Anomalous Duality of 4f Electrons in Filled Skutterudite $CeOs_4Sb_{12}$

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We study the electronic structure of the filled skutterudite $CeOs_4Sb_{12}$ using photoemission spectroscopy (PES). Soft x-ray excited Ce 3d-4f resonant PES confirms the existence of Ce 4f states at the Fermi level (E_F). Temperature dependent high-resolution laser-PES spectra reveal a pseudogap formation around E_F, which can be explained in terms of the hybridization gap. Simultaneously, a sharp feature is formed just above E_F with decreasing temperature. The heavy-fermion-like specific heat is attributed to the occupation of this feature. The results identify the origin of the anomalous coexistence of heavy-fermion and pseudogap behavior in terms of a symmetry dependent hybridization.

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It is well known that strongly correlated f-electron systems exhibit various ground states, including heavy-fermion metal, magnetically ordered metal, a Kondo semiconductor, and so on. Such a variety of phenomena is derived from a competition or an interplay of the localized and itinerant degrees of freedom of the f electrons. This f-electron duality is considered as a basic ingredient of quantum critical behavior, leading to exotic phenomena such as the coexistence of magnetism and superconductivity [1–4]. Aside from this, an anomalous dichotomy was also identified in several f-electron systems [5–7], namely, the coexistence of an electrically semiconducting behavior which is typical of very low carriers or a gap in the electronic density of states (DOS) and a significantly high specific heat at low temperature (T) which is usually observed in heavy-fermion metals.

In this Letter, we address the origin of this dichotomy in $CeOs_4Sb_{12}$ by means of photoemission spectroscopy (PES). $CeOs_4Sb_{12}$ crystallizes in the filled-skutterudite structure and exhibits anomalous physical properties. The electrical resistivity shows a typical metallic behavior above ~50 K, but increases rapidly below 50 K [7,8]. The Hall coefficient follows T^{-1} behavior in the wide T range (0.3–300 K), indicating the reduction of the carrier density with decreasing T [8]. The optical conductivity revealed an energy gap formation at low T due to the hybridization between conduction (c) band and Ce 4f states [9]. However, the electronic specific heat at low T shows a significantly enhanced value (92–180 mJ/K^2 mol) [7,10], indicating the existence of heavy-electron carriers. A simple localized f-electron picture due to the crystalline-electric-field (CEF) splitting between the doublet ground state and the quartet excited state suggested from the magnetic susceptibility [7], has been excluded by the neutron scattering [11] and the ultrasonic measurement [12]. In addition, a spin- or charge-density-wave transition at lower T (=0.8 K) has been proposed [10,13,14]. Consequently, the ground state properties of $CeOs_4Sb_{12}$ are not consistently explained, especially in the absence of electronic-structure studies in the vicinity of the Fermi level (E_F). Our detailed PES study shows that the dual character of Ce 4f electrons gives a good account for such anomalous properties: a coherent hybridization with c band forms the pseudogap below E_F, and a sharp feature just above E_F contributes to the heavy-fermion-like specific heat. The pseudogap and sharp feature are derived from the Γ_5^- and Γ_{67}^- states due to CEF splitting for T_h symmetry, respectively, (corresponding to Γ_7^- and Γ_8^- states for O_h symmetry, respectively [15]). The character of 4f electrons can be determined by the specific symmetry dependence of hybridization with the c bands based on the filled-skutterudite structure. Thus, the dual character represents an unconventional class of correlated f-electron systems.

Single crystals of $CeOs_4Sb_{12}$ were grown by the Sb-flux method [8]. PES was performed using soft x-ray synchrotron radiation and vacuum-ultraviolet laser source. Soft x-ray excited Ce 3d-4f resonant PES and x-ray absorption spectroscopy (XAS) were performed at undulator beam line BL17SU in SPring-8. PES spectra were measured using a hemispherical electron analyzer, Scienta SES-2002 [16]. The total energy resolution was set to ~200 and 100 meV at $T = 22$ K for the measurement of overall valence-band region and near E_F region, respectively. XAS was recorded using the total electron yield method. T-dependent laser PES was performed using a Scienta R4000WAL electron analyzer and a vacuum-ultraviolet laser ($h\nu = 6.994$ eV) [17]. The total energy resolution was set to 6 meV for T dependent measurements and 2 meV for the lowest T (4.2 K) measurement. For all experiments, a clean sample surface was obtained by fracturing or cleaving *in situ* at low T. The vacuum during all the measurements was below 4×10^{-8} Pa. All the PES spectra did not show angle-resolved effects, and hence are discussed in terms of the angle-integrated electronic structure in $CeOs_4Sb_{12}$.

Figure 1(a) shows the Ce $3d_{5/2}$-$4f$ XAS spectrum for $CeOs_4Sb_{12}$. The main peak at 882 eV is due to the $3d^9 4f^2$ final state, and no clear satellite structure is observed at higher photon energy. In strongly c-f hybridized systems, a satellite structure is observed at ~887 eV due to $3d^9 4f^1$ final state (from $4f^0$ ground state) [18–20]. Thus, $CeOs_4Sb_{12}$ can be considered to be a weakly mixed-valence system with an f-electron count $n_f = 0.97$–1 on the basis of single impurity Anderson model (SIAM) generally used for Kondo metals. The Ce $3d$-$4f$ resonant PES spectra for $CeOs_4Sb_{12}$ are shown in Fig. 1(b) and 1(c). The photon energies used are marked in the XAS spectrum by arrows in Fig. 1(a). All the spectra are normalized to the incident photon flux, measured as the drain current at the focusing mirror. The off-resonance spectrum is multiplied by 10 for clarity. Taking into account the photoionization cross sections [21], the off-resonance spectrum is expected to be dominated by Os $5d$ partial (p) DOS, while the on-resonance data are dominated by Ce $4f$ pDOS due to a resonance enhancement. The Ce $4f$ and Os $5d$ pDOS calculated using the local density approximation (LDA) [22] is also shown in Fig. 1(b), in comparison with the on- and off-resonance spectrum, respectively. For the off-resonance spectrum, the overall line shape is well reproduced by Os $5d$ pDOS in the LDA calculation. On the other hand, for the on-resonance spectrum, a deviation from the LDA calculation is observed. This result can be understood in terms of the f-weight distribution between the ionization peak (f^0 final state) at ~3.2 eV and the Kondo resonance peak (f^1 final state) around E_F [23], and is also consistent with the weakly mixed-valence character for $CeOs_4Sb_{12}$, as inferred from XAS. Figure 1(c) shows the higher-energy resolution ($\Delta E = 100$ meV) resonant PES spectra near E_F. The f^1 final state around E_F is accompanied by the shoulder at ~0.25 eV due to spin-orbit splitting. The Fermi edge is clearly observed for the on-resonance spectrum with the midpoint of the leading edge slightly above E_F [23,24]. This situation is more apparent in the spectral DOS as shown in Fig. 1(d). The on-resonance data shows a sharp rise above E_F, but off-resonance data shows monotonic decrease. This indicates that the Ce $4f$ states dominate the electronic structure at and around E_F.

Figure 2 shows the T dependence of laser-PES spectra for $CeOs_4Sb_{12}$, normalized for the integrated intensity between -0.1 and 0.3 eV. The key points in the spectra are (i) a pseudogap formation within ~50 meV coupled with a spectral-weight transfer up to ~120 meV with decreasing T, and (ii) a residual DOS (in-gap states) around E_F at low T in connection with unoccupied DOS. The inset of Fig. 2 shows the higher-resolution laser-PES spectrum at 4.2 K and the corresponding spectral DOS after dividing by the Fermi-Dirac function (plotted up to $5k_BT$ above E_F). The sharp rise above E_F is definitely confirmed. Thus, while the spectral weight of laser-PES data seems to

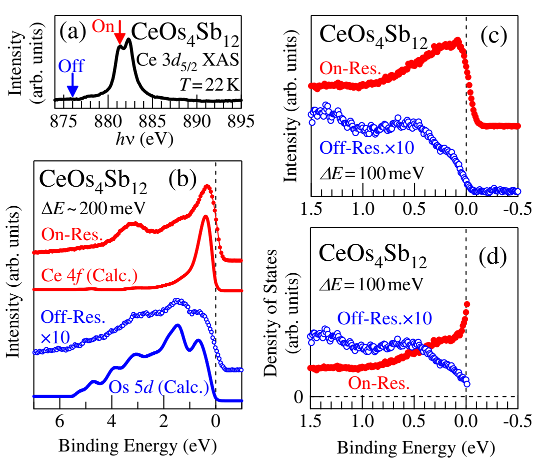

FIG. 1 (color online). (a) Ce $3d_{5/2}$ x-ray absorption spectrum for $CeOs_4Sb_{12}$. Arrows indicate the energies at which off- and on-resonant photoemission (PES) spectra were measured. (b) Ce $3d$-$4f$ resonant PES spectra for $CeOs_4Sb_{12}$ in comparison with the band-structure calculation. (c) Higher-resolution ($\Delta E = 100$ meV) resonant PES spectra near the Fermi level. (d) Spectral density of states, obtained by divided the on- and off-resonance PES spectra by resolution-convoluted Fermi-Dirac function.

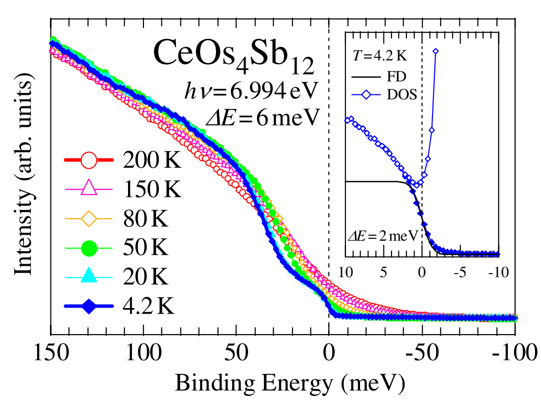

FIG. 2 (color online). Temperature dependence of laser photoemission spectra for $CeOs_4Sb_{12}$, normalized at the integrated intensity between -0.1 and 0.3 eV ($\Delta E = 6$ meV). The inset shows the higher-resolution ($\Delta E = 2$ meV) data at 4.2 K, and the spectral density of states obtained by dividing the corresponding Fermi-Dirac function.

show a monotonic decrease till E_F similar to the off-resonance spectrum near E_F as shown in Fig. 1(c), a clear sharp feature exists even in the laser-PES data just as is observed in the on-resonance spectrum.

In order to see the pseudogap behavior in detail, we also evaluated the T-dependent spectral DOS as shown in Fig. 3(a). A clear evolution of the pseudogap is observed. More importantly, the DOS just above E_F also shows evolution from a broad structure at 200 K to a sharp feature at low T. Figure 3(b) shows the T dependence of normalized spectral DOS, which is obtained by dividing each DOS by that at 200 K. The pseudogap magnitude is effectively estimated as the energy at which spectral weight of the normalized DOS starts to deplete, as indicated by arrows in Fig. 3(b). Figure 3(c) shows the obtained T variation of the pseudogap magnitude. It increases with decreasing T, together with the optical gap [9] also plotted in Fig. 3(c). In addition, the pseudogap magnitude obtained in this laser-PES coincides with approximately half or more than half of the optical gap. Considering that optical conductivity probes the electronic excitations from occupied DOS to unoccupied DOS, this behavior is consistent with each other. The pseudogap feature is attributed to the c-f hybridization gap [9], as is known from theoretical studies of a Kondo semiconductor based on the periodic Anderson model (PAM) [25], while it cannot be explained in the SIAM. The T dependence of the pseudogap indicates an evolution of c-f hybridization. According to the LDA calculation, the hybridization occurs between the a_u (Γ_5^-) main c band and Ce-4f Γ_5^- states [22]. Note that the pseudogap magnitude (~50 meV) is strongly renormalized

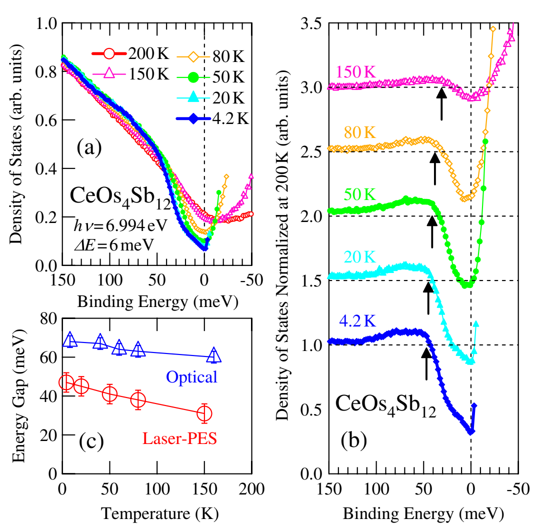

FIG. 3 (color online). (a) Spectral density of states (DOS) for $CeOs_4Sb_{12}$ as a function of temperature (T), obtained by dividing the resolution-convoluted Fermi-Dirac function for each T. (b) DOS for $CeOs_4Sb_{12}$ as a function of T, normalized to that at 200 K. For clarity, each spectrum is offset by 0.5. Arrows indicate the pseudogap energy. (c) The T dependence of the pseudogap energy in this laser-PES plotted with that obtained from the optical conductivity [9].

from that obtained by the LDA calculation (~250 meV). Thus, the 4f-Γ_5^- states play the main role in the pseudogap formation.

Next, we focus on the origin of the feature just above E_F. The laser-PES spectra certainly has a residual DOS around E_F even at low T in connection with the sharp unoccupied states seen in the inset of Fig. 2 and Fig. 3(a). Considering the sharp rise above E_F for the on-resonance (Ce 4f) spectrum in contrast to the monotonic decrease for the off-resonance (Os 5d) spectrum [Fig. 1(d)], the Ce 4f states should be responsible for the sharp feature in the unoccupied DOS just above E_F. In fact, the LDA calculation for $CeOs_4Sb_{12}$ predicted the presence of a sharp peak in the DOS just at E_F. The sharp peak is derived from the 4f-Γ_{67}^- states positioned just at E_F and the states cannot hybridize at the Γ point in the Brillouin zone with a_g (Γ_5^+) c band located above E_F because of opposite parity [22]. As shown in Fig. 3(a), the DOS for the laser-PES spectra shows a broad feature just above E_F at high T, which becomes sharper with decreasing T. This T dependence is thus derived from the fractional hybridization between f-Γ_{67}^- states and a_g-c band except for Γ point. Such a sharp feature provides a high DOS at and just above E_F, resulting in the heavy-electron carriers, possibly in the form of a Kondo resonance coexisting with the hybridization gap.

The schematic electronic structure for $CeOs_4Sb_{12}$ near E_F inferred from the present study is shown in Fig. 4. Figure 4(a) shows the discrete Γ_5^- and Γ_{67}^- states, which locate below and above E_F, respectively, without hybridization with c band. The a_u main c band hybridizes well with only Γ_5^- states, leading to a hybridization gap formation around E_F. As a result, two hybridized bands are formed, which are centered at Γ_5^- states before hybridiza-

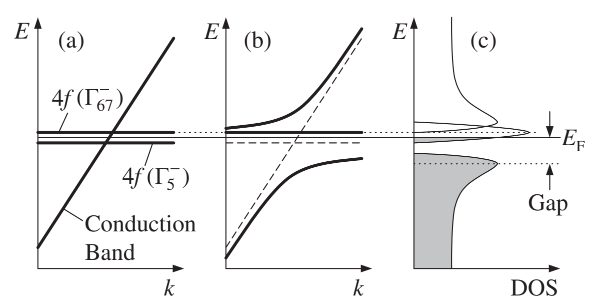

FIG. 4. Schematic picture of band dispersion and density of states (DOS) realized in $CeOs_4Sb_{12}$. (a) The dispersive conduction band and two discrete Ce 4f states without hybridization. The Γ_5^- and Γ_{67}^- states are located below and above Fermi level (E_F), respectively. (b) Only Γ_5^- states hybridize with the a_u (Γ_5^-) main conduction band, and two hybridized bands are formed below and above E_F. Γ_{67}^- states remain nearly dispersionless because they hardly hybridize with the opposite parity a_g (Γ_5^+) band (not shown) [22]. (c) DOS in the case of (b). The arrow represents the effective pseudogap magnitude observed in this laser photoemission study. The sharp f-DOS just above E_F due to Γ_{67}^- states is partially occupied.

tion as shown in Fig. 4(b). On the other hand, Γ_{67}^- states, which remain dispersionless, hardly contribute to the transport properties because of fractional hybridization with a_g-c band. In addition, the a_g-c band does not also provide metallic carriers, even though it exists near E_F. The rapid reduction in the electrical resistivity below 20 K under an applied magnetic field [8] suggests a suppressed scattering involving Γ_{67}^- states [26]. Consequently, the semiconducting behavior is naturally reflected in the resistivity, the Hall coefficient [8], and the far-infrared optical conductivity [9], because they should be strongly affected by the reduction of carrier concentration induced by the evolution of c-f (Γ_5^-) hybridization gap. It should also be noted that the absence of a clear CEF excitation in neutron scattering [11] could be explained in terms of the delocalized- and broadened-Γ_5^- states due to the c-f hybridization. On the other hand, the mass enhancement observed by the specific heat [7,10] can be provided by the sharp f DOS just above E_F due to mainly Γ_{67}^- states. Future work using angle-resolved PES is necessary for a comprehensive insight into the k-dependent electronic structure of $CeOs_4Sb_{12}$.

The in-gap states between two c-f hybridized bands are also obtained by an asymmetric PAM study [27]. In this model, a particle-hole asymmetry ($n_f = 2 - n_c \neq 1$, where n_c is c-electron number) gives a similar DOS as observed here and in agreement with the optical conductivity of $CeOs_4Sb_{12}$ [9]. However, the model involves a highly mixed-valence state ($n_f = 0.73$) in contrast with our XAS or resonant PES results ($n_f = 0.97$–1) and hence is not fully compatible with experimental results in $CeOs_4Sb_{12}$.

Usually, an f-electron duality has been regarded as an itinerant (coherent) character near E_F and a localized (incoherent) character in the higher binding energy side [28,29]. Such a duality is closely related to the coexistence of magnetism and superconductivity. In contrast, the present study indicates the dual character of a pseudogap due to c-f hybridization below E_F and a sharp feature just above E_F, resulting in the anomalous coexistence of hybridization-gap semiconducting and heavy-fermion behavior. This duality originates from the symmetry dependent hybridization of the c bands with the Ce-4f CEF states (Γ_5^- and Γ_{67}^-) based on the crystal structure of the filled-skutterudite compounds. Also, this unique electronic structure is related with the fact that $CeOs_4Sb_{12}$ locates in the vicinity of quantum critical point as was discussed recently [13].

In summary, we have performed PES on filled-skutterudite $CeOs_4Sb_{12}$. High-resolution laser-PES spectra reveal the pseudogap formation with finite DOS at E_F. Its T evolution can be explained in terms of the hybridization gap between the a_u-c band and $4f$-Γ_5^- states. Simultaneously, a sharp feature just above E_F was observed in the Ce $3d$-$4f$ resonant PES and laser PES, which arises from the $4f$-Γ_{67}^- states. The character of $4f$ electrons can be determined by the specific symmetry dependence of hybridization with the c bands. We believe the dual character observed here is responsible for anomalous coexistence of the hybridization-gap semiconducting and heavy-fermion thermal behavior.

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