ELECTRONIC STRUCTURE OF THE PYROCHLORE-TYPE Ru OXIDES THROUGH THE METAL–INSULATOR TRANSITION*

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The electronic structures of the pyrochlore-type Ru oxides $Sm_{2-x}Ca_xRu_2O_7$ and $Sm_{2-x}Bi_xRu_2O_7$, which show metal–insulator transition with increasing Ca or Bi concentration, have been studied by ultraviolet photoemission spectroscopy. Spectral changes near the Fermi level are different but reflect the tendency of their transport properties in both systems. The $Sm_{2-x}Ca_xRu_2O_7$ system shows an energy shift, which is expected from the increase of hole in the Ru $4d$ t_{2g} band and the $Sm_{2-x}Bi_xRu_2O_7$ system shows spectral weight transfer within the Ru $4d$ t_{2g} band, which is expected to be observed in bandwidth-control Mott-Hubbard system.

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1. Introduction

It has been reported that pyrochlore-type Ru oxides $A_2Ru_2O_7$ show a wide range of electrical properties for different A-site ions [1]. It is expected that the effect of electron correlation plays important roles in their electronic structure and physical properties. $Sm_{2-x}Bi_xRu_2O_7 (0 \leq x \leq 2.0)$ exhibits a Mott insulator-to-metal transition at $x \sim 0.6$ with increasing Bi concentration, *i.e.*, through changing the Ru t_{2g} band width [2,3]. $Sm_{2-x}Ca_xRu_2O_7$

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($0 \leq x \leq 0.6$) also shows a metal–insulator transition at x $\sim$ 0.45 with increasing Ca concentration, *i.e.*, through doping holes to the Ru t_{2g} band [4]. We have studied the electronic structures of $Sm_{2-x}Bi_xRu_2O_7$ and $Sm_{2-x}Ca_xRu_2O_7$ systematically through the metal–insulator transition by ultra-violet photoemission spectroscopy (UPS). We discuss the mechanism of the metal–insulator transition by comparing those two systems.

2. Experimental

Sintered samples of $Sm_{2-x}Ca_xRu_2O_7$ and $Sm_{2-x}Bi_xRu_2O_7$ were synthesized by the solid reaction [3,4]. UPS measurements were done under ultra high vacuum ($\sim 10^{-10}$Torr) by using a He discharge lamp (He I:$h\nu = 21.2$ eV). Energy resolution of the measurements are 40 meV and 5 meV for UPS measurements in $Sm_{2-x}Ca_xRu_2O_7$ and $Sm_{2-x}Bi_xRu_2O_7$, respectively. Before each measurement we made sample surface clean by scraping with a diamond file in ultra high vacuum. The spectra were taken at liquid nitrogen temperature for $Sm_2Ru_2O_7$, at 26 K for $Sm_{2-x}Ca_xRu_2O_7$ ($0.1 \leq x \leq 0.6$), and at 14 K for $Sm_{2-x}Bi_xRu_2O_7$ ($0.2 \leq x \leq 2.0$).

3. Results and discussions

Figure 1 shows the UPS spectra of $Sm_{2-x}Ca_xRu_2O_7$ through the metal–insulator transition. The region from above the Fermi level to 2 $\sim$ 3 eV below it is mainly composed of the Ru 4*d* t_{2g} states and has much influence on the physical properties of $Sm_{2-x}Ca_xRu_2O_7$. With increasing Ca concentration, the spectral intensity near the Fermi level increases and the Fermi edge is established at $x \sim 0.4$. This corresponds well to the transport properties of $Sm_{2-x}Ca_xRu_2O_7$. Another influence of the Ca doping can be observed in the spectral change around 2.5 eV, which corresponds to the edge of the O 2*p* band. With increasing Ca concentration, the O 2*p* band edge is shifted closer to the Fermi level without changes in the shape of Ru 4*d* t_{2g} band. Therefore, the energy shift can be well explained by doping holes to the Ru 4*d* t_{2g} band.

Figure 2 shows the UPS spectra of $Sm_{2-x}Bi_xRu_2O_7$ through the metal–insulator transition. The spectra have been normalized intensity integrated from the Fermi level to 2 eV below it equal. This normalization is based on the assumption that the integrated density of the Ru 4*d* t_{2g} states does not change. With increasing Bi concentration, the spectral intensity near the Fermi level increases and the Fermi edge appears at $x \sim 0.6$, which resembles the phenomena occurring in $Sm_{2-x}Ca_xRu_2O_7$. As for the spectral change of the entire Ru 4*d* t_{2g} band is, however, very different from that in $Sm_{2-x}Ca_xRu_2O_7$. The spectral weight near the Fermi level which has close

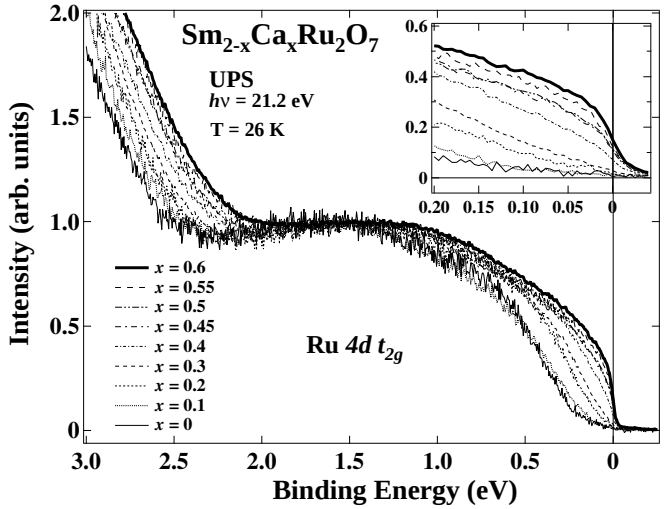

Fig. 1. UPS spectra of $Sm_{2-x}Ca_xRu_2O_7$ ($0 \leq x \leq 0.6$) across the metal–insulator transition. Inset shows spectral changes near the Fermi level.

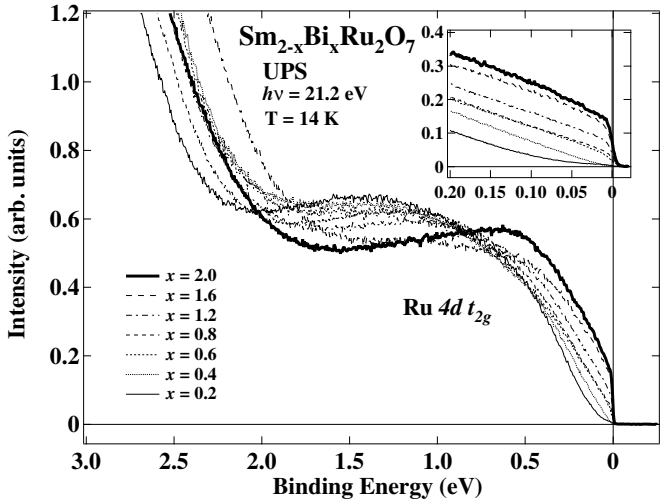

Fig. 2. UPS spectra of $Sm_{2-x}Bi_xRu_2O_7$ ($0.2 \leq x \leq 2.0$) across the metal–insulator transition. Inset shows spectral changes near the Fermi level.

relationship with metallic conductivity is transferred from the higher binding energy region through the metal–insulator transition. This spectral weight transfer is anticipated during the metal–insulator transition in a bandwidth-control Mott-Hubbard system [5].

4. Conclusion

As for the spectral change near the Fermi level, in both systems spectral intensity near the Fermi level increases monotonically through the metal–insulator transition, which well corresponds to the doping dependence of the transport properties. Spectral changes in the entire Ru $4d\,t_{2g}$ band, however, are different from each other. It is concluded that this difference has close relationship with the different routes of the metal–insulator transition in those systems, hole-doping or band-width control.

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