Electronic structure of $CaCu_3Ru_4O_{12}$ studied by x-ray photoemission spectroscopy

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We have studied the electronic structure of the *d*-electron heavy-fermion system $CaCu_3Ru_4O_{12}$ using x-ray photoemission spectroscopy and a cluster model calculation. The Ru 3*d* core level spectrum shows a double-peak structure as commonly observed in metallic Ru oxides. In $CaCu_3Ru_4O_{12}$, the well-screened peak has dominating intensity, indicating that the Ru 4*d* electrons in $CaCu_3Ru_4O_{12}$ are highly itinerant. On the other hand, the Cu $2p_{3/2}$ core level peak is accompanied by a satellite and shows that the valence state of Cu is close to $3d^9$ (Cu^{2+}) with localized character. In addition, the main Cu $2p_{3/2}$ peak shows an asymmetric line shape due to the screening effect, suggesting the hybridization effect between the Cu 3*d* and Ru 4*d* orbitals. The present results show that, among the *d*-electron heavy-fermion materials, the electronic structure of $CaCu_3Ru_4O_{12}$ best resembles that of the *f*-electron Kondo system.

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Research on heavy-fermion materials was started by the discovery of an enormous electronic heat capacity coefficient in $CeAl_3$,[1] and has been accelerated by the discovery of superconductivity in $CeCu_2Si_2$,[2] and recently by observations of heavy-fermion behavior in transition-metal oxides.[3] While in *f*-electron heavy-fermion compounds the Kondo lattice model gives the essentials of the underlying physics, the routes to the formation of heavy quasiparticle masses would be very different in transition-metal oxides. This makes research on *d*-electron heavy-fermion systems a hot topic in strongly correlated material science and attracts the interest of many researchers, both experimentalists and theoreticians.[3]

$CaCu_3Ru_4O_{12}$ is a newly discovered *d*-electron heavy-fermion system[4] in which a transport study indicates that the heavy-fermion behavior comes from the Kondo mechanism just as in an *f*-electron heavy-fermion system. In this scenario, Cu 3*d* and Ru 4*d*, respectively, play the roles of the localized *f* electron and the conduction electron. This point makes $CaCu_3Ru_4O_{12}$ different from other *d*-electron heavy-fermion systems, such as LiV_2O_4, in which only V 3*d* electrons have important roles.[5] $CaCu_3Ru_4O_{12}$ has the perovskite-type crystal structure as shown in Fig. 1. While the Ca and Cu ions occupy the *A* site coordinated by the 12 oxygen ions, the Ru ions occupy the *B* site octahedrally coordinated by the six oxygen ions. The corner-sharing Ru-O network is expected to provide a relatively wide Ru 4*d*−O 2*p*band near the Fermi level just as in other perovskite-type Ru oxides such as $SrRuO_3$ and Sr_2RuO_4. On the other hand, the hybridization between the Cu 3*d* and O 2*p* orbitals would be different from that in typical perovskite-type Cu oxides such as $LaCuO_3$ and La_2CuO_4. In our experiment, we examine the electronic structure of $CaCu_3Ru_4O_{12}$ by x-ray photoemission spectroscopy (XPS), in order to get information about the above scenario.

Our XPS measurements were carried out at room temperature using JPS9200 spectrometer. Monochromatic Al$K\alpha$ (1486.6 eV) was used as an x-ray source. The pass energy of the electron analyzer was set to 10 eV. The total energy resolution including the x-ray source and the electron analyzer was about 0.6 eV. The binding energy was calibrated using the Fermi edge and the Au 4*f* core level (84.0 eV) of the gold reference sample. The polycrystalline samples of $CaCu_3Ru_4O_{12}$ prepared by a solid-state reaction were fractured *in situ* to obtain a clean surface. The base pressure of the chamber was 7×10^{-8} Pa.

Figure 2 shows the valence band XPS spectrum of $CaCu_3Ru_4O_{12}$. Three main structures (*A*, *B*, and *C*) were observed. Compared with the XPS result for Sr_2RuO_4 and its analysis,[6] we can conclude that the peak at around −0.8 eV (structure *C*) and the broad structure at around −6 eV (structure *A*) are derived from, respectively, the Ru $4dt_{2g}$ band (hybridized with the O 2*p* states) and the O 2*p* band (hybridized with the Ru 4*d* states). Therefore, structure *B*, which does not appear in the spectrum of Sr_2RuO_4, is mainly constructed from the Cu 3*d* states. The Cu 3*d* band is located at ∼−2.5 eV. In the case of CuO, the main Cu 3*d* band is located at ∼−3.1 eV and the Zhang-Rice singlet level with the $^1A_1$ symmetry is located at ∼−1.3 eV.[7,8] Assuming that the

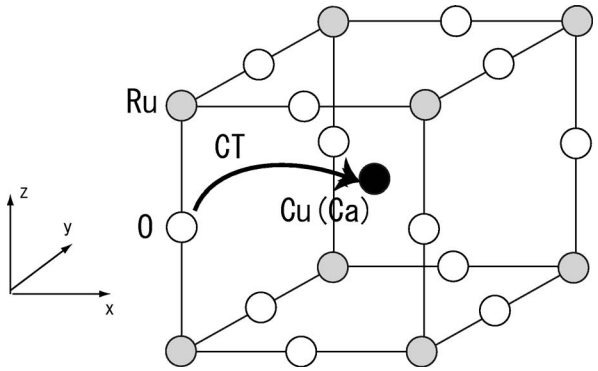

FIG. 1. Schematic drawing of the crystal structure of $CaCu_3Ru_4O_{12}$. The arrow indicates the charge transfer from the O 2*p* to Cu 3*d* orbitals.

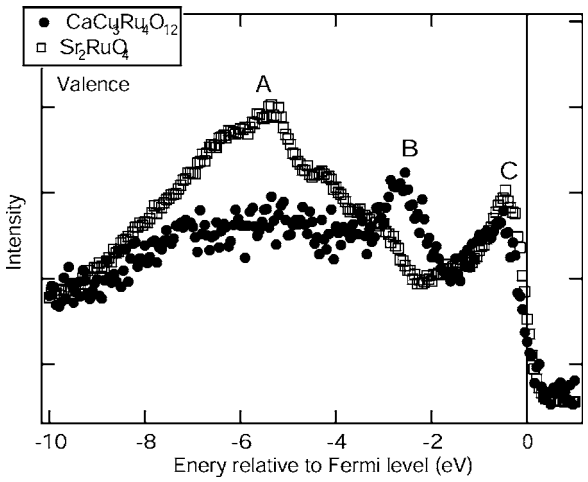

FIG. 2. Valence band XPS spectra of $CaCu_3Ru_4O_{12}$ (closed circles) and Sr_2RuO_4 (open squares).

energy separation between the main Cu 3*d* band and the Zhang-Rice singlet level in $CaCu_3Ru_4O_{12}$ is comparable or smaller than CuO, the Zhang-Rice singlet level does not reach the Fermi level. This assumption is reasonable since the Cu 3*d*–O 2*p* hybridization of $CaCu_3Ru_4O_{12}$ is rather weak compared to that of CuO, as indicated from the cluster model analysis of the Cu 2*p* spectra. Therefore, the electronic states at the Fermi level is dominated by the Ru $4dt_{2g}$ states and the Zhang-Rice singlet level derived from the Cu 3*d* states is buried in the Ru $4dt_{2g}$ band. Therefore, in the ground state, the Cu ion takes the d^9 electronic configuration with localized spin 1/2. The Zhang-Rice singlet state is the final state of the photoemission process from this d^9 ground state. As shown in Fig. 2, the Ru $4dt_{2g}$ bandwidth and the density of states at the Fermi level in $CaCu_3Ru_4O_{12}$ are similar to those in Sr_2RuO_4. The high density of states near the Fermi level is the origin of the strong screening effects on core holes as discussed below.

The Ru 3*d* core level XPS result for $CaCu_3Ru_4O_{12}$ is shown in Fig. 3 together with the same result in Sr_2RuO_4. Both spectra show a clear double-peak structure which can be assigned as poorly screened (*A*) and well-screened (*B*) peaks due to the screening effect of the conduction electrons.[14] The theory states that satellite structure may occur when the core-valence Coulomb interaction is strong enough to form well-screened and poorly screened final states. The main and satellite structures correspond to the well-screened and poorly screened final states, respectively. In metallic Ru oxides such as $SrRuO_3$ and Sr_2RuO_4, the intensity of the well-screened peak is dominant while the intensity of the poorly screened peak becomes dominant in insulating Ru oxides such as Ca_2RuO_4.[9–11] In $CaCu_3Ru_4O_{12}$, the intensity of the well-screened peak is more dominant than those in $SrRuO_3$ and Sr_2RuO_4 and is comparable to that in RuO_2,[12] indicating that the Ru 4*d* electrons in $CaCu_3Ru_4O_{12}$ are much more itinerant than those in $SrRuO_3$ and Sr_2RuO_4. Since the screening process of the Ru 3*d* core level involves the extended Ru 4*d* electrons, quantitative analysis of the Ru 3*d* spectrum is very difficult. It would be interesting to develop a new theoretical method to analyze

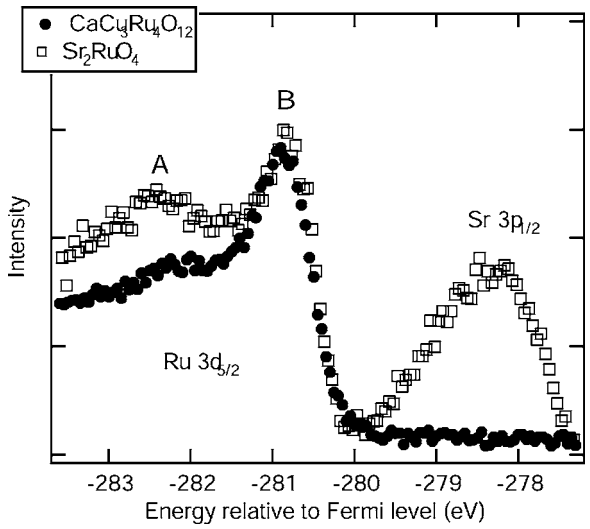

FIG. 3. Ru 3*d* core level XPS spectra of $CaCu_3Ru_4O_{12}$ (closed circles) and Sr_2RuO_4 (open squares).

the Ru 3*d* spectrum of the metallic Ru oxides. For example, Anderson impurity model would be useful to analyze the Ru 3*d* spectrum as applied to the Cu 2*p* spectrum by Koitzsch and co-workers.[13]

Figure 4 shows XPS result for the Cu $2p_{3/2}$ core level. It shows the satellite structure (*A*) and the main peak (*C*). A shoulder structure (*B*) of the main peak is also observed. The satellite structure is commonly observed in insulating transition-metal oxides such as CuO and NiO. The existence of the satellite structure shows that the Cu 3*d* level is partially filled and that the O 2*p* electrons can be transferred to the empty Cu 3*d* orbitals to screen the Cu 2*p* core hole. In addition, the line shape of the satellite structure is similar to those observed in Cu^{2+} oxides such as CuO and La_2CuO_4. Therefore, it is reasonable to conclude that the valence state of Cu is close to $3d^9$ (Cu^{2+}) and that the Cu 3*d* electrons in this system are almost localized. In order to confirm this interpretation, we have analyzed the main and satellite structures using the configuration interaction calculation on the CuO_{12} cluster model (see Fig. 1).[15,17,18] In this description,

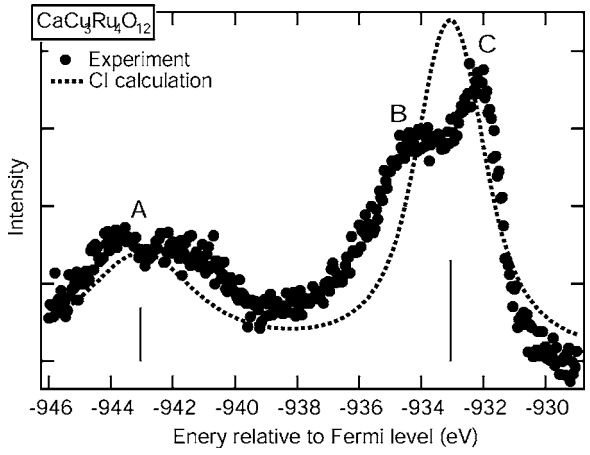

FIG. 4. Cu 2*p* photoemission spectrum of $CaCu_3Ru_4O_{12}$ (closed circles) and the cluster model analysis (dotted curve).

the ground state is given by the linear combination of $3d^9$ and $3d^{10}\underline{L}$ states:

$$\Psi_g = \alpha_1|d^9\rangle + \alpha_2|d^{10}\underline{L}\rangle, \quad (1)$$

where d implies a Cu $3d$ electron and $\underline{L}$ denotes an O $2p$ ligand hole. The final states are given by the linear combinations of $\underline{c}3d^9$ and $\underline{c}3d^{10}\underline{L}$ where c represents the Cu $2p_{3/2}$ core hole:

$$\Psi_f = \beta_1|\underline{c}d^9\rangle + \beta_2|\underline{c}d^{10}\underline{L}\rangle. \quad (2)$$

Adjustable parameters are the charge-transfer energy from the O $2p$ orbitals to the empty Cu $3d$ orbitals, Δ, the Coulomb interaction between the Cu $3d$ electron and the Cu $2p$ core hole, Q, and the transfer integrals between the Cu $3d$ and O $2p$ orbitals, which can be expressed by Slater-Koster parameters $(pd\pi)$ and $(pd\sigma)$. Here, the ratio $(pd\sigma)/(pd\pi)$ is -2.2. The energy difference between the $3d^9$ and $3d^{10}\underline{L}$ states is given by Δ and that between the $\underline{c}3d^9$and $\underline{c}3d^{10}\underline{L}$ by $\Delta - Q$. The hybridization term between the $3d^9$ ($\underline{c}3d^9$) and $3d^{10}\underline{L}$ ($\underline{c}3d^{10}\underline{L}$) states is given by the transfer integrals. The calculated Cu $2p$ core level photoemission spectrum is broadened with an energy-dependent Lorentzian such that the Lorentzian full width at half maximum is

$$2\Gamma = 2\Gamma_0(1 + \alpha\Delta E), \quad (3)$$

where Γ_0 and Γ are, respectively, the lifetime broadening of the main and satellite peaks, ΔE denotes the energy separation from the main peak, while α is the broadening parameter. We adopted the values $\Gamma_0 = 1.0$ eV and $\alpha = 0.1$.[17] The Gaussian broadening of 1.0 eV is also used for the entire spectrum to simulate the instrumental resolution and other broadening effects. We have obtained the best-fit result by setting $Q = 10.0$ eV, $\Delta = 0.2$ eV, and $(pd\sigma) = -1.0$ eV. Since the charge transfer energy $\Delta = 0.2$ is smaller than the Coulomb interaction between the Cu $3d$ electron and the Cu $2p$ core hole, Q, the satellite structure in Cu $2p$ spectra has $\underline{c}3d^9$character and the main peak has $\underline{c}3d^{10}\underline{L}$ character. The transfer integral between the Cu $3d$ and O $2p$ orbitals is much smaller than those reported for CuO and La_2CuO_4.[8,17,18] This is consistent with the fact that the Cu ions occupy A site of the perovskite lattice. The charge transfer energy Δ is also smaller than those reported for the Cu^{2+} oxides.[17,18] While the smallness of transfer integral tends to make the Cu $3d$ electrons in the present system more localized than those in La_2CuO_4 or Nd_2CuO_4, the smallness of the charge-transfer energy tends to make the Cu $3d$ electrons in the present system more delocalized than those in La_2CuO_4or Nd_2CuO_4. Probably these two effects cancel with each other to some extent and the localization of the Cu $3d$ electrons in $CaCu_3Ru_4O_{12}$ would be more or less similar to that in La_2CuO_4 or Nd_2CuO_4.

The calculated result is plotted in Fig. 4. We could not reproduce the shoulder structure of the main peak since we employed the single-site cluster model in our calculation. The shoulder structure (B) of the main peak is caused by the nonlocal screening mechanism:[16] screening by transferring an electron from the outside of the CuO_{12} cluster considered above. In the present system, the nonlocal screening due to the Ru $4d$ electrons is expected to be dominant since the Ru $4d$ density of states at the Fermi level is considerably high. Recently, an x-ray absorption study has shown that the Cu valence in $CaCu_3Ti_4O_{12}$ is also +2.[19] However, it is expected that the nonlocal screening channel is almost suppressed in $CaCu_3Ti_4O_{12}$ where the Ti $3d$ orbitals are unoccupied and the Cu ion is essentially isolated.

The Cu $2p$ spectrum with the satellite structure indicates that the Cu $3d$ electrons are relatively localized in contrast to the itinerant Ru $4d$ electrons. In this sense, the electronic structure of $CaCu_3Ru_4O_{12}$ is rather similar to that of $4f$-electron heavy-fermion materials in which the highly localized $4f$ electrons hybridize with the conduction electrons. However, the asymmetric line shape of the Cu $2p$ main peak indicates that the Ru $4d$–Cu $3d$ screening channel is very active to screen the Cu $2p$ core hole. Actually, the cluster model analysis of the Cu $2p$ spectrum shows that the transfer integral between the Cu $3d$ and O $2p$ orbitals is as large as ~ 1 eV and the Ru $4d$–Cu $3d$ hybridization via the O $2p$ orbitals is expected to large compared with the $4f$-electron heavy-fermion systems. Here, one can speculate that the Cu $3d$ electrons would be less localized than the $4f$-electron systems and would be comparable to the $5f$-electron systems. In future, further experiments should be performed on $CaCu_3Ru_4O_{12}$ to reveal to what extent the Kondo picture can be applicable to $CaCu_3Ru_4O_{12}$. One of the most important experiments is the photoemission spectroscopy experiment with high-energy resolution in which one would observe a Kondo peak at the Fermi level.

In conclusion, we have performed the XPS measurement of $CaCu_3Ru_4O_{12}$. The Ru $3d$ spectrum indicates that Ru $4d$ electrons are highly itinerant while Cu $2p$ spectrum reveals the localization of Cu $3d$ electrons. This supports the scenario which Kobayashi *et al.* proposed about the mechanism of the heavy-fermion behavior in $CaCu_3Ru_4O_{12}$ and shows that, among the d-electron heavy-fermion materials, the electronic structure of $CaCu_3Ru_4O_{12}$ best resembles that of the f-electron Kondo system.

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