Momentum-Dependent Hybridization Gap of The Kondo Semiconductor SmB$_6$

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(Dated: June 20, 2011)

We report the temperature-dependent three-dimensional angle-resolved photoemission spectra of the Kondo semiconductor SmB$_6$. We found a difference in the temperature dependence of the peaks at the X and Γ points, due to hybridization between the Sm 5d conduction band and the nearly localized Sm 4f state. The peak intensity at the X point has the same temperature dependence as the valence transition below 120 K, while that at the Γ point is consistent with the magnetic excitation at $Q = (0.5, 0.5, 0.5)$ below 30 K. This suggests that the hybridization with the valence transition mainly occurs at the X point, and the initial state of the magnetic excitation is located at the Γ point. The anomalous temperature dependence of the physical properties of SmB$_6$ is considered to originate in the coexistence between the hybridization and magnetic states.

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

Materials with strong electron correlation have exotic physical properties that cannot be predicted from first-principle band calculations. One example may be seen in a semiconductor with a very small energy gap, which appears in rare-earth compounds such as the Kondo semiconductor/insulator (KI) [1]. At high temperatures, KI behaves like a dense Kondo metal, while an energy gap with activation energy of several 10 meV appears at low temperature. The energy gap is believed to originate from hybridization between the nearly localized 4f state near the Fermi level ($E_F$) and the conduction band (c-f hybridization).

Numerous studies have investigated the energy gap of KI, using optical conductivity [2, 3], point contact spectroscopy [4], angle-integrated photoemission spectroscopy [8, 6], and other methods. However, the momentum dependence of the c-f hybridization gap, as well as the relation of the electronic structure to other physical properties, has yet to be studied. Because the c-f hybridization occurs at a specific momentum vector, the most direct method of observing the band dispersion of the c-f hybridization gap is three-dimensional angle-resolved photoemission spectroscopy (3D-ARPES) using a tunable photon source from synchrotron radiation. Thus, we measured the 3D-ARPES spectra to observe the c-f hybridization gap creation of a typical KI, SmB$_6$.

SmB$_6$ is a valence-fluctuation material in between Sm$^{2+}$($4f^6$) and Sm$^{3+}$($4f^5$) ions [7]. The electrical resistivity ($\rho$) decreases on cooling, like a metal, above the temperature of 100 K, but then reveals a semiconductor-like character with activation energy of 15 meV [8]. There are two characteristic temperatures on SmB$_6$; one is valence transition below 120 K, and the other is magnetic excitation below 30 K. The mean valence changes from 2.57 at 120 K to 2.50 at 40 K on cooling [9]. Coincidentally, the lattice constant, which normally shrinks above 120 K on cooling, anomalously expands from 120 K to a few tens K indicating the valence change from Sm$^{3+}$ to Sm$^{2+}$ [10]. On the other hand, the magnetic excitation at the scattering vector of $Q = (0.5, 0.5, 0.5)$, observed by inelastic neutron scattering (INS), rapidly increases below 30 K [11]. Then the mean valence slightly recovers from 2.50 to 2.52 below 30 K, and the lattice constant shrinks again. The reason for the different temperature dependence between the magnetic excitation and the valence transition has yet to be determined. At temperatures lower than 10 K, another gap (in-gap state) has been noted at about 4 meV through the observations of optical conductivity [3, 12], point-contact spectroscopy [4], and angle-integrated photoemission spectroscopy [8]. Below 3 K, $\rho$ becomes saturated and has a residual resistivity of several $\Omega\cdot$cm [13]. Recently, the residual resistivity has been suggested to originate from metallic behavior at the edge state on the surface [topological KI (TKI)] [14], but the relation of the electronic state to the in-gap state, has never been investigated experimentally.

In this Letter, we report the temperature dependence of the dispersion curve of the hybridization state using temperature-dependent 3D-ARPES, in order to determine the electronic structure and the reason for the different temperature dependence of the valence transition and magnetic excitation. We found that the hybridization band with a peak at the binding energy ($E_B$) of 15 meV at the X point gradually appears on cooling from 150 to 40 K, which has the same temperature dependence as the valence transition. At the Γ point, on the other hand, the peak at $E_B \sim$18 meV has the same temperature dependence as the magnetic excitation at $Q = (0.5, 0.5, 0.5)$, which differs from the 15-meV peak at the X point. This suggests that the magnetic excitation originates from the
hybridization band at the Γ point. In addition, another dispersion curve at \( E_B \approx 5 \) meV appears at 10 K, which corresponds to the in-gap state and is considered to be the origin of the residual resistivity.

A high purity single crystal of SmB\(_6\) was grown by the floating-zone method \[13\]. The sample cut along the (001) plane was cleaned by argon sputtering and annealing at 1400 °C, by using an infrared heating system under a vacuum of \( 10^{-8} \) Pa. The low-energy electron diffraction (LEED) image of the clean surface is shown in Fig. 1(a). The LEED image indicates that the SmB\(_6\) (001) surface has not only \( 1 \times 1 \) of the bulk but also a superlattice structure of \( 2 \times 1 \) of the surface, which is similar to the previous result \[16\]. The superlattice structure implies that the surface state is mostly boron-terminated B\(_6\); i.e., the Sm atoms do not appear as much on the surface. Therefore the surface state derived from Sm is expected to be suppressed.

Normal-emission and in-plane ARPES experiments in the vacuum-ultraviolet region were performed at beamlines 5U \[17\] and 7U \[18\], respectively, of the UVSOR-II storage ring, Institute for Molecular Science. The photon energies corresponding to high symmetry \( k \_F \) points, as shown in Fig. 1(b) were determined by using normal emission ARPES taken at BL5U (Fig. 1). Using the obtained high symmetry points, the temperature dependence of high-resolution ARPES spectra at the Γ and X points was measured at BL7U. The total energy resolutions were about 50 meV at BL5U and 5 meV at BL7U, and the vacuum during the measurement was less than \( 5 \times 10^{-9} \) Pa. LDA band structure calculation was performed by the full potential linearized augmented plane wave plus local orbital (LAPW+lo) method including spin-orbit coupling implemented in the WIEN2K code \[19\].

Figures 1(d1)–1(d3) are the ARPES images of the M–X–M, X–Γ–X, and R–M–R lines, taken at photon energies of 45.8, 70.0, and 48.2 eV, respectively, and the corresponding band calculation results. The photon energies at the high symmetry points are consistent with a previous work \[20\]. The flat bands at the binding energies \( (E_B) \) of 0, 0.2, 1, and 3 eV can be recognized as the multiplet structures of \( ^6H_{5/2}, ^6H_{7/2}, ^6P \), and \( ^6F \) of Sm\(^{2+}\) final state, respectively. There is another flat band at \( E_B \approx 1.5 \) eV, which seems to originate from the surface state of Sm \(^{4f}\), but the intensity is not great, because the surface is terminated by boron atoms, and the amount of Sm atoms is not large. The highly dispersive valence bands at \( E_B \geq 1.4 \) eV and the conduction band at \( E_B \leq 1.5 \) eV at the X point originate from the sp covalent state of the B\(_6\) network and the Sm \( 5d \) state, respectively. These bands are in good agreement with the band structure calculation. The band calculation indicated that the hybridization gap opens near the X point in Fig. 1(d1). Actually, the intensities of the Sm\(^{2+}\) final state multiplet \( ^6H \) and \( ^6F \) are greater near the X point than those at the M point. This implies that the hybridization occurs near the X point.

To investigate the \( c \)-\( f \) hybridization gap formation, we measured the temperature dependence of the Sm \( 5d \) character of the hybridization gap (peak) in energy distribution curves (EDCs) at the X and Γ points, as shown in Fig. 2. Because of the hybridization between the Sm \( 5d \) and \( 4f \) states, the \( 4f \) feature must appear in the Sm \( 5d \) EDC. Then we used low photon energies of 10.6 eV for the X point and 26 eV for the Γ point, because the Sm \( 4f \) cross section can be strongly suppressed by using lower energy photons below 30 eV \[21\]. The temperature dependence of EDCs obtained at the X and Γ points is shown in Figs. 2(a1) and 2(a2). At 10 K, there are peaks at \( E_B \approx 15 \) meV at the X point, and at 18 meV at the Γ point. These peaks have different temperature dependence. Figures 2(b1) and (b2) are the symmetrized spectra with respect to \( E_F \) of Figs. 2(a1) and 2(a2), respectively. Clear energy gaps with peaks appear at \( E_F \) at both the X and Γ points. Because the EDCs originate from the Sm \( 5d \) states, the peaks at the gap edges are evidence of the hybridization with the Sm \( 4f \) states. At the X point, the peak becomes visible at 100 K and increases on cooling. To clarify the relation of these peaks to other physical properties, the temperature dependence of the peak is plotted in Fig. 2(c1). The peak intensity...
FIG. 2: (Color online) Temperature dependence of energy distribution curves (EDCs) at the X point \( (hν = 10.6 \text{ eV}, \text{a1}) \) and the Γ point \( (26 \text{ eV}, \text{a2}) \), and their symmetrized spectra \( \text{(b1, b2)} \). EDCs were normalized at the binding energy and the Γ point \( (26 \text{ eV}, \text{a2}) \), and their symmetrized spectra \( \text{(b1, b2)} \) are offset by 0.2 for clarity. The temperature-dependent peak intensities relative to the intensity at 200 K of the 15-meV peak at the X point \( (c1) \) and of the 18-meV peak at the Γ point \( (c2) \). The mean valence number evaluated by the X-ray absorption spectroscopy (XAS) \( [9] \) and the peak intensity of the inelastic neutron scattering (INS) at \( Q = (0.5, 0.5, 0.5) \) \( [10] \), are also plotted.

Gradually increases below 150 K. The temperature dependence of the peak is very similar to the valence transition \( (2.57 \text{ at } 120 \text{ K} \rightarrow 2.50 \text{ at } 40 \text{ K}) \) observed by using X-ray absorption spectroscopy (XAS) at the Sm \( L_3 \) edge, as shown in Fig. \( \text{c1} \). Therefore the temperature dependence of the 15-meV peak at the X point indicates the change in the hybridization intensity, i.e., the hybridization gap opens at the X point. This is consistent with the LSDA+\( U \) band calculation with Sm\(^{2+} \) ions \( [22] \). The band calculation showed that the hybridization between the Sm\(^{2+} \)\( 5d \) conduction band and \( 4f_{5/2} \) states appears near the X point. On cooling, the hybridization becomes stable, and the mean valence shifts to divalent.

At the Γ point, on the other hand, the temperature dependence of the 18-meV peak is not the same as the 15-meV peak at the X point. The symmetrized spectrum in Fig. \( \text{c2} \) has no energy gap above 80 K. However, the energy gap with the 18-meV peak rapidly appears below 40 K, which differs from the temperature dependence of the 15-meV peak at the X point. In Fig. \( \text{c2} \), the temperature dependence of the relative intensity at \( E_B = 18 \text{ meV} \) is plotted, and its peak intensity has the same temperature dependence as the magnetic excitation at \( Q = (0.5, 0.5, 0.5) \) by INS \( [11] \). The temperature dependence of the 18-meV peak is consistent with that of the magnetic excitation, suggesting that the 18-meV peak at the Γ point (i.e., the hybridization band at the Γ point) is the initial state of the magnetic excitation. Strictly speaking, however, the peak energies of the magnetic excitations observed by INS and the Raman scattering \( [23] \) are about 14 and 16 meV, respectively, which is slightly lower energy than the 18-meV EDC peak. This might indicate the property of the magnetic exciton investigated in other KI, Yb\( B_{12} \) \( [24] \).

In the LSDA+\( U \) band calculation with Sm\(^{3+} \) ions \( [22] \), the energy level of the Sm\(^{3+} \)\( 5d \) state is close to that of the \( 4f_{7/2} \) state near the Γ point. Then the hybridization between these states would occur at the Γ point. Due to the opposite logic of the hybridization in the Sm\(^{2+} \) ions at the X point, the hybridization in the Sm\(^{3+} \) ions means that the mean valence shifts to trivalent. This is consistent with the evidence of the increase in the mean valence below 30 K \( [9] \).

FIG. 3: (Color online) (a) Temperature dependence of energy distribution curves divided by the Fermi-Dirac distribution curve in the X \( (0 \text{ Å}^{-1}) \)-M \( (0.76 \text{ Å}^{-1}) \) line, using 10.6-eV photon energy. The hybridization band dispersions are shown by marks, and the observed dispersive in-gap state is shown by vertical lines. Temperature dependence of the hybridization band in the X–M line \( (hν = 10.6 \text{ eV}) \) and the Γ–X line \( (hν = 26.0 \text{ eV}) \). The band dispersion derived from the LDA calculation (Fig. \( \text{H1} \)) with the energy scale in the right axis is also plotted by a solid line (b).
The creation of the hybridization gap is here described in detail. The temperature-dependent ARPES spectra, divided by the Fermi-Dirac distribution curve along the X–M line, are plotted in Figs. 2(a). At $T = 40$ K in Fig. 2(a), the $k$-dependence of the peak at $E_B = 15$ meV is almost flat. The band becomes dispersive below 20 K, as shown in Fig. 2(b). At 10 K, the band dispersion is very similar to that of the LDA band calculation, but the energy of the peak at $k_{(100)} = 0.4$ Å$^{-1}$ is about 18 meV, which is much lower than the calculated result of 70 meV. This suggests that the band dispersion far from the X point is strongly renormalized by the electron correlation with the renormalization factor $z$ of 0.26. Note that the band dispersion near the $\Gamma$ point shown in Fig. 2(c) is almost flat, and is also located at much lower energy than that in the LDA calculation ($E_B \sim 0.3$ eV), as shown by vertical lines in Fig. 2(a). Because the band dispersion of the in-gap state is almost flat at 20 K, it only appears at 10 K. The dispersive ARPES spectra suggest that the in-gap state is not a local state, such as an impurity state, but has a periodicity of the lattice constant. The electrical resistivity data indicates that the transport property changes from an activation type to residual resistivity below about 5 K. The ARPES data seem to be consistent with the electrical resistivity; i.e., the hybridization gap of 14 meV is dominant above 20 K, while the in-gap state originating the residual resistivity becomes dominant below 10 K. The in-gap state is a quasiparticle state with extremely low carrier density and with very low scattering rate. The origin of the carriers is thought to be the appearance of an edge state, but has a periodicity of the lattice constant. The hybridization gap opens at the X point, while the initial state of the magnetic excitation is the $\Gamma$ point.

At $T = 10$ K, another band dispersion, with an electron pocket at $k \sim 0.25$ Å$^{-1}$, appears around $E_B \sim 5$ meV, as shown by vertical lines in Fig. 2(a). Because the band dispersion of the in-gap state is almost flat at 20 K, it only appears at 10 K. The dispersive ARPES spectra suggest that the in-gap state is not a local state, such as an impurity state, but has a periodicity of the lattice constant. The electrical resistivity data indicates that the transport property changes from an activation type to residual resistivity below about 5 K. The ARPES data seem to be consistent with the electrical resistivity; i.e., the hybridization gap of 14 meV is dominant above 20 K, while the in-gap state originating the residual resistivity becomes dominant below 10 K. The in-gap state is a quasiparticle state with extremely low carrier density and with very low scattering rate. The origin of the carriers is thought to be the appearance of an edge state, but the actual cause is yet unclear. To determine the origin of the in-gap state, ARPES with higher energy and momentum resolution would be helpful.

To summarize, we have investigated the momentum-dependent hybridization state between the conduction band and 4$f$ states of SmB$_6$ by using a three-dimensional angle-resolved photoemission spectroscopy. The temperature dependence of the energy distribution curves suggests that the hybridization state at the binding energy of 15 meV at the X point is the energy gap and the origin of the valence transition below 120 K, while that at 18 meV at the $\Gamma$ point is the initial state of the magnetic excitation at $Q = (0.5, 0.5, 0.5)$. A dispersive in-gap state was also observed only at 10 K. The origin of the in-gap state is yet unclear, but it seems to be an intrinsic quasiparticle electronic state.

We would like to thank Prof. Dzero, Prof. Coleman, and Dr. Matsunami for their fruitful discussion. Part of this work was performed by the Use-of-UVSOR Facility Program of the Institute for Molecular Science. The work was partly supported by a Grant-in-Aid for Scientific Research (B) from MEXT of Japan (Grant No. 22340107).

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