses with temperature, alloying, and magnetic field, one may be able to answer such questions. In this paper, we present a photoemission spectroscopy (PES) study of the alloy system $Yb_{1-x}Lu_xB_{12}$, in which the gap closes as Lu is substituted for Yb. We have observed both the $4f$- and valence-band electronic structures using various photon energies and discussed how the $4f$ and conduction electrons interact with each other and evolve with Lu substitution.

$Yb_{1-x}Lu_xB_{12}$ has a UB_{12}-type crystal structure in the whole composition range $0 \leqslant x \leqslant 1$. The electrical resistivity measurements have shown that the semiconducting behavior of YbB_{12} persists up to $x \sim 0.5$.[11] The magnetic susceptibility rapidly decreases below ~60 K in the Yb-rich region while it saturates to a constant value in the Lu-rich region.[11] It shows a broad maximum at about 75 K and follows a Curie-Weiss law above ~150 K. Magnetic contributions to the low-temperature specific heat of $Yb_{1-x}Lu_xB_{12}$ show a T-linear behavior in Lu-rich ($x \geqslant 0.5$) samples while in $x \sim 0.25$ samples they show a clear Schottky-type behavior similar to pure YbB_{12} with its maximum at ~40 K,[6] again showing that the gap disappears only for a large amount of Lu substitution. The Lu $4f$ level forms the closed-shell $4f^{14}$ configuration and is located well below E_F.[12] 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 (~2.86+).[4]

Polycrystalline samples of $Yb_{0.5}Lu_{0.5}B_{12}$ and LuB_{12} were prepared by reducing Yb_2O_3 and Lu_2O_3 at 2200 °C. The LuB_{12} samples contained a trace amount (~3%) of Yb. 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 21–25, ~28, and ~55 meV for He I, He II, and $h\nu = 125$ eV, respectively. All the measurements were done at ~ 30 K. The base pressure of the spectrometer was $\sim 5 \times 10^{-11}$ Torr for the He I and He II measurements and $\sim 3.5 \times 10^{-10}$ Torr for the synchrotron radiation measurements. The sample surfaces were repeatedly scraped *in situ* with a diamond file.

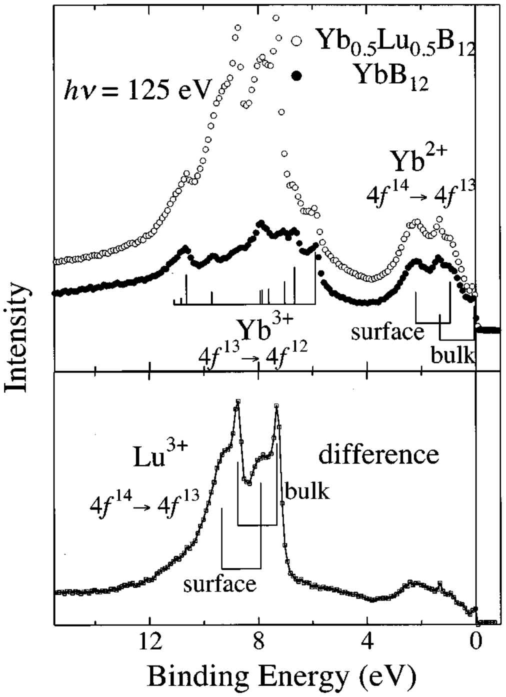

FIG. 1. Upper panel: valence-band photoemission spectra of $Yb_{0.5}Lu_{0.5}B_{12}$ and YbB_{12}. Calculated multiplet structures (Ref. 16) are also shown by vertical bars. Lower panel: the difference spectrum between $Yb_{0.5}Lu_{0.5}B_{12}$ and YbB_{12}.

Figure 1 shows the entire valence-band spectra of $Yb_{0.5}Lu_{0.5}B_{12}$ and YbB_{12} (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 ($4f^{14} \rightarrow 4f^{13}$) and trivalent ($4f^{13} \rightarrow 4f^{12}$) parts. The divalent part is further decomposed into surface and bulk components[4,14,15] as shown in the figure. For $Yb_{0.5}Lu_{0.5}B_{12}$, signals from the Lu $4f^{14} \rightarrow 4f^{13}$ 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 E_F, 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 YbB_{12}, the Yb valence in $Yb_{0.5}Lu_{0.5}B_{12}$ is estimated to be ~2.82 compared with Yb valence ~2.86 in YbB_{12}.[4]

The $h\nu = 125$ eV spectra in the upper panel of Fig. 2 (dots) show the Kondo peak corresponding to the $j = 7/2$ final state of the $4f^{14} \rightarrow 4f^{13}$ doublet. One notices distinct differences between the two spectra: (i) the peak for $Yb_{0.5}Lu_{0.5}B_{12}$ is shifted toward higher binding energy by about 10 meV, and (ii) is broadened compared to that for YbB_{12}. In order to discuss the Yb $4f$ signal with better resolution (~ 28 meV for $Yb_{0.5}Lu_{0.5}B_{12}$ and ~ 42 meV[4] for YbB_{12}) 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 $h\nu = 125$ eV the B $2s$ contribution, which is relatively small for He I, is not negligible[13] 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[17] convoluted with a Gaussian, the Gaussian width corresponding to the instrumental resolution was sufficient to fit the spectrum of YbB_{12} while larger Gaussian broadening was needed for $Yb_{0.5}Lu_{0.5}B_{12}$. The fits show that the peak position is ~23 meV below E_F for YbB_{12} and ~31 meV for $Yb_{0.5}Lu_{0.5}B_{12}$.

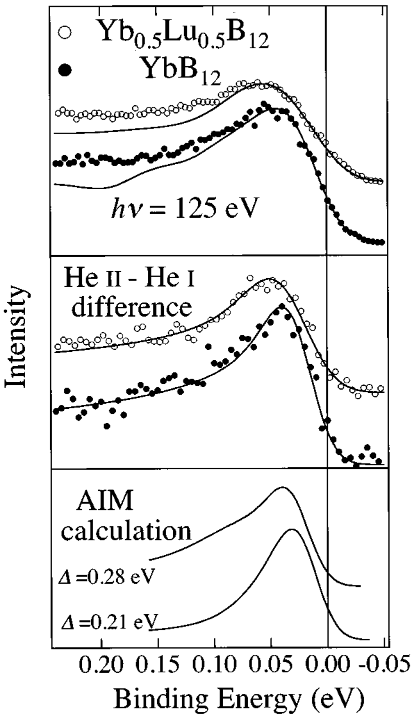

FIG. 2. Photoemission spectra of $Yb_{0.5}Lu_{0.5}B_{12}$ and YbB_{12} near E_F. Upper panel: Spectra taken with $h\nu = 125$ eV (dots) and broadened He II − He I difference spectra (solid curves). Middle panel: He II − He I difference spectra (dots) and fits using Mahan's line shape (solid curves). Lower panel: Calculated spectra using the AIM convoluted with a Gaussian of FWHM 40 meV.

We compare the He I spectra of YbB_{12}, $Yb_{0.5}Lu_{0.5}B_{12}$, and LuB_{12} 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 E_F 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 YbB_{12} (~6 meV). The spectrum of LuB_{12} 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 $Yb_{0.5}Lu_{0.5}B_{12}$ and YbB_{12} have a dip or pseudogap (produced by subtracting Gaussians from the linear DOS) around E_F. The spectral intensity at E_F for YbB_{12} thus turned out to be depressed by ~25% compared to

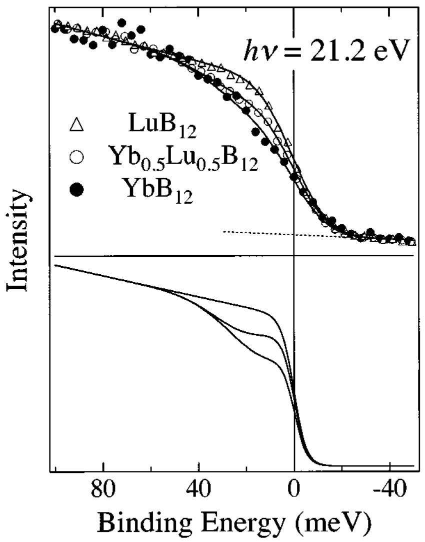

FIG. 3. Upper panel: He I spectra of $Yb_{1-x}Lu_xB_{12}$ and YbB_{12}. The solid curves have been obtained by convoluting the curves in the lower panel with a Gaussian. Lower panel: the assumed DOS multiplied by the Fermi distribution function.

LuB_{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 ~40 meV width and the ~6 meV transport gap is not clear at present. A recent electron tunneling study of SmB_6, which is another Kondo insulator with a transport activation energy of ~4 meV,[18] has revealed a broad dip of ~40 meV width around E_F.[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[7]

$$\delta = B\exp\left(-\frac{\pi\varepsilon_f^0}{N_f\Delta}\right), \qquad \overline{n}_f = \frac{\Delta}{\Delta+\pi\delta/N_f}, \tag{1}$$

to lowest order in $1/N_f$ with $U_{ff}=\infty$, where $\delta \equiv k_B T_K$ is the Kondo peak position in the PES spectra, B is the conduction-band width above E_F, ε_f^0 is the bare f ($f^{13}\rightarrow f^{14}$) level measured from E_F ($\varepsilon_f^0>0$), $N_f=8$ is the degeneracy of the $4f_{7/2}$ level, and $\overline{n}_f$ denotes the f-hole occupancy. We define the hybridization strength by $\Delta=(\pi/B)\int_0^B\rho(\varepsilon)|V(\varepsilon)|^2 d\varepsilon$, where $\rho(\varepsilon)$ is the conduction-band DOS and $V(\varepsilon)$ is the hybridization matrix element between the f and conduction electrons.[20] In $Yb_{1-x}Lu_xB_{12}$, Lu substitution may change two parameters of the model: (i) electron doping raises the Fermi level and thus reduces ε_f^0; (ii) the recovery of the B sp band DOS $\rho(\varepsilon)$ around E_F increases Δ. With these changes in ε_f^0 and Δ, δ increases and hence $\overline{n}_f$ 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 $4f$ photoemission spectra at $T=0$ K to second order in $1/N_f$.[21] A flat DOS of 0.3 eV width is considered for the conduction band with E_F in the middle.[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[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-n} state stands for the state with n holes in the f level and 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 and 14), and the Kondo peak position in the YbB_{12} spectrum with $\Delta=0.21$ eV, $\varepsilon_f^0=0.7$ eV, and $U_{ff}=7$ eV.[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.[24,25]

As already clear in Eq. (1), both decreasing Δ and increasing ε_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 $4f^{13}\rightarrow 4f^{12}$ transition increases; the f-hole occupancy $\overline{n}_f$ approaches unity. As ε_f^0 changes, the position of the $4f^{13}\rightarrow 4f^{12}$ structure at the binding energy of about $-\varepsilon_f^0+U_{ff}$ should be shifted by the same amount. Since the shift of the $4f^{13}\rightarrow 4f^{12}$ signal is much less than 0.1 eV (Fig. 1), we conclude that the change of Δ rather than that of ε_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_{12} to $Yb_{0.5}Lu_{0.5}B_{12}$, Δ 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 Δ 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 $4f$ spectra and the B sp DOS mean that the presence of the $4f$-derived spectral weight near E_F affects the B sp DOS, which in turn affects the $4f$ states on neighboring Yb atoms. That is, the $4f$ states at different Yb sites are interacting with each other through the hybridization, indicating that the Kondo singlet in YbB_{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 (~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 $\overline{n}_f$) conserved and that the high-energy $4f^{13}\rightarrow 4f^{12}$ structure did not change at all. Experimentally we have indeed observed the narrowing of the Kondo peak in going from $Yb_{0.5}Lu_{0.5}B_{12}$ to YbB_{12} but a substantial change in $\overline{n}_f$. Therefore the changes in the $4f$ 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[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 of the insulating $\mathrm{Yb}_{1-x}\mathrm{Lu}_x\mathrm{B}_{12}$ might simply have originated from the absence of the Pauli paramagnetism owing to the gap opening itself. The validity of the AIM, which has only one characteristic temperature T_K, remains to be checked for YbB_{12}.

In summary, we have studied how Lu substitution into YbB_{12} changes the low-energy electronic structure. In going from YbB_{12} to LuB_{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_F. Since the recovery of the conduction-band DOS is certainly caused by the disappearance of the Yb $4f$ spectral weight near E_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_{12}.

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[23] In our calculation, the equation $I(4f^{13} \rightarrow 4f^{12}) / I(4f^{14} \rightarrow 4f^{13}) = [(N_f - 1)\overline{n}_f]/[N_f(1 - \overline{n}_f)]$ underestimates $\overline{n}_f$ 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.

[24] P. Weibel *et al.* [Z. Phys. B **91**, 337 (1993)] have reported that the Kondo peak is asymmetric and broader than the single-impurity calculation for YbAgCu_4.

[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 **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.