Temperature-Dependent High-Resolution Photoemission Study of the Kondo Insulator YbB_{12}

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We have performed a detailed temperature-dependent photoemission study of the conduction-band states in the Kondo insulator YbB_{12} using single crystalline samples. Measurements with improved energy resolution have revealed (pseudo)gaps of two energy scales. The size of the narrower gap $\sim$10 meV and its disappearance at high temperatures are consistent with the temperature dependence of the electrical resistivity and the magnetic susceptibility. The larger pseudogap of $\sim$100 meV depends on temperature even at room temperature. We discuss how the characteristics of the Kondo insulator are reflected in the conduction-band photoemission spectra. [S0031-9007(98)08323-9]

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The formation of a nonmagnetic insulating ground state in the Kondo insulator from a higher-temperature metallic state, where itinerant electrons are scattered by local moments, is one of the most intriguing phenomena in strongly correlated systems [1]. Among them YbB_{12} is the only Yb-based Kondo insulator [2]. In Yb compounds, because a large part of the $4f$ density of states (DOS) is on the occupied side of the Fermi level (E_F) in contrast to Ce compounds, one can study the main part of the f states by photoemission spectroscopy (PES). Actually, the peculiar temperature dependence of the $4f$ emission in Yb compounds has been studied extensively with high-resolution PES [3]. However, few PES studies have so far focused on the non-f conduction-band states. Schlesinger *et al.* remarked on the optical spectra of a "3d Kondo insulator" FeSi [4] that the entire conduction band, which screens all the local moments, could depend on the temperature. Such a temperature dependence could appear in the formation of the Kondo singlet irrespective of whether the system becomes a renormalized metal or insulator. The electrical resistivity of the Kondo insulator is expected to be dominated by the Kondo effect at high temperatures and to show activated behavior at low temperatures. Thus a significant temperature dependence is expected in the conduction-band states and such a temperature dependence may give a clue to understanding the Kondo insulators. In the preceding work using YbB_{12} polycrystals, we have studied the low-temperature electronic structure [5] and its Lu-substitution effects [6] by PES. For the conduction-band states of B $2sp$–Yb $5d$ hybridized character, we have found that a broad dip or a pseudogap of $\sim$40 meV width is present and is filled gradually with Lu substitution. YbB_{12} has a cubic UB_{12}-type structure [7] and is believed to develop a rather isotropic gap at low temperatures. In this work, we have made a PES study of YbB_{12} single crystals with higher energy resolution to investigate how the (pseudo)gap evolves as a function of temperature.

Single crystalline YbB_{12} samples were prepared using the traveling-solvent floating-zone method [8]. YbB_{12} forms by a peritectic reaction at 2200 °C, which temperature is close to the peritectic temperature of the adjacent phase YbB_{66} (2150 °C) [9]. In order to keep the temperature inhomogeneity less than 50 °C at 2200 °C we used an image furnace with four xenon lamps. Laue photographs and x-ray powder diffraction confirmed large samples to be single crystalline. Figure 1 shows the electrical resistivity and the magnetic susceptibility of the best rod grown

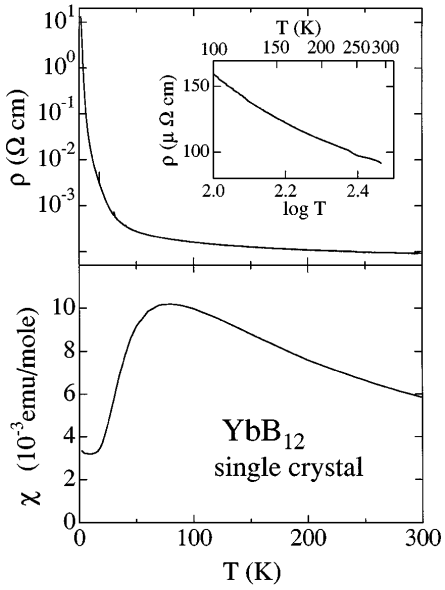

FIG. 1. Electrical resistivity and magnetic susceptibility of the YbB_{12} single crystal used in the present work. High-temperature ($100 < T < 300$ K) resistivity is plotted in the inset.

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in this way [8]. The resistivity increases monotonously by more than 5 orders of magnitude as the temperature is decreased from 300 to 1.3 K. The activation energy (Δ_{act}) for $15 < T < 40$ K is 68 K. The inset shows the high-temperature (>100 K) resistivity, which follows $-\log T$. The magnetic susceptibility is characteristic of the Kondo insulator: It follows a Curie-Weiss law above ~170 K and as the temperature decreases it shows a broad maximum at $T_{max} \sim 75$ K and then rapidly decreases. The low-temperature upturn of the magnetic susceptibility is very small compared with that of polycrystals, indicating a much reduced amount of magnetic impurities.

All the photoemission measurements were performed for samples cut from the rod whose magnetic and electrical properties are profiled in Fig. 1. We used a He I resonance line ($h\nu = 21.2$ eV) from a Gammadata He discharge lamp and a synchrotron radiation ($h\nu =$ 125 eV) for excitation light sources. Scienta SES-200 analyzers were used for energy analysis. The He I measurements were done at Hiroshima University and the synchrotron radiation measurements were done at beam line BL-3B of the Photon Factory, High Energy Accelerator Research Organization. The base pressure of the spectrometer was $\sim 1.4 \times 10^{-10}$ Torr for the He I measurements and $\sim 3.5 \times 10^{-10}$ Torr for the synchrotron radiation measurements. Liquid-He flow cryostats were used to rapidly cool the samples. The sample surfaces were scraped *in situ* with a diamond file, and therefore the measured spectra represent the angle-integrated spectral functions, namely, the spectral densities of states. We evaporated Au on the samples after every measurement to determine the Fermi-level (E_F) position and the energy resolution. The resolution was 7 meV for $h\nu = 21.2$ eV and ~0.14 eV for $h\nu = 125$ eV. The data acquisition system of the He I measurements was very stable for many hours and the accuracy of E_F, including its fluctuation with time, was less than ~0.1 meV.

Figure 2 shows the entire valence band of single crystalline YbB_{12} taken with the photon energy of $h\nu =$ 125 eV. The Yb $4f$ contribution is relatively large for $h\nu = 125$ eV [10]. The measurement temperature was ~20 K, low enough compared with $T_{max} \sim 75$ K, where the magnetic susceptibility shows a broad maximum. The spectrum consists of two sets of structures characteristic of intermediate-valence Yb compounds, namely, the divalent ($4f^{14} \rightarrow 4f^{13}$) and trivalent ($4f^{13} \rightarrow 4f^{12}$) parts [11–13]. The divalent part is further decomposed into surface and bulk signals as shown in the figure. The present spectra are almost identical to those of polycrystals reported earlier [5] except (a) that a broad non-f contribution around ~8 eV is reduced [14] and (b) that the surface signal increases (probably due to the difference in the irregularity of the scraped surfaces) for the single crystal. The decrease in the non-f contribution would correspond to the improved sample quality. A possible origin of the non-f emission around ~8 eV for the polycrystals, which does not depend much on exposing time, may be impurities in grain boundaries.

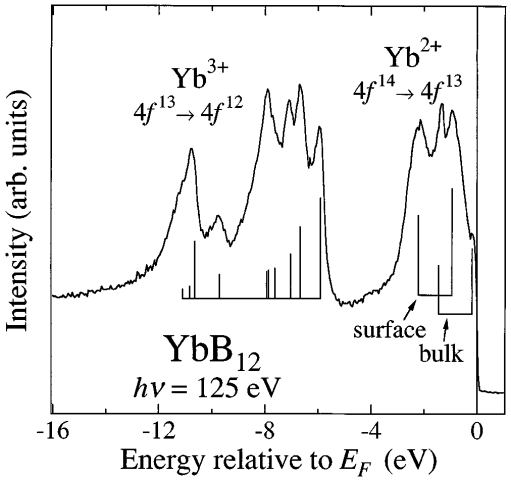

FIG. 2. Valence-band photoemission spectrum of single crystalline YbB_{12} ($h\nu = 125$ eV). Vertical bars for the trivalent part are multiplet structures calculated by Gerken [27].

Figure 3 shows high-resolution temperature-dependent PES spectra taken with the He I resonance line. According to the photoionization cross-sections, He I probes the B $2sp$–Yb $5d$-derived DOS [10]. We have made a series of temperature-dependent measurements without intermediate scraping: First we scraped the sample at 305 K and took spectra at that temperature. Then we measured

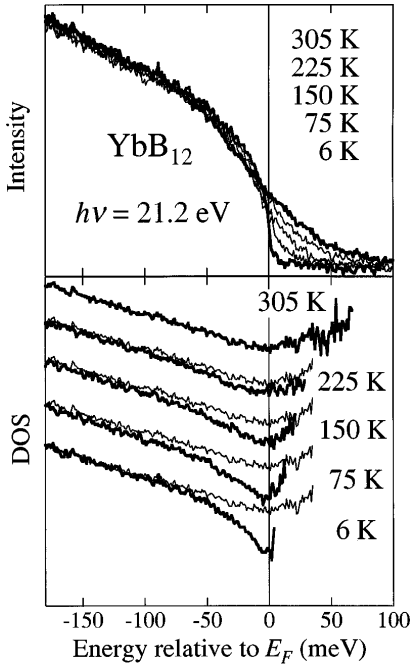

FIG. 3. Top: High-resolution photoemission spectra of YbB_{12} near E_F ($h\nu = 21.2$ eV). Bottom: Spectral DOS at each temperature (thick curve) together with the DOS at 305 K (thin curve). The bottom line is the zero for the DOS at 6 K and the other densities of states have been offset.

spectra while lowering the temperature from 225 to 6 K without rescraping it. All the spectra were taken in less than two hours after scraping. The spectrum taken at 6 K in this way was identical to that taken just after scraping. Several series of such measurement cycles were made and the spectra were all reproducible. The upper panel of Fig. 3 shows the accumulation of five series of such temperature-dependent measurements. The spectra have been normalized to the intensity below -0.2 eV. The two thick curves are the spectra taken at 305 and 6 K. With increasing temperature, significant spectral weight is distributed above E_F in spite of small changes below E_F, although in a simple metal an increase in the spectral weight above E_F should compensate with a decrease below E_F.

In order to isolate the temperature dependence of the spectral DOS, including the phonon effect, from that of the Fermi-Dirac (FD) distribution function, we have divided the spectra by the FD distribution function (convoluted with a Gaussian corresponding to the instrumental resolution) [15–17] as shown in the lower panel of Fig. 3. We present the spectral DOS up to $\sim 2k_BT$ above E_F where the FD function falls off to ~ 0.1 [18]. The results show that the DOS with a V-shaped dip varies with temperature in such a wide energy region as ~ 100 meV around E_F. This widely extended dip compared with the activation energy of 6 meV has already been implied in the previous measurements on polycrystalline YbB_{12} [5]. Here, the improved energy resolution has clarified the shape of the dip at low temperatures: The closer to E_F one goes, the steeper the slope appears. From the measurements on polycrystals at ~ 30 K we estimated that the spectral DOS at E_F was depressed by $\sim 25\%$ compared with that of LuB_{12}. Here, the depression amounts to more than 40% in going from 305 to 6 K because of the improved energy resolution and the extended temperature range. The width of the sharp cusplike depression in the very vicinity of E_F, which has not been observed in the previous work, is ~ 10 meV. This energy scale falls in the same range as the transport gap of $2\Delta_{\mathrm{act}} \sim 12$ meV. The appearance of this sharp depression only at low temperatures (6 to 75 K) is parallel to the temperature dependence of the magnetic susceptibility and the electrical resistivity: Below $T_{\mathrm{max}} \sim 75$ K the magnetic susceptibility decreases due to the missing Pauli paramagnetism. The electrical resistivity follows an activated form only below ~ 50 K. Above ~ 100 K it decreases slowly with temperature following $-\log T$, like a metallic Kondo material [19]. Except for the residual DOS at E_F at low temperatures the spectra imply that a narrow gap is formed at low temperatures while a Fermi edge exists at high temperatures. Here, we note that the bottom of the pseudogap in YbB_{12} is not located exactly at E_F but slightly below E_F. This may indicate that the dip feature is caused by hybridization of the conduction-band states with the $4f$ states since the $4f$ states are located largely below E_F.

A recent reflectivity study by Okamura *et al.* [20] has also revealed two energy scales in the spectrum of YbB_{12}: a gap of ~ 25 meV (threshold) with a shoulder at ~ 40 meV develops below 70 K in the optical conductivity. They are superposed on a broad dip with a shoulder at ~ 0.25 eV, which is present at all temperatures. Okamura *et al.* have attributed the broad structure to a $4f$-$5d$ transition, which has no direct relation with the peculiar behavior of the Kondo insulator. That the energy of the optical threshold is larger than the transport gap ($2\Delta_{\mathrm{act}} \sim 12$ meV) is characteristic of an indirect gap, implying a formation of a renormalized hybridization gap [21]. This is contrasted with the behavior of FeSi, in which the valence-band edge is located ~ 35 meV below E_F [22], nearly half of the optical gap (threshold) of ~ 60 meV [4]. The origin of the residual DOS at E_F in FeSi as well as in YbB_{12} remains unclear at present. This may be due to an extrinsic signal from a possibly metallic surface layer. Also, the residual DOS may have been caused partly by the finite energy resolution.

The high-temperature spectra of the conduction band is also worth remarking. The spectral DOS continues to be recovered even above 150 K and the broad V-shaped dip still survives at 305 K. The lower panel of Fig. 3 shows that the DOS is not conserved within ~ 100 meV of E_F, indicating spectral weight transfer with temperature over an energy scale larger than ~ 100 meV. Such a temperature dependence is most likely associated with changes in the $4f$ electronic states because the presence of the Yb $4f$ states has been shown to affect the conduction-band states over a wide (~ 40 meV) energy range in the study of $Yb_{1-x}Lu_xB_{12}$ [6].

Recently, Breuer *et al.* [23] reported the non-f photoemission spectra of another Kondo insulator $Ce_3Bi_4Pt_3$ ($T_{\mathrm{max}} \sim 80$ K and $\Delta_{\mathrm{act}} \sim 4$ meV) in comparison with a Kondo metal $CeSi_2$. The spectrum of $Ce_3Bi_4Pt_3$ showed a shallow dip of ~ 20 meV around E_F and the spectrum of $CeSi_2$ was identical to a simple Fermi edge. Very recently, it was found by Takeda *et al.* [24] that $Ce_3Bi_4Pt_3$ exhibited a sharp depression of the DOS at E_F as in the present case of YbB_{12}. The magnitude of the depression is smaller than that of YbB_{12}, corresponding to the weaker temperature dependence of the electrical resistivity in $Ce_3Bi_4Pt_3$ [25].

In Fig. 4 the spectral DOS at several energies are plotted as a function of temperature and are compared with the dc electrical conductivity. All the intensities are normalized at 305 K. A decrease in the intensity from 75 K to 6 K, which is expected from the dc conductivity, is present only in the vicinity (within ~ 10 meV) of E_F. For larger energy separation (>20 meV) from E_F, the DOS at 6 K is almost the same as or even higher than the value at 75 K. This means that in that high energy region no characteristic behavior of the Kondo insulator appears in the conduction-band spectra. Here, it should be remembered that the Kondo peak of YbB_{12} appears at ~ -25 meV[5], which sets a higher energy scale than the transport activation energy, and is similar to that of a

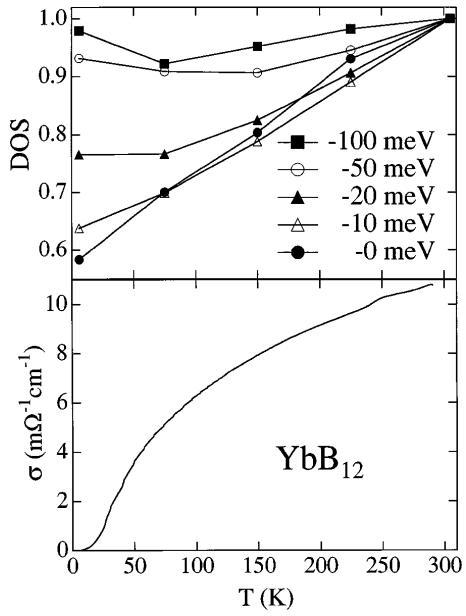

FIG. 4. Top: Spectral DOS of YbB_{12} at several energy positions as a function of temperature. Bottom: Electrical conductivity of the same sample as a function of temperature.

Kondo metal having a similar Kondo temperature: The Kondo peak position ($k_B T_K$) of YbB_{12} scales with $T_{\max}$ as in metallic Kondo systems [26]. Thus a crossover from a Kondo metal to a Kondo insulator is expected to be observed as a function of energy separation from E_F as well as of temperature. In order to clarify the crossover, a PES study of the conduction-band states in a metallic valence-fluctuating Yb system would provide valuable information. The difference between the conduction-band states of Yb compounds and those of Ce compounds is also an important issue to be clarified in the future.

To conclude, the temperature-dependent electronic structure of the conduction band of YbB_{12} has been studied by high-resolution PES. We have found that a sharp dip of $\sim$10 meV width appears at low temperatures in addition to the broad pseudogap of $\sim$100 meV, which survives at room temperature. The size of the sharp gap is consistent with the transport gap of $\sim$12 meV. The missing sharp gap at high temperature is also consistent with both the high-temperature electrical resistivity and the magnetic susceptibility, where no characteristic behavior of the Kondo insulator appears.

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