Hybridization gap formation in Kondo insulator YbB$_{12}$ observed using time-resolved photoemission spectroscopy

M. Okawa, Y. Ishida, M. Takahashi, T. Shimada, F. Iga, T. Takabatake, T. Saitoh and S. Shin

1Department of Applied Physics, Tokyo University of Science, Katsushika, Tokyo 125-8585, Japan
2Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
3College of Science, Ibaraki University, Mito, Ibaraki 310-8512, Japan
4Department of Quantum Matter and Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima 739-8530, Japan
5CREST, Japan Science and Technology Agency, Chiyoda, Tokyo 102-0075, Japan

(Dated: July 3, 2014)

PACS numbers: 71.27.+a, 75.30.Mb, 79.60.-i

Due to the strong electron correlation, lanthanide and actinide $f$ electron systems exhibit various ground states such as the Fermi liquid metal with valence fluctuation, magnetic order, quantum criticality, and exotic superconductivity. Among them, there is a class of rare-earth compounds called the Kondo insulators/semiconductors that show a metal-to-insulator crossover accompanied by a loss of local magnetic moment [1]. YbB$_{12}$ is a typical Kondo insulator with the fluctuating Yb valence around 2.9+ [1, 4, 5]. According to infrared spectroscopy studies [6], the Drude response is sharply decreased below $\sim$2.9+ [4, 5]. Inelastic neutron scattering studies reported the spin gap $\sim 80$ K and an indirect gap of $\sim 110$ K. In harmony with this, the latter discovered a very long recombination time exceeding 100 ps below $\sim T^*$. This is a clear manifestation of photoexcited electron-hole pairs accumulating at the pseudogap edges, which is interpreted as a developing hard gap. The finite spectral weight of the 15-meV pseudogap at the Fermi level implies a possibility of a topological Kondo insulator, which has recently been predicted in theory.

Detailed low-energy electronic structure of a Kondo insulator YbB$_{12}$ was revealed by a synergistic combination of ultrahigh-resolution laser photoemission spectroscopy (PES) and time-resolved PES. The former confirmed a 25-meV pseudogap corresponding to the Kondo temperature of this material, and more importantly, it also revealed that a 15-meV pseudogap and a Kondo-peak feature developed below a crossover temperature $T^* \sim 110$ K. In harmony with this, the latter discovered a very long recombination time exceeding 100 ps below $\sim T^*$. This is a clear manifestation of photoexcited electron-hole pairs accumulating at the pseudogap edges, which is interpreted as a developing hard gap. The finite spectral weight of the 15-meV pseudogap at the Fermi level implies a possibility of a topological Kondo insulator, which has recently been predicted in theory.

Single crystals of YbB$_{12}$ were grown by the floating zone method [3]. In both ultrahigh-resolution laser-PES and TrPES measurements, the samples were fractured in situ under the base pressure of $\sim 2 \times 10^{-11}$ Torr, and the spectra were recorded using a VG Scienta R4000 analyzer. In ultrahigh-resolution laser-PES, the incident light was the 6th harmonic (6.994 eV) of a Nd:YVO$_4$ quasi-cw laser (Spectra-Physics Vanguard) and the energy resolution was set to 1 meV. In TrPES [19], the samples were excited by a $\sim 170$-fs pump pulse of $h\nu_1 = 1.47$ eV at a repetition rate of 250 kHz delivered from a Ti:Sapphire amplifier (Coherent RegA 9000), and the transient was probed by $h\nu_2 = 5.88$ eV, which is the 4th harmonic of $h\nu_1$ generated by two $\beta$-BaB$_2$O$_4$ non-linear optical crystals. To strictly avoid the multiphoton photoelectrons which start to appear at the laser fluence of $\geq 20 \mu J/cm^2$, we set it to 15 $\mu J/cm^2$, which induces surface heating of $\sim 10$ K at most, throughout the TrPES measurements. The energy and time resolutions were 12 meV and 0.41 ps, respectively, and the origin of pump-probe delay, $t = 0$, was calibrated in situ using TrPES of graphite attached next to the sample [19]. $E_F$ was...
spectra were normalized to the area at $110 \pm 7$ K. (d) Spectral intensity at $12$ meV, $15$ meV, $30$ meV, and $45$ meV as functions of temperature. Solid lines are guides to the eye.

FIG. 1. Temperature dependence of the valence band spectra of YbB$_{12}$ in the near-$E_F$ region recorded by 7-eV laser. (a) Near-$E_F$ valence-band spectra at various temperatures. The inset shows a magnified view at $E_F$. (b) Experimental DOS. (c) Intensity of the experimental DOS relative to that at 225 K. (d) Spectral intensity at $E_F$, 15 meV, 30 meV, and 45 meV as functions of temperature. Solid lines are guides to the eye.

The spectral weight at $12$ meV and $15$ meV on cooling; the 25-meV pseudogap starts opening already at 200 K, the size of which is comparable with the Kondo temperature of YbB$_{12}$, 240 K. Furthermore, the spectroscopic studies of Yb-diluted Yb$_{1-x}$Lu$_x$B$_{12}$ [14, 22] reported that this pseudogap persists in a wide range of $x$. Therefore the 25-meV pseudogap should be attributed to the single-site Kondo effect. On the other hand, identifying the characteristic temperature of the 15-meV pseudogap is a little more complex; Fig. 1(d) shows the spectral intensity at $E_F$, 15 meV, 30 meV, and 45 meV (from Fig. 1(a)) as functions of temperature. In the upper panel of Fig. 1(d), one can observe a subtle kink in the $E_F$ spectral weight at $T^* \sim 110$ K, resulting in a faster depletion below $T^*$. Remarkably, $T^*$ coincides with a distinct upturn of the 15-meV spectral weight that develops into a peak (upper panel) and an onset of development of the 30- and 45-meV spectral weight (lower panel) upon cooling. These facts demonstrate that the 15-meV pseudogap is a manifestation of hybridization-gap opening at the characteristic temperature $T^*$. We discuss this issue in depth later in terms of TrPES data.

calibrated using the Fermi cutoff of evaporated Au [20].

Figure 1(a) shows temperature dependence of the ultrahigh-resolution laser-PES spectra of YbB$_{12}$. These spectra were normalized to the area at $110 \pm 10$ meV. We also show the experimental density of states (DOS) in Fig. 1(b), which was obtained by dividing the laser-PES spectra by a Gaussian-broadened Fermi-Dirac distribution function. The spectral weight at $12$ meV decreases on cooling, reflecting the opening of a pseudogap. It is also apparent from the inset to Fig. 1(a) that the Fermi edge is present even at the lowest temperature, which is a clear evidence of in-gap states coexisting with the pseudogap. A sharp peak at 15 meV and a broad peak at 45 meV were observed in the previous PES studies [13, 14]. The former corresponds to the renormalized band by the $c$-$f$ hybridization, while the latter 45-meV structure corresponds to the main peak of the Yb 4$f_{7/2}$ state, which can be found more clearly at 30–50 meV in hard x-ray PES spectra [3] because of a higher photoionization cross section ratio [21]. In addition, we also find another small peak at 30 meV. Such fine structures observed using ultrahigh-resolution PES could be considered as the crystal field splitting of the Yb 4$f$ state.

To investigate how the pseudogap and the peak develop in detail, we plot the normalized experimental DOS with respect to the 225-K DOS in Fig. 1(c). We can observe different evolutions of the two pseudogaps of 25 meV and 15 meV on cooling; the 25-meV pseudogap starts opening already at 200 K, the size of which is comparable with the Kondo temperature of YbB$_{12}$, 240 K [3]. Furthermore, the spectroscopic studies of Yb-diluted Yb$_{1-x}$Lu$_x$B$_{12}$ [14, 22] reported that this pseudogap persists in a wide range of $x$. Therefore the 25-meV pseudogap should be attributed to the single-site Kondo effect. On the other hand, identifying the characteristic temperature of the 15-meV pseudogap is a little more complex; Fig. 1(d) shows the spectral intensity at $E_F$, 15 meV, 30 meV, and 45 meV (from Fig. 1(a)) as functions of temperature. In the upper panel of Fig. 1(d), one can observe a subtle kink in the $E_F$ spectral weight at $T^* \sim 110$ K, resulting in a faster depletion below $T^*$. Remarkably, $T^*$ coincides with a distinct upturn of the 15-meV spectral weight that develops into a peak (upper panel) and an onset of development of the 30- and 45-meV spectral weight (lower panel) upon cooling. These facts demonstrate that the 15-meV pseudogap is a manifestation of hybridization-gap opening at the characteristic temperature $T^*$. We discuss this issue in depth later in terms of TrPES data.
Figures 2(a) and 2(b) show the spectral weight in the unoccupied side in the transient process, which is highlighted in a logarithmic TrPES intensity image [2(a)] and their delay profiles at −5 and −35 meV [2(b)]. When the pump pulse $h\nu_1$ is irradiated at $t = 0$, the valence-band electrons are photoexcited, so that the spectral intensity in the occupied side decreases and tails into the unoccupied side. We observed that the high-energy ($< -30$ meV) hot electrons relaxed into low-energy thermalized electrons through intraband transitions within $<1$ ps, similar to the case in a typical metal Au 22. Nevertheless, it is apparent that the electron distribution is not completely recovered even at $>1$ ps, which is clearly seen as the shaded area in Fig. 2(c). This indicates that the recovery dynamics of the electronic system is bottlenecked.

To clarify the features in the anomalously long recovery, the difference spectra $\Delta I(E_B) = I(E_B, t = 5.87 \text{ ps}) - I_{eq}(E_B)$ is also shown in Fig. 2(c), where $E_B$ is the binding energy, $I(E_B, t)$ is the PES spectrum before the pump irradiation, $\Delta I(E_B)$ exhibits a peak-and-valley feature throughout the transient, revealing the accumulation of the photoexcited electrons due to the bottleneck in the recovery dynamics. The valley bottom coincides with the 15-meV peak position observed in the valence-band spectra [Fig. 1] that should be identified as the charge-gap edge in the occupied side. The counterpart in the unoccupied side is the peak top located just above $E_F$. The charge gap thus does not have an electron-hole symmetry, but is asymmetric regarding $E_F$, resulting in the gap bottom centered below $E_F$. This is consistent with a recent infrared spectroscopy which reported an interband gap size of $\sim 15$ meV 6.

It is noteworthy that the photoexcited electrons and holes do not recombine through the in-gap metallic states. Our detection of the bottlenecked electronic recovery thus has twofold implications: (i) The scattering between the states consisting of the charge-gap and the in-gap states is negligibly small, which will impose tight constraints on the origin of the in-gap states (discussed later); (ii) TrPES can spectroscopically identify the real charge gap that may be buried in the in-gap states, which strongly motivates us to investigate the $T$-dependent dynamical response of the charge gap as below.

Now we discuss the temperature-dependence of the transient response. We show time-dependent spectra at several temperatures between 6 K and 175 K in the Supplemental Material 24. Here, we found that the accumulation of hot electrons gradually weakened on warming and was hardly observed at $T > T^* \sim 110$ K. This behavior can be explained by the fact that the photoexcited hot electrons rapidly go back into the occupied state via the intraband relaxation at high $T$, indicating the insulator-to-metal crossover with $T$. Since the time resolution of the TrPES measurements was over 400 fs, such an intraband rapid relaxation could not be observed clearly.

To discuss the temperature-dependence of the long-lived component as a measure of the hard-gap formation, the spectral weight evolutions due to the accumulated hot electrons at 6–175 K are shown in Fig. 3(a). These are defined as the integrated intensity in the region of the unoccupied side at each temperature. The long-lived component emerges on cooling and increasingly grows below $\sim 100$ K. As shown in Fig. 3(b), this long-lived component does not go back to the equilibrium state over 100 ps. This feature can be seen more clearly in the temperature dependence of the integrated intensity between 10 and 90 ps obtained from data shown in (a). The intensities were normalized to the lowest-temperature data. The characteristic temperature ($T^*$) shown in Fig. 3 is indicated by a dashed line at 110 K.

FIG. 3. (a) Time-dependence of the integrated intensities in the unoccupied region (−45 meV $< E_B < E_F$) at several temperatures. Dashed lines correspond to the zero intensity. (b) The long range decay behaviors ($\gg 100$ ps) at 8 K and 175 K. (c) Temperature dependence of the integrated intensity between 10 and 90 ps obtained from data shown in (a). The intensities were normalized to the lowest-temperature data. The characteristic temperature ($T^*$) shown in Fig. 3 is indicated by a dashed line at 110 K.

TrPES measurements.

Figures 3(a), 3(b) and 3(c) show schematic diagrams of the electron relaxation processes in metallic, crossover, and insulating (ground state) phases. In the metallic phase ($T > T^*$), a photoexcited electron can rapidly recombine with a hole through the intraband relaxation process. In the ground state, the c-f hybridization makes a narrow and indirect charge gap at $E_F$. The long-lived component is caused by the electron-hole recombination between the indirect charge gap, which should be assisted by phonon or magnon scattering with a large momentum ($k$) [dashed arrow in Fig. 3(c)]. A computational study on the Kondo lattice model based on the nonequilibrium
Kondo insulators SmB$_6$ band insulator creates much interest in topological insulators. Such a gapless surface states in the observed in-gap state includes a contribution from the non-hybridized conduction band, the localized $f$ state, and the $c$-$f$ hybridized band, respectively.

Thus we will not rule out the possibility that the in-gap state event at the lowest $T$. In TrPES measurements, we found that the long-lived ($\approx$100 ps) component that gradually develop upon cooling through $T^*$, which is taken as a signature of the charge-gap evolution. Thus we experimentally determined the characteristic temperature $T^*$ determined to be $\sim$110 K as the metal-to-insulator crossover in YbB$_{12}$. Coexistence with the metallic in-gap state observed even at the lowest temperature implies possible topological nature of the surface metallic state in YbB$_{12}$.

The authors thank T. Oka, P. Werner, K. Tsunetsugu, and K. Ueda for useful discussions. This work was supported by MEXT KAKENHI Grant Number 20102004 and JSPS KAKENHI Grant Numbers 23540413, 23840039, 23740256, and 26800165. JSPS supported this research also through the FIRST Program, initiated by the Council for Science and Technology Policy.

\[ \text{FIG. 4. Schematic electron (c)-hole (h) recombination processes in (a) the metallic state (} T > T^*\text{), (b) the crossover state (} T \lesssim T^*\text{), and (c) the insulating ground state (} T = 0\text{).} \]

\[ \text{\textit{E}_F, \text{\textit{E}}_c, \text{\textit{E}}_f, \text{\textit{h}}_F, \text{\textit{k}}_F, \text{\textit{p}}_f, \text{\textit{T}}_F \]
SUPPLEMENTAL MATERIAL

For the spectra acquired without pump pulses, we determined the Fermi level $E_F$ using the Fermi-edge position of evaporated Au film which was electrically connected to the sample. However, in the spectra with pump pulses, we found a rigid spectral shift. Figure 5(a) shows pump-off and -on spectra at several temperatures. In the pump-on spectra, the delay time was set to $-2$ ps. At $T = 10$ K, a clear spectral shift of 10 meV appears by irradiating pump pulses, although delay $t$ is before 0 ps. The lineshapes of these spectra at 10 K are completely identical to each other as shown in the inset of Fig. 5. Such a spectral shift can also be observed in the 50-K spectra (the shift of 1 meV), while it was not observed in the spectra at 110 and 140 K ($\leq T^* \sim 110$ K). The shift in our data is not induced by the space charge effect because the spectra move to the higher binding energy side which is the opposite direction of the effect [29]. Taking into account that the spectral shift can be found only at low temperatures where YbB$_{12}$ shows the insulating feature, this may be due to the surface photovoltage (SPV) effect [30].

The SPV effect, if exists, is also a possible evidence for a charge-gap formation at $E_F$. To get rid of this effect, we aligned the binding energies of the time-resolved spectra to those without pump irradiation.

$$\text{Binding energy (meV)}$$

-100
-50
0
50
100

$$\text{Intensity (arb. units)}$$

1.66
1.64
1.62
1.60
1.58

$$\text{Pump power (mW)}$$

0 mW
1 mW
2 mW
5 mW
10 mW
15 mW

$$\text{Energy shift (meV)}$$

-40
0
40

$T = 10$ K

FIG. 5. (a) Comparison between pump-off and pump-on (delay of $-2$ ps) spectra at various temperatures. The inset shows the 10-meV shifted pump-on spectrum and the raw pump-off spectrum at 10 K. (b) Pump power dependence of near-$E_F$ spectra at 10 K. (c) Pump power dependence of the energy shift relative to the pump-off (0 mW) spectrum at 10 K.