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Electronic structure of the filled skutterudite compound $CeRu_4Sb_{12}$

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Ultrahigh-resolution photoemission spectra of $CeRu_4Sb_{12}$ reveal crossover behavior into a low carrier state. The density of states (DOS) around the Fermi level (E_F) decreases on lowering temperature and the semimetalliclike DOS is observed at 5.9 K. The temperature dependence of DOS at E_F is explained in terms of the development of the coherence. The smaller hybridization strength between the Ru-d state and the Ce-4f state prevents the hybridization gap from opening in $CeRu_4Sb_{12}$, which is realized in $CeRu_4P_{12}$.

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The rare-earth filled skutterudites $RETM_4X_{12}$ (RE: rare earth; TM: Fe, Ru, and Os; X: P, As, and Sb) have recently attracted much attention. Some of them exhibit a large positive peak in thermoelectric power, so that it is expected to apply them to advanced thermoelectric materials.[1–4] From a viewpoint of the condensed matter physics, they provide very interesting objects to study; a rich variety of ground state is realized in this series of compounds, e.g., superconductivity in all LaT_4X_{12} compounds, heavy-fermion behavior in $PrFe_4P_{12}$,[5] anomalous metal-insulator phase transition in $PrRu_4P_{12}$ and $SmRu_4P_{12}$, and so on.[6,7] It has been revealed that both TM and X play an important role in the emergence of such a wide variety of features in physical properties. Hybridization between TM-d, X-p, and RE-4f states must be responsible for the band structure in the vicinity of the Fermi level, E_F, especially the top of the valence band.[8,9]

The band calculation predicts a semiconducting ground state in all the family of Ce-based compounds $CeTM_4X_{12}$.[8,9] In fact, $CeTM_4P_{12}$ (TM=Fe, Ru, and Os) are semiconductors with a small energy gap, which is reported to increase from $CeOs_4P_{12}$ to $CeFe_4P_{12}$ with the valence of Ce.[10] This TM dependence of the semiconducting gap is consistent with the results of the band calculation. It is believed that the c-f hybridization brings about the energy gap of $CeTM_4P_{12}$ in a similar way to Kondo semiconductors (or Kondo semimetals). However, $CeRu_4Sb_{12}$ shows a metallic ground state contrary to the prediction. The $\rho(T)$ of $CeRu_4Sb_{12}$ has a well-defined hump around 80 K and it drops off at lower temperatures, which may be characterized as a valence-fluctuating system.[11,12] This difference between $CeRu_4P_{12}$ and $CeRu_4Sb_{12}$ indicates the fact that the decrease in the c-f hybridization from $CeRu_4P_{12}$ to $CeRu_4Sb_{12}$ makes a continuous transition from an insulating phase into a metallic phase of $CeTM_4X_{12}$ systems. If this would be the case, it gives a lucid explanation for the relationship between c-f hybridization and semiconducting gap formation.

Recently, upturn of the Hall coefficient and loss of the low-frequency intensities in the optical conductivity at low temperatures were reported in $CeRu_4Sb_{12}$.[13,14] These experimental results suggest the reduction in the carrier density at low temperatures. It would be important to examine what kind of ground state is realized in $CeRu_4Sb_{12}$ in order to get some insight into the metal-insulator border in Ce-based filled skutterudites.

In this Rapid Communication, we present the temperature dependent ultrahigh-resolution photoemission (UHRPE) spectra of $CeRu_4Sb_{12}$ down to 5.9 K. The electronic structure just below E_F was directly probed. The valence band spectra show that the 4f-band has much weight just below E_F. The spectra in the vicinity of E_F reveal that the density of states (DOS) at E_F decreases below $\sim$80 K, suggesting a crossover into the semimetalliclike state. This result can be described in a similar way to the hybridization gap model.

The $CeRu_4Sb_{12}$ sample preparation and characterization have been presented elsewhere.[15] Measurements were carried out in an ultrahigh-vacuum chamber where the base pressure is under 5×10^{-11} Torr. Samples were cooled by using the ^{4}He flow-type cryostat. Clean sample surfaces were obtained by scraping or fracturing these surfaces with a diamond file in the measurement chamber every $\sim$40 minutes in temperature equilibrium. We checked the valence spectra to confirm the surface cleanliness periodically. The UHRPE measurement system consists of a SCIENTA SES-2002 analyzer and a GAMMADATA discharging lamp. The position of E_F and an energy resolution of the system were determined by referring to the Fermi edge in the UHRPE spectra of Au which was evaporated on the sample holder. The energy resolution of the system was estimated to be $\sim$3.9 meV.

We present the valence-band spectra of $CeRu_4Sb_{12}$ measured by using He Iα and He IIβ resonance lines in Fig. 1. The He IIβ spectrum has a larger contribution from the 4f states and we can obtain information about 4f electronic structure effectively. The broad structure around 1.5 eV in both spectra is due to the valence band which is mainly made up by Ru-4d and Sb-5p states. To pick up information about the 4f electronic structure from the two similar spectra, the difference spectrum obtained by subtracting the He Iα spectrum from the He IIβ spectrum is presented in the bottom of the figure. Since the ratio of the photoemission cross section of Ce 4f orbital in He IIβ line to that in He Iα line is much larger than that of other orbitals, the difference spectrum effectively extracts the 4f states from the He IIβ spectrum. The remarkable point is the appearance of a peak just below E_F. This peak stands for the 4f-band which is caused by a strong hybridization between the Ce-4f state and the Ru-4d

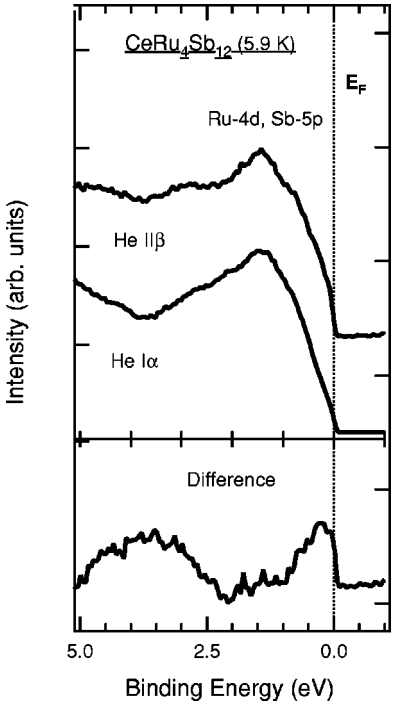

FIG. 1. Photoemission spectra of $CeRu_4Sb_{12}$ at 5.9 K. The spectra were measured by using the He IIβ (top) and the He Iα (middle) resonance lines. The difference spectrum (bottom) was obtained by subtracting the He I spectrum from the He II spectrum. The spectral intensity were normalized to the peak intensity at 1.5 eV.

state, suggesting large weights of the $4f$ states just below E_F. Large though the Ce-Ru spacing is, 12 Ru nearest neighbors make such strong hybridization possible. The problem of how to subtract the backgrounds and surface contribution without any ambiguity remains unclear, so that it is too complicated to discuss the components on higher binding energy. Assuming that the difference spectrum in higher binding-energy region reflects the $4f$ electronic structure, the

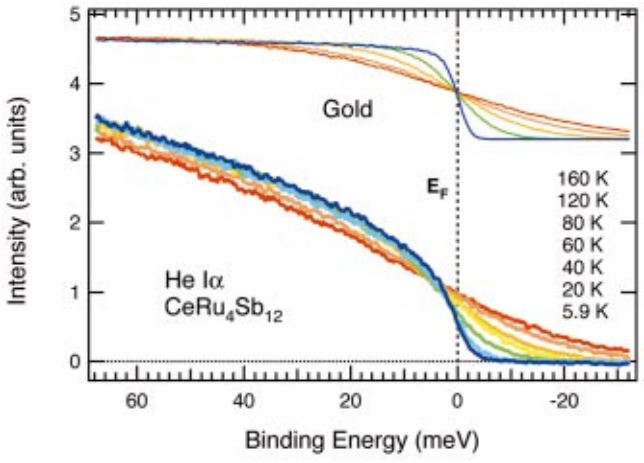

FIG. 2. (Color) UHRPE spectra of $CeRu_4Sb_{12}$ as a function of temperature. The spectral intensities are normalized to the integrated intensities of the valence band spectra, assuming that the $4f$-electron number is conserved within wide energy range ($\leqslant$2.5 eV). The spectra of gold are presented for a comparison.

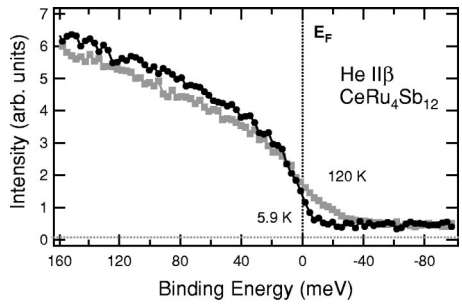

FIG. 3. UHRPE spectra of $CeRu_4Sb_{12}$ which were measured at 5.9 K and 120 K by using He IIβ resonance line.

broad structure beyond 2.5 eV may reflect the deeper $4f$ level ($\geqslant$2.5 eV). It must indicate an unusual coexistence of the deeper $4f$-level and the strong hybridized $4f$ states around E_F in $CeRu_4Sb_{12}$. But, the resonant-photoemission spectroscopy is necessary to specify the exact $4f$-level.

Figure 2 shows the temperature dependence of UHRPE spectra in the vicinity of E_F of $CeRu_4Sb_{12}$. The spectra of gold are added for a comparison. The Fermi edge of the spectra broadens by raising temperature due to the thermal excitation of the electron. But the spectra of gold at any temperature have midpoints of the leading edge with the same intensity at E_F. On the other hand, we can see that the spectra of $CeRu_4Sb_{12}$ do not have the same intensity at E_F in contrast with the gold. The intensity of the spectra at E_F, D(E_F), which is related to the DOS at E_F, gradually reduces with lowering temperature. The reduction in D(E_F) is also observed in the spectra measured by He IIβ line, as shown in Fig. 3. The D(E_F) at 5.9 K is lower than that at 120 K. It is expected that the reduction in DOS at E_F occurs in both the conduction states and the $4f$ states. These temperature dependences of the UHRPE spectra are reminiscent of those observed in Kondo semiconductors CeRhAs, CeRhSb, and

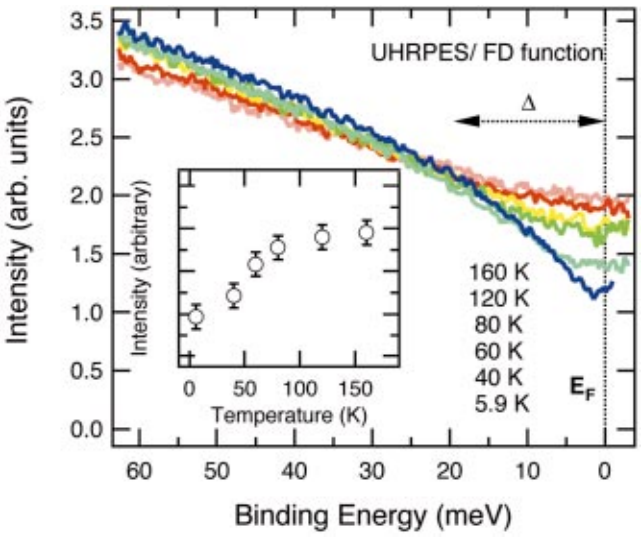

FIG. 4. (Color) Temperature dependence of UHRPE spectra of $CeRu_4Sb_{12}$ measured by He Iα line, which were divided by FD function. The inset represents the D(E_F) estimated from the UHRPE spectra as a function of temperature.

$Ce_3Bi_4Pt_3$, which are interpreted as an opening of a small energy gap.[16,17]

In order to eliminate the thermal broadening effect, the UHRPE spectra by He Iα line in Fig. 2 are divided by the Fermi–Dirac (FD) distribution function which is convoluted by the experimental energy resolution as presented in Fig. 4.[16] The spectra directly reflect the DOS as a function of temperature. The DOS below ~ 20 meV is nearly constant at 160 K and gradually decreases by lowering temperature. The spectral intensity transfers from the neighborhood of E_F to the higher binding-energy region ($\geqslant 30$ meV). It should be noted that this reduction in the DOS is apparently caused by the many-body effect. This fact reveals the reduction in carrier concentration of $CeRu_4Sb_{12}$ at low temperatures, whereas the large $D(E_F)$ at 5.9 K still remains, indicating the existence of some residual carriers. This result is consistent with the small residual resistivity ratio and the large Hall coefficient which also suggests the lower carrier concentration at low temperatures. The $D(E_F)$ of the spectra against temperature is plotted in the inset. We can see the remarkable decrease in $D(E_F)$ below $T^* \sim 80$ K. The $D(E_F)$ which directly reflects the carrier concentration is clearly scaled by T^*. T^* is defined as a coherence temperature, which is characteristic of Kondo lattice. The hump at $T^* \sim 80$ K in $\rho(T)$, which is followed by a steep decrease, corresponds to the onset of the coherent Fermi liquid formation.[11,15] It is noted here that $D(E_F)$ doesn't represent exact carrier concentration because the surface state must contribute to the background and the $4f$ cross section is small in the He Iα excitation energy. But we can see the behavior of the carrier concentration by monitoring the $D(E_F)$.

We speculate that the coherence among Kondo centers leads to the development of the renormalized $4f$-band and a semimetalliclike band structure is realized at the temperatures far below T^*. This scenario is very similar to that of Kondo semiconductor. The appearance of the gaplike structure in the optical conductivity which is very similar to the Kondo semiconductor's case supports this idea.[18] The mean-field solution of the Kondo lattice model predicts the existence of a hybridization gap between the renormalized $4f$-bands.[19] When the coherence is developed, a small gap arises from the hybridization of the Kondo compensated magnetic moments. The filling of the conduction electron is a unique parameter that determines whether the insulating ground state is realized. One of the key predictions of the hybridization gap model is a simple scaling relationship between T^* and the magnitude of the direct energy gap 2Δ.[20] The Δ of $CeRu_4Sb_{12}$ is estimated by a gaplike threshold in Figs. 2 and 4 at about 20 meV at 5.9 K. The magnitude of Δ is the same order of high Kondo temperature ($T_K \sim 100$ K) conjectured from the maximums in the magnetic susceptibility and the thermoelectric power.[11,13]. We find an agreement between this Δ value and that extracted from the interband transition in the optical conductivity.[14] The value of the ratio Δ/k_BT_K of $CeRu_4Sb_{12}$ is estimated to be about 2.3, which is in good agreement with those of Kondo semiconductors obtained by the photoemission and the optical measurements. The Δ/k_BT_K of CeRhAs, CeRhSb, and $Ce_3Bi_4Pt_3$ ranges between 1.7–2.3.[16,18,21] This shows that the direct gap Δ of $CeRu_4Sb_{12}$ has a similar relationship with T_K (or T^*) to Kondo semiconductors. Because the gap opening is caused by the involvement of the conduction electron into the singlet formation, the decrease in the carrier density should be related with the increase of Δ. That is to say, the predicted scaling behavior of Δ is mirrored in the scaling behavior of $D(E_F)$. In fact, the onset of the decrease in the $D(E_F)$ of $CeRu_4Sb_{12}$ is corresponding to the T^* as shown in the inset of Fig. 4. This fact proves that the formation of the pseudogap around E_F in DOS has much to do with the long-range coherence development.

The residual $D(E_F)$ at 5.9 K indicates that the hybridization gap does not completely open in $CeRu_4Sb_{12}$. We speculate that $CeRu_4Sb_{12}$ may be classified to a ''Kondo semimetal'' like CeNiSn. It is interesting that $CeFe_4Sb_{12}$ and $CeRu_4Sb_{12}$ are metallic and have some characteristics of a heavy fermion whereas the series of $CeTM_4P_{12}$ (TM=Fe, Ru and Os) compounds and $CeFe_4As_{12}$ are semiconductors with small hybridization gaps.[22,23,8] It is reasonable to suppose that the smaller hybridization between transition metal-d state and Ce-$4f$ state in $CeFe_4Sb_{12}$ and $CeRu_4Sb_{12}$, as compared with that in the phosphide, is insufficient for the gap formation. The local density approximation (LDA) calculation predicts the semiconducting gap in both $CeFe_4Sb_{12}$ and $CeRu_4Sb_{12}$ though the experiments show metallic character in both.[8] The LDA calculation has a tendency to overestimate the gap size because it tends to underestimate the intra-atomic correlation between the $4f$ electrons and hence overestimate the hybridization. This may be the reason for the discrepancy between the calculation and experiments.

Note that the process of decreasing the carrier concentration due to the reduction in $D(E_F)$ is not accompanied by activating behavior in $\rho(T)$. The effects of the decrease in the carrier number occur even in the metallic phase. A kind of the longevity of the quasiparticles at low temperatures is necessary to explain that the metallic behavior persists down to 0 K in $CeRu_4Sb_{12}$. The extension of the lifetime of the quasiparticle needs to overcome the reduction in the carrier concentration. A similar coexistence of a decrease in carrier number and a metallic ground state is realized in Kondo semimetals, such as CeNiSn and CeRhSb.[24,25] In fact, the microwave complex conductivity measurements on CeNiSn show a rapid decrease in the scattering rate of the quasiparticles, whose excitation spectrum is dramatically changed with the hybridization gap formation at low temperatures.[26]

We would like to point out that $CeRu_4Sb_{12}$ has features of valence-fluctuating as well as heavy-fermion system. The very high T_K, the large $4f$-DOS around E_F, and the semimetalliclike low carrier state induced through the c-f hybridization belong to the former, and the lower $4f$-level, the small Weiss temperature ($\Theta_W = -26$ K) and the non-Fermi liquid (NFL) behavior observed below 5 K belong to the latter.[15] The characteristic crystal structure of the rare earth filled skutterudites must be one of the reasons for the dual character of the $4f$ electron in $CeRu_4Sb_{12}$.

Finally, attention should be paid to the possibility of the NFL ground state of $CeRu_4Sb_{12}$ because of the unusual be-

havior in $\rho(T)$.[11] And then, we cannot conclude the semimetallic ground state of $CeRu_4Sb_{12}$ because it is described within a simple Fermi liquid picture.

In this work, the UHRPE spectroscopy on $CeRu_4Sb_{12}$ is reported. The valence band spectra show the strongly hybridized $4f$-band just below E_F. On the other hand, from the results of the UHRPE spectra near E_F, we found that a semimetalliclike DOS of $CeRu_4Sb_{12}$ is realized at low temperatures. The temperature dependence of the $D(E_F)$ shows a simple scaling relationship with T^*. The reduction in c-f hybridization strength in $CeRu_4Sb_{12}$, which is caused from the enhancement of the unit-cell volume, prevents the formation of the hybridization gap which is realized in $CeRu_4P_{12}$. We intend to carry out further measurements on this and other Ce-based filled skutterudites in order to further elucidate the relationship between the c-f hybridization and the metal-insulator crossover line in the series of the compounds.

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[1] T. Uchiumi, I. Shirotani, C. Sekine, S. Todo, T. Yagi, Y. Nakagawa, and K. Kanoda, J. Phys. Chem. Solids **60**, 689 (1999).
[2] G.P. Meisner, Physica B **108**, 763 (1980).
[3] M.S. Torikachvili, J.W. Chem, Y. Dalichaouch, R.P. Guertin, M.W. McElfresh, C. Rossel, M.B. Maple, and G.P. Meisner, Phys. Rev. B **36**, 8660 (1987).
[4] I. Shirotani, T. Adachi, K. Tachi, S. Todo, K. Nozawa, T. Yagi, and M. Kinoshita, J. Phys. Chem. Solids **57**, 211 (1996).
[5] T. Matsuda, H. Okada, H. Sugawara, Y. Aoki, H. Sato, A.V. Andreev, Y. Shiokawa, V. Sechovsky, T. Honma, E. Yamamoto, and Y. Onuki, Physica B **281&282**, 220 (2000).
[6] C. Sekine, T. Uchiumi, I. Shirotani, and T. Yagi, Phys. Rev. Lett. **79**, 3218 (1997).
[7] C. Sekine, H. Saito, T. Uchiumi, A. Sakai, and I. Shirotani, Solid State Commun. **106**, 441 (1997).
[8] L. Nordstrom and D.J. Singh, Phys. Rev. B **53**, 1103 (1996).
[9] H. Harima (private communication).
[10] C.H. Lee, H. Oyanagi, C. Sekine and I. Shirotani (in preparation).
[11] N. Takeda and M. Ishikawa, J. Phys. Soc. Jpn. **69**, 868 (2000).
[12] N. Takeda and M. Ishikawa, Physica B **281&282**, 388 (2000).
[13] K. Abe, T.D. Matsuda, F. Watanuki, H. Sugawara, Y. Aoki, and T. Sato, (unpublished).
[14] S.V. Dordevic, D.N. Basov, N.R. Dilley, E.D. Bucher, and M.B. Maple, Phys. Rev. Lett. **86**, 684 (2001).
[15] N. Takeda and M. Ishikawa, Physica B **259&261**, 92 (1999).
[16] H. Kumigashira, T. Sato, T. Yokoya, and T. Takahashi, Phys. Rev. Lett. **82**, 1943 (1997); H. Kumigashira, T. Sato, T. Yokoya, T. Takahashi, S. Yoshii, and M. Kasaya, Jpn. J. Appl. Phys., Part 1 **11**, 91 (1998).
[17] T. Susaki, A. Fujimori, T. Takeda, M. Taniguchi, M. Arita, K. Shimada, H. Namatame, S. Hiura, F. Iga, and T. Takabatake, J. Phys. Soc. Jpn. **70**, 756 (2001).
[18] B. Bucher, Z. Schlesinger, P.C. Canfield, and Z. Fisk, Phys. Rev. Lett. **72**, 522 (1995).
[19] T.M. Rice and K. Ueda, Phys. Rev. Lett. **55**, 995 (1985).
[20] G. Aeppli and Z. Fisk, Comments Condens. Matter Phys. **16**, 155 (1992).
[21] K. Breuer, S. Messerli, D. Purdie, M. Garnier, M. Hengsberger, G. Panaccione, Y. Baer, T. Takahashi, S. Yoshii, M. Kasaya, K. Katoh, and T. Takabatake, Europhys. Lett. **41**, 563 (1998).
[22] H. Sugawara, Y. Abe, Y. Aoki, H. Sato, M. Hedo, R. Settai, Y. Onuki, and H. Harima, J. Phys. Soc. Jpn. **69**, 2938 (2000).
[23] D.T. Morelli and G.P. Meisner, J. Appl. Phys. **77**, 3777 (1995).
[24] K. Izawa, T. Suzuki, T. Fujita, T. Takabatake, G. Nakamoto, H. Fujii, and K. Maezawa, Phys. Rev. B **59**, 2599 (1999).
[25] T. Takabatake, T. Yoshino, H. Tanaka, Y. Bando, H. Fujii, T. Fujita, H. Shida, and T. Suzuki, Physica B **206&207**, 804 (1995).
[26] T. Shibauchi, N. Katase, T. Tamegai, K. Uchinokura, T. Takabatake, G. Nakamoto, and A.A. Menovsky, Phys. Rev. B **57**, 8277 (1997).