High-resolution photoemission study of the temperature-dependent *c-f* hybridization gap in the Kondo semiconductor YbB_{12}

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The temperature-dependent metal-to-insulator transition in the Kondo semiconductor YbB_{12} single crystal has been studied by means of high-resolution photoemission spectroscopy with a tunable photon energy. An energy gap in the valence band is gradually formed below $T_1 \sim 150$ K, and at the same time, the Yb $4f_{7/2}$ Kondo peak at 55 meV grows and shifts to a lower binding energy. Below $T_2 \sim 60$ K, an additional spectral feature at 15 meV becomes apparent in the Yb $4f$ and Yb $5d$ derived spectra, indicating a strongly hybridized character. The 15 meV feature in the Yb $4f$ derived spectra is intense at the L point of the Brillouin zone and diminishes away from the L point. These results indicate that the energy gap is formed by the hybridization between the Yb $4f$ and Yb $5d$ states.

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Among $4f$ electron systems, Kondo semiconductors have attracted much interest for their unusual metal-to-insulator transition (MIT) at a characteristic temperature T^*.[1] In the temperature regime $T^* < T < T_K$ (Kondo temperature), the Kondo semiconductor seems to behave as a metal with a local moment. As the temperature decreases below T^*, the local moment gradually disappears, and an energy gap opens at the Fermi level (E_F).[1] The mechanism of the MIT in Kondo semiconductors is still an unsolved issue. Rare-earth Kondo semiconductors are located at the boundary between the valence fluctuation regime with an itinerant $4f$ state and the Kondo regime with a localized $4f$ state, where unusual physical phenomena are often observed.[2] YbB_{12}, with a cubic crystal structure, has been regarded as one of the most typical Kondo semiconductors,[1,3,4] and a detailed study of YbB_{12} should provide us with a clue to understand physics of the Kondo semiconductors. X-ray absorption spectroscopy measurement of YbB_{12} shows that the valence of Yb (v) is close to $+3$ ($v > +2.95$).[5] This suggests that YbB_{12} is located in the mixed valence regime very close to the Kondo regime and the slight appearance of the Yb^{2+} components should play an important role in the energy gap formation. Transport measurements on single-crystal samples indicated that an isotropic gap ($2\Delta_t = 6-8$ meV) is formed at a low temperature.[3] A significant reduction of the optical conductivity below ~ 80 K has been reported, which leads to the magnitude of the direct gap being $2\Delta_{opt} \sim 25$ meV.[7] Since the gap magnitude measured by optical reflectivity is larger than the transport gap ($\Delta_{opt} > \Delta_t$), the gap should be indirect and, therefore, the energy gap probably derives from the hybridization between a wide conduction band and a narrow $4f$ band ($c-f$ hybridization).[7]

A photoemission spectroscopy (PES) study, using a He lamp ($h\nu = 21.2$ eV), indicated a temperature-dependent reduction of the spectral intensity at E_F on cooling.[6] It is noteworthy that photoemission spectra of YbB_{12} taken at $h\nu = 21.2$ eV mainly reflect the valence bands derived from the Yb $5d$ and B $2sp$ states.[8] Although a Yb $4f$ spectrum at 30 K at $h\nu = 125$ eV with energy resolution $\Delta E \sim 55$ meV has been reported,[9,10] the details of the temperature dependence of the Yb $4f$ states near E_F has not thus far been clarified. Furthermore, there has been no angle-resolved photoemission (ARPES) study on YbB_{12}, and no direct evidence that the Yb $4f$ states are responsible for the energy gap formation.

In this paper, we present temperature-dependent ultraviolet PES spectra of a YbB_{12} single crystal taken at selected two-photon energies, $h\nu = 15.8$ and 100 eV, with improved energy resolution, $\Delta E = 5$ and 15 meV. The ratio of the Yb5 d/B$2p$ photoionization cross sections passes through a maximum at $h\nu \sim 16$ eV.[8] On the other hand, the photoemission spectrum taken at $h\nu \sim 100$ eV reflects the Yb $4f$ state due to the high photoionization cross section compared with other orbitals in the valence band.[8] With an improved energy resolution, the temperature-dependent energy gap formation in the valence bands and in the Yb $4f$ states have been directly revealed. Moreover, a peak at 15 meV was clearly observed at a low temperature for the first time. ARPES measurements clearly indicate that the peak is enhanced near the L point of the Brillouin zone. We will discuss a mechanism for the creation of the c-f hybridization gap in YbB_{12} taking into account the result of the LDA+U calculation,[11] and inelastic neutron scattering (INS) measurements.[12–15]

The single crystals of YbB_{12} and, as a metallic reference LuB_{12}, were grown by the floating zone method using an image furnace with four xenon lamps.[3] The high quality of the YbB_{12} crystal was confirmed by the fact that its resistivity increased by more than five orders of magnitude as the temperature decreased from 300 to 1.3 K.[1,3,6] For the temperature regime 15 K $< T <$ 40 K, the energy gap estimated from the electrical resistivity and Hall coefficients is 68 and 90 K, respectively.[3] The magnetic susceptibility follows a Curie-Weiss law down to 170 K, passes through a broad maximum at $T_{max} \sim 80$ K, and decreases on further cooling.[3,4] Angle-integrated and angle-resolved high-resolution PES measurements were performed using high-resolution hemispherical electron-energy analyzers

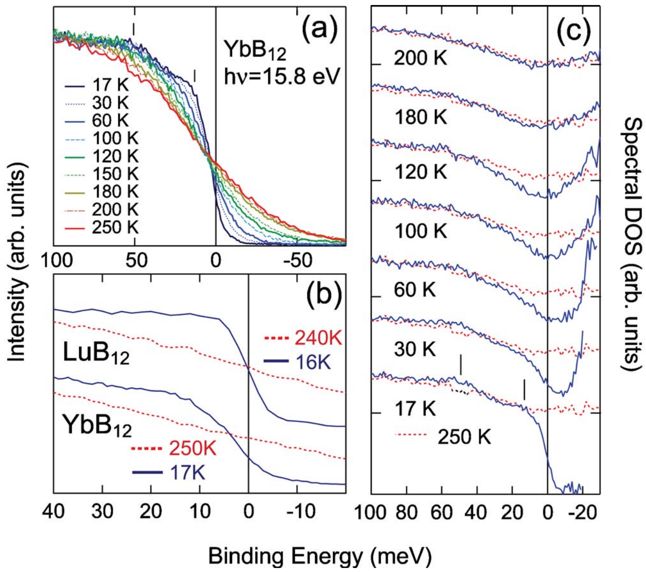

FIG. 1. (Color online) (a) Temperature-dependent high-resolution photoemission spectra of YbB_{12} taken at $h\nu=15.8$ eV. (b) Comparison with LuB_{12}. (c) Photoemission spectra divided by a Gaussian-broadened Fermi-Dirac function.

(GAMMADATA-SCIENTA SES200 and SES2002) installed on beamlines BL-1 ($h\nu=27-300$ eV)[16] and BL-9 ($h\nu=5-40$ eV)[17] of the electron-storage ring (HiSOR) at Hiroshima Synchrotron Radiation Center (HSRC), Hiroshima University. Energy calibration was performed using the Au Fermi edge at a low temperature. In order to obtain clean sample surfaces, we cleaved the single-crystal samples *in situ*. A cleaved (110) surface was used for the ARPES measurements. The base pressure was below 1.0×10^{-10} Torr.

Figure 1(a) shows temperature-dependent high-resolution PES spectra of YbB_{12} taken with $h\nu=15.8$ eV photons. The spectral intensity at E_F gradually decreases on cooling, indicating temperature-dependent energy gap formation. This behavior is similar to that seen in a previous experiment using HeI radiation[6] except that we now see clear spectral features at 15 and 50 meV. These spectral features become apparent due to stronger Yb 5d contribution. The reference system of metallic LuB_{12}, on the other hand, clearly exhibits a Fermi edge down to 16 K, confirming the importance of the Yb 4f contribution near E_F to the MIT in YbB_{12} [Fig. 1(b)]. In order to derive the spectral density-of-states (spectral DOS) of the valence states, the photoemission spectra were divided by a Gaussian-broadened ($\Delta E=5$ meV) Fermi-Dirac distribution function [Fig. 1(c)].[6] From these spectra, we obtained the spectral intensities at E_F and 15 meV as a function of temperature. As Fig. 2(a) shows, the spectral intensity at E_F decreases on cooling below ~150 K. The spectral feature at 15 meV, which was not observed in the previous experiment using a He lamp,[6] becomes apparent only below ~60 K.

Figure 3(a) exhibits Yb^{3+} and Yb^{2+} 4f derived spectral features at $h\nu=100$ eV over a wide binding energy region. Figure 3(b) shows two sharp peaks at 35 meV and 1.3 eV, which are derived from the Yb $4f_{7/2}$ and Yb $4f_{5/2}$ states in the bulk, respectively. Each of them is accompanied by a broad peak at 0.9 and 2.2 eV derived from the surface states.[18] The

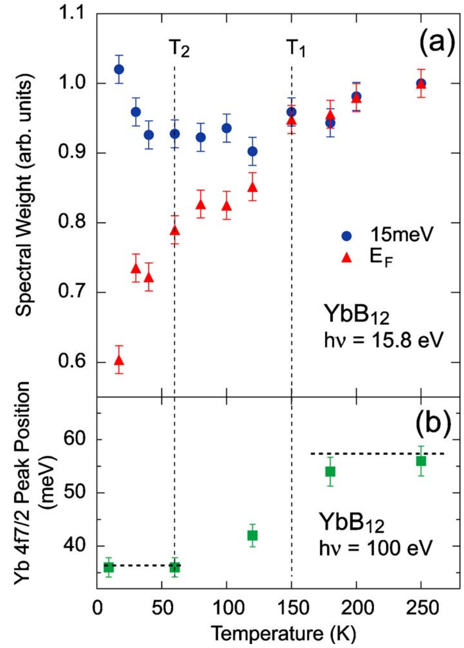

FIG. 2. (Color online) (a) Temperature dependence of spectral intensities of the valence bands at a binding energy of 15 meV and at E_F. (b) Peak position of the Yb $4f_{7/2}$ peak as a function of temperature. Below ~150 K, the peak is shifted to a lower binding energy by ~20 meV.

surface and bulk components are well separated and most of the spectral weight near E_F is derived from the bulk component. It should be noted that the spectral intensity from the bulk component with respect to the surface component is much larger in the present data compared with that seen in previous experiments on the scraped sample surface.[9,10] We can see significant temperature dependence only in the bulk component. Figure 3(c) shows the temperature dependence

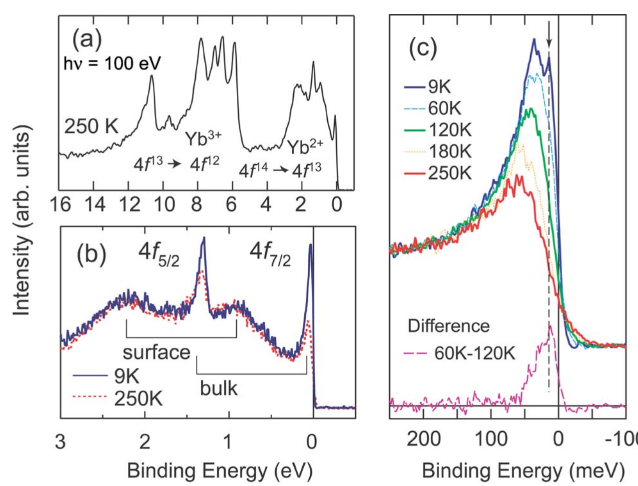

FIG. 3. (Color online) (a) Valence-band spectrum taken at $h\nu=100$ eV at 250 K in a wide energy range. (b) The Yb^{2+} 4f derived spectra at 9 and 250 K. (c) Temperature-dependent Yb $4f_{7/2}$ spectra near E_F. A difference spectrum obtained by subtracting the 120 K spectrum from the 60 K spectrum is plotted. The 15 meV peak appears below ~60 K.

of the Yb $4f_{7/2}$ states near E_F. On cooling, the intensity of the Yb $4f_{7/2}$ derived structure is increased and this peak is shifted to lower binding energy.[19] Figure 2(b) shows the binding energy of the $4f_{7/2}$ peak position as a function of temperature. The peak position stays at ~55 meV down to ~180 K, below which it shifts to reach a value of ~35 meV by ~60 K, after which it remains almost constant at ~35 meV.

An enhancement of the Yb $4f_{7/2}$ peak at low temperatures was also observed in the Kondo metal $YbAl_3$,[20] and was reasonably explained within the scheme of the single-impurity Anderson model (SIAM). The temperature-dependent enhancement and shift of the Yb $4f_{7/2}$ peak are indicated by a calculation based on the periodic Anderson model (PAM).[21] A theoretical investigation of the Seebeck coefficient also supports the notion of a shift of the $4f$ energy level towards E_F on cooling.[22]

Since our energy resolution is improved to 15 meV, a small peak at 15 meV in the Yb $4f$ spectrum at 9 K, which was not resolved in the previous photoemission measurements,[9] is now clearly resolved in addition to the main peak at ~35 meV. Even at 60 K, one can discern a shoulder on the lower binding energy side of the main peak at ~35 meV [see a difference spectrum in Fig. 3(c)]. The appearance of the 15 meV peak structure cannot be explained in the framework of the SIAM, indicating clearly that we should take into account the periodicity of the $4f$ states. Although the energy gap at E_F is obscured by the intense 15 meV peak whose binding energy is comparable to the energy resolution, as Figs. 1(a) and 1(c) show, a corresponding spectral feature is also present at 15 meV in the Yb $5d$ spectra.[23] We should note that the spectral feature at 15 meV in the Yb $5d$ state also becomes prominent below 60 K [Fig. 2(a)]. These observations indicate that the 15 meV peak is derived from the hybridization between the Yb $4f$ and Yb $5d$ states ($d-f$ hybridization).

We thus find two characteristic temperatures, namely the onset of the energy gap formation and the start of the Yb $4f_{7/2}$ peak shift at $T_1 \sim 150$ K, and the appearance of the 15 meV structure at a second, $T_2 \sim 60$ K. Although there is no anomaly in the physical properties at around T_1, we assume this temperature provides a measurement of the onset of the gradual crossover from the metallic to insulating states on cooling. On the other hand, T_2 is close to the temperature for the maximum of the magnetic susceptibility ~80 K,[3,4] and the temperature ~50 K from which the electrical resistivity increases rapidly.[1] The observed spectral DOS near E_F at 17 K forms a narrow energy gap of <15 meV, visible in the spectrum at the bottom of Fig. 1(c), which is close to the value of the transport gap, $2\Delta_t = 6-8$ meV.[3] We assume, therefore, that the coherent nature of the Yb $4f$ state manifests itself below T_2.

In order to further examine the nature of the 15 meV peak, we performed ARPES measurements around the L point and away from the L point (on the Σ line) by rotating the (110) axis as shown in Fig. 4. In this way one can examine energy bands in the ΓKLUX mirror plane along a line (in green) as indicated in the figure. In order to improve statistics, the spectra were averaged over the shaded region in Fig. 4. An inner potential was assumed to be 10 eV. The spectrum at the L point exhibits the 15 meV peak, but the peak disappears as we move away from the L point. Thus, the 15 meV peak is localized in k space. On the other hand, the peak at ~35 meV exists both at the L point and along the Σ line, but with much broader width. These observations imply that the 35 meV peak is not spatially delocalized. It is reasonable to assume that the 35 meV peak corresponds to the Kondo resonance as described by the SIAM, while it is difficult to interpret the 15 meV peak in the ARPES spectrum within a localized Kondo picture.[2] The present observations strongly suggest again that the 15 meV peak around the L point originates from the $4f$ states which are responsible for the $d-f$ hybridization-gap formation below T_2.

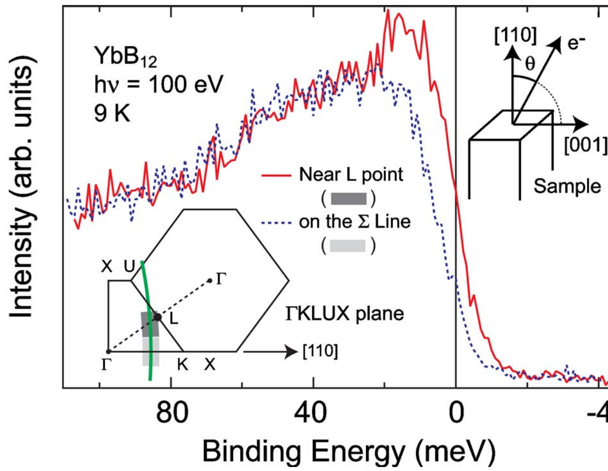

FIG. 4. (Color online) Angle resolved photoemission spectra of the Yb $4f_{7/2}$ peak at 9 K using $h\nu = 100$ eV.

Finally we discuss the 15 meV peak in relation to INS measurements.[12–15] Magnetic excitations were observed at ~15, ~20, and ~37 meV at low temperatures. The peak at 15 meV appeared below ~60 K, and became enhanced as temperature decreases.[13] The intensity of the 15 meV peak showed strong q dependence while that of the peak at ~37 meV did not. Recent INS results indicate that the peak at ~15 meV in YbB_{12} is related to the energy gap formation.[13–15] The 15 meV peak intensity is strongly enhanced at $\Delta q = (3/2, 3/2, 3/2)$.[14] It is surprising that the temperature dependence and the energy of the 15 meV peak in the magnetic response have many similarities with the PES spectral features seen in the present study.

Although the physical properties involved in the PES and INS measurements are different, we are tempted by these similarities to compare these two sets of results. If the 15 meV peak in the magnetic response corresponds to the indirect gap excitation at a low temperature,[4] it is reasonable to interpret the 15 meV peak based on the energy bands given by the LDA+U calculation.[11] Since the calculation can explain the specific heat measurement,[11] we assume that it gives the correct ground state. The calculation indicates that the conduction-band minimum (CBM) exists at the X and W points, and the valence-band maximum (VBM) is at the L point.[11] The calculation also reveals that around the L point there exist Yb $4f$ derived states with a binding energy of ~95 meV. The corresponding peak in the ARPES spectrum is located at 15 meV, the energy is smaller than the calculated one due to significant electron correlation effects. The flat VBM in the calculation originates in the Yb $4f$ and $5d$ states, which is consistent with the present PES results. The electrons at the VBM around the L point can be excited to the X points in the CBM, with a momentum transfer of $\Delta q = (3/2, 3/2, 3/2)$ and an energy transfer corresponding to the indirect energy gap of $\sim$15 meV. Thus, the peak at 15 meV in both the magnetic response and PES can be interpreted consistently within this framework.

It has been claimed that the magnetic excitations at 20 and 37 meV should derive from the many-body interactions.[12] In the PES spectrum, the peak at $\sim$35 meV is broad, which may correspond to the presence of two superimposed peaks at 20 and 37 meV. The two peak structure, is not resolved since these peaks are broadened due to the lifetime, and additionally broadened with the energy resolution $\sim$15 meV.

In summary, the temperature-dependent energy gap formation in both the valence bands and the Yb $4f$ states of YbB_{12} have been examined by means of high-resolution PES. An energy gap ($<$15 meV) is gradually formed in the valence band on cooling. Two characteristic temperatures are found at $T_1 \sim 150$ K and at $T_2 \sim 60$ K. The 55 meV peak at 250 K is shifted slightly toward lower binding energy by $\sim$20 meV on cooling below T_1. The appearance of a 15 meV peak in the Yb $4f$ and Yb $5d$ states is clearly observed below T_2. The 15 meV peak in the Yb $4f$ state is enhanced near the L point. The present results give direct evidence that the coherent nature of the Yb $4f$ state plays an important role in the energy gap formation via the d-f hybridization below T_2.

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[1] T. Takabatake, F. Iga, T. Yoshino, Y. Echizen, K. Katoh, K. Kobayashi, M. Higa, N. Shimizu, Y. Bando, G. Nakamoto, H. Fujii, K. Izawa, T. Suzuki, T. Fujita, M. Sera, M. Hiroi, K. Maezawa, S. Mock, H. v. Lohneysen, A. Bruckl, K. Neumaier, and K. Andres, J. Magn. Magn. Mater. **177-181**, 277 (1998).
[2] T. Kasuya, J. Phys. Soc. Jpn. **65**, 2548 (1996).
[3] F. Iga, N. Shimizu, and T. Takabatake, J. Magn. Magn. Mater. **177-181**, 337 (1998).
[4] F. Iga, S. Hiura, and T. Takabatake, Physica B **259-261**, 312 (1999).
[5] P. A. Alekseev, E. V. Nefeodova, U. Staub, J. -M. Mignot, V. N. Lazukov, I. P. Sadikov, L. Soderholm, S. R. Wassermann, Yu. B. Paderno, N. Yu. Shitsevalova, and A. Murani, Phys. Rev. B **63**, 064411 (2001).
[6] T. Susaki, Y. Takeda, M. Arita, K. Mamiya, A. Fujimori, K. Shimada, H. Namatame, M. Taniguchi, N. Shimizu, F. Iga, and T. Takabatake, Phys. Rev. Lett. **82**, 992 (1999).
[7] H. Okamura, S. Kimura, H. Shinozaki, T. Nanba, F. Iga, N. Shimizu, and T. Takabatake, Phys. Rev. B **58**, R7496 (1998).
[8] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).
[9] T. Susaki, A. Sekiyama, K. Kobayashi, T. Mizokawa, A. Fujimori, M. Tsunekawa, T. Muro, T. Matsushita, S. Suga, H. Ishii, T. Hanyu, A. Kimura, H. Namatame, M. Taniguchi, T. Mayahara, F. Iga, M. Kasaya, and H. Harima, Phys. Rev. Lett. **77**, 4269 (1996).
[10] T. Susaki, T. Konishi, A. Sekiyama, T. Mizokawa, A. Fujimori, T. Iwasaki, S. Ueda, T. Matsushita, S. Suga, H. Ishii, F. Iga, and M. Kasaya, Phys. Rev. B **56**, 13727 (1997).
[11] T. Saso and H. Harima, J. Phys. Soc. Jpn. **72**, 1131 (2003).
[12] A. Bouvet, T. Kasuya, M. Bonnet, L. P. Regnault, J. Rossat-Mignod, F. Iga, B. Fåk, and A. Severing, J. Phys.: Condens. Matter **10**, 5667 (1998).
[13] F. Iga, A. Bouvet, L. P. Regnault, T. Takabatake, A. Hiess, and T. Kasuya, J. Phys. Chem. Solids **60**, 1193 (1999).
[14] J. M. Mignot, P. A. Alekseev, K. Nemkovski, L. P. Regnault, and F. Iga (unpublished).
[15] E. V. Nefeodova, P. A. Alekseev, J.-M. Mignot, V. N. Lazukov, I. P. Sadikov, Yu. B. Paderno, N. Yu. Shitsevalova, and R. S. Eccleston, Phys. Rev. B **60**, 13507 (1999).
[16] K. Shimada, M. Arita, Y. Takea, H. Fujino, K. Kobayashi, T. Narimura, H. Namatame, and M. Taniguchi, Surf. Rev. Lett. **9**, 529 (2002).
[17] M. Arita, K. Shimada, H. Namatame, and M. Taniguchi, Surf. Rev. Lett. **9**, 535 (2002).
[18] See for example, S. Hüfner, *Photoelectron spectroscopy* (Springer-Verlag, Berlin, 2003), Chap. 8.
[19] We have conducted temperature-dependent hard x-ray PES using $h\nu$=5.95 keV, and found the similar temperature dependence [Y. Takeda *et al.*, Physica B **351**, 286 (2004)].
[20] L. H. Tjeng, S.-J. Oh, E.-J. Cho, H.-J. Lin, C. T. Chen, G.-H. Gweon, J.-H. Park, J. W. Allen, T. Suzuki, M. S. Makivić, and D. L. Cox, Phys. Rev. Lett. **71**, 1419 (1993).
[21] T. Mutou and D. S. Hirashima, J. Phys. Soc. Jpn. **63**, 4475 (1994).
[22] T. Saso and K. Urasaki, J. Phys. Soc. Jpn. **71**, Suppl 288 (2002).
[23] Recent photoconductivity measurements by H. Okamura, T. Michizawa, T. Nanba, S. Kimura, F. Iga, and T. Takabatake, J. Phys. Soc. Jpn. **74**, 1954 (2005), show also a structure at 15 meV at low temperature.