Pseudogap behavior of RuP probed by photoemission spectroscopy

K. Sato$^{1}$, D. Ootsuki$^{2}$, Y. Wakisaka$^{1}$, N. L. Saini$^{3,1}$, T. Mizokawa$^{1,2}$, M. Arita$^{4}$, H. Anzai$^{4}$, H. Namatame$^{4}$, M. Taniguchi$^{4,5}$, D. Hirai$^{6}$, and H. Takagi$^{2,6}$

$^1$Department of Complexity Science and Engineering, University of Tokyo, 5-1-5 Kashiwanoha, Chiba 277-8561, Japan
$^2$Department of Physics, University of Tokyo, 5-1-5 Kashiwanoha, Chiba 277-8561, Japan
$^3$Department of Physics, University of Roma "La Sapienza" Piazzale Aldo Moro 2, 00185 Roma, Italy
$^4$Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-hiroshima 739-0046, Japan
$^5$Graduate School of Science, Hiroshima University, Hiroshi-hiroshima 739-8526, Japan and
$^6$Department of Advanced Materials, University of Tokyo, 5-1-5 Kashiwanoha, Chiba 277-8561, Japan

(Dated: May 1, 2014)

We have studied the electronic structure of RuP and related Ru pnictides using photoemission spectroscopy. Ru 3d core-level and valence-band spectra of RuP show that the Ru valence is +3 with $t_{2g}$ configuration. The photoemission spectral weight near the Fermi level is moderately suppressed in the pseudogap phase of RuP, consistent with the pseudogap opening of $2\Delta/k_BT_c \sim 3$ (gap size $\Delta \sim 50$ meV and transition temperature $T_c \sim 330$ K). The Ru 3d peak remains sharp in the pseudogap phase and the insulating phase of RuP, suggesting that the electronic orderings responsible for the phase transitions are different from the conventional charge density wave.

PACS numbers: 74.70.Xa, 74.25.Jb, 71.30.+h, 71.20.-b

Intensive and extensive research activities have been dedicated to understand the electronic phase diagram of Fe pnictide family since the discovery of superconductivity and magnetism in LaFeAsO$_{1-x}$F$_x$.$^{2,5}$ The Fe pnictide superconductors show an interesting interplay between superconductivity and magnetism which is similar to cuprate superconductors. In the case of the cuprate superconductors, pseudogap behavior is believed to be one of the key ingredients to understand the relationship between the superconductivity and the magnetism. On the other hand, pseudogap behavior has never been established in the Fe pnictide superconductors although it was claimed in an early photoemission study.$^{2}$ Very recently, Hirai et al. have discovered that Ru pnictides have a unique electronic phase diagram with insulating, superconducting, and pseudogap phases.$^{4}$ This has opened up a new opportunity to study the relationship between superconductivity and pseudogap in the pnictides. Ru pnictides have a complicated three-dimensional structure (MnP-type structure) as schematically shown in Fig. 1 and shows a transition from a metal to a non-magnetic insulator. Transitions from metals to non-magnetic (or almost non-magnetic) insulators have been reported in various transition-metal compounds including pyrochlore-type $\text{Tb}_2\text{Ru}_2\text{O}_7$,$^{6}$ spinel-type $\text{CuIr}_2\text{S}_4$,$^{6}$ $\text{LiRh}_2\text{O}_4$,$^{6}$ $\text{MgTi}_2\text{O}_4$,$^{7}$,$^{11}$ hollandite-type $\text{K}_2\text{V}_8\text{O}_{16}$.$^{12,13}$ However, superconductivity has not been realized in any of these by destroying the non-magnetic insulating phases. In this context, the non-magnetic insulating phase of RuP is very interesting and important since the superconductivity is induced by Rh doping.$^4$ The electric resistivity of RuP takes a minimum at $T_1 = 330$ K with a drastic increase due to the metal-to-insulator transition around $T_2 = 270$ K. The magnetic susceptibility of RuP shows Pauli paramagnetic behavior above $T_1$ and gradually decreases below $T_1$ with an almost discontinuous drop around $T_2$ to a negative value which is comparable to the expected core diamagnetism.$^4$ This suggests that RuP is a normal metal above $T_1$ and an non-magnetic insulator below $T_2$. In the temperature range between $T_1$ and $T_2$, RuP shows the pseudogap behavior. RuAs resembles RuP with $T_1 = 280$ K and $T_2 = 200$ K while RuSb is a normal metal down to the lowest temperature. In this paper, we report core-level and valence-band x-ray photoemission spectroscopy (XPS) and valence-band ultraviolet photoemission spectroscopy (UPS) of RuP and related Ru pnictides. While XPS provides information on the fundamental electronic structure of Ru$^{3+}$ ($t_{2g}^5$) in RuP, spectral evidence of pseudogap opening is obtained by UPS measurement of RuP.

Polycrystalline samples of RuP, Ru$_{0.75}$Rh$_{0.25}$As, and RuSb were prepared as reported in ref. 4.$^2$ The XPS measurements were performed using a JPS-9200 spectrometer equipped with a monochromatized Al K$_x$ x-ray source ($\hbar\nu = 1486.6$ eV). The total energy resolution was 600 meV. The base pressure of the spectrometer was in the $1.0 \times 10^{-7}$ Pa range. The UPS measurements were performed using SES-100 analyzer with the He I line ($\hbar\nu = 21.2$eV). The total energy resolution was 30 meV. The base pressure of the spectrometer was $5.0 \times 10^{-8}$ Pa. The high-energy resolution UPS measurements have been performed at beamline 9A at Hiroshima Synchrotron Radiation Center (HiSOR). The photon energy from the normal incidence beamline was set to $\hbar\nu=10$ eV. The total energy resolution was 8 meV. The binding energy was calibrated using the Fermi edge of the gold reference sample. The base pressure of the chamber was $2.0 \times 10^{-9}$ Pa. The polycrystalline samples of RuP were fractured in situ at 300 K in order to obtain clean surfaces for the XPS and UPS measurements.

Figure 2 shows the Ru 3d core level XPS spectra of RuP measured at 300K and 40 K which are compared
Ru 4$d$ photo-ionization cross section relative to $P\ 3p$ increases from 10 eV to 1486.6 eV; the spectral weight from $E_F$ to 1.0 eV has stronger Ru $4d$ character than that from 1 eV to 2.5 eV. In Figs. 3(b) and (c), the near-$E_F$ UPS spectrum of RuP taken at 300 K is compared with that of $Ru_{0.75}Rh_{0.25}$As and RuSb. In Fig. 3(c), the photoemission spectra are divided by Fermi distribution functions for each temperature convoluted with a Gaussian function of FWHM of 8 meV. The spectral weight from $E_F$ to $\sim 50$ meV is suppressed in RuP compared to those $Ru_{0.75}Rh_{0.25}$As and RuSb. This spectral weight suppression is consistent with the pseudogap phase of RuP between $T_1 = 330$ K and $T_2 = 270$ K. The energy scale of pseudogap $\Delta \sim 50$ meV is roughly consistent with the pseudogap transition temperature $T_c \sim 330$ K since the $2\Delta/k_BT_c$ value is $\sim 3$ close to the BCS value.

Figure 4(a) shows the near-$E_F$ UPS spectra of RuP taken at 300K, 230K 120K and 40K at $h\nu=10$ eV. They are normalized to the integrated spectral weight from 0.2 eV to -0.1 eV. Across the metal-to-insulator transition temperature, the spectral weight at $E_F$ does not decrease in spite of the metal-to-insulator transition. This indicates that the surface region of RuP remains metallic even when the bulk undergoes the metal-to-insulator transition. Although the main part of the surface-sensitive UPS spectrum does not represent the interesting phase transition of the bulk, the electronic structural change of the bulk can be picked up in the UPS spectra as discussed below. In order to identify the spectral change at $E_F$, the photoemission spectra are divided by Fermi distribution functions for each temperature convoluted with a Gaussian function of FWHM of 8 meV. In Fig. 4(b), the data up to $3k_BT$ above $E_F$ are plot-
creases with cooling. Although the full gap opening as-

Interestingly, the magnitude of pseudogap apparently de-

50 meV is suppressed ∼75 Rh doping.

330 K and Tg = 270 K show different responses to the

The authors would like to thank valuable discussions with D. I. Khomskii. The synchrotron radiation experi-

ments were performed with the approval of HSRC (Proposal No.11-A-7).

1 Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).

2 H. Takahashi, K. Iwasa, K. Arii, Y. Kamihara, M. Hirano, and H. Hosono, Nature 453, 376 (2008).

3 Y. Ishida, T. Shimojima, K. Ishizaka, T. Kiss, M. Okawa, T. Togashi, S. Watanabe, X.-Y. Wang, C.-T. Chen, Y. Kamihara, M. Hirano, H. Hosono, and S. Shin, Phys. Rev. B 79, 060503(R) (2009).

4 D. I. Khomskii. The synchrotron radiation experiment was performed with the approval of HSRC (Proposal No.11-A-7).
5. H.S. Jarrett, A.W. Sleight, J.F. Weiher, J.L. Gillson, C.G. Frederick, G.A. Jones, R.S. Swingle, D. Swartzfager, J.E. Gulley, P.C. Hoell, *Valence Instabilities and Related Narrow-Band Phenomena*, p. 545 (Plenum, New York, 1977).

6. S. Lee, J.-G. Park, D. T. Adroja, D. Khomskii, S. Streltsov, K. A. McEwen, H. Sakai, K. Yoshimura, V. I. Anisimov, D. Mori, R. Kanno and R. Ibberson, Nature Mat. **5**, 471 (2006).

7. S. Nagata, N. Matsumoto, Y. Kato, T. Furubayashi, T. Matsumoto, J. P. Sanchez and P. Vulliet, Phys. Rev. B **58**, 6844 (1998).

8. P. G. Radaelli, Y. Horibe, M. J. Gutmann, H. Ishibashi, C. H. Chen, R. M. Ibberson, Y. Koyama, Y. S. Hor, V. Kirykhin, and S. W. Cheong, Nature **416**, 155 (2002).

9. Y. Okamoto, S. Niitaka, M. Uchida, T. Waki, M. Takigawa, Y. Nakatsu, A. Sekiyama, S. Suga, R. Arita, and H. Takagi, Phys. Rev. Lett. **101**, 086404 (2008).

10. M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **71**, 1848 (2002).

11. M. Schmidt, W. Ratcliff, P.G. Radaelli, K. Refson, N.M. Harrison, and S.W. Cheong, Phys. Rev. Lett. **92**, 056402 (2004).

12. M. Isobe, S. Koishi, N. Kouno, J. Yamaura, T. Yamauchi, H. Ueda, H. Gotou, T. Yagi, and Y. Ueda, J. Phys. Soc. Jpn. **75**, 073801 (2006).

13. A. C. Komarek, M. Isobe, J. Hemberger, D. Meier, T. Lorenz, D. Trots, A. Cervellino, M. T. Fernandez-Diaz, Y. Ueda, and M. Braden, Phys. Rev. Lett. **107**, 027201 (2011).

14. T. T. Tran, T. Mizokawa, S. Nakatsuji, H. Fukazawa, and Y. Maeno, Phys. Rev. B **70**, 153106 (2004).

15. K. Horiba, K. Ono, J. H. Oh, T. Kihara, S. Nakazono, M. Oshima, O. Shiino, H. W. Yeom, A. Kakizaki, and Y. Aiura, Phys. Rev. B **66**, 073106 (2002).

16. K. Takubo, S. Hirata, J. Y. Son, J. W. Quilty, T. Mizokawa, N. Matsumoto, and S. Nagata, Phys. Rev. Lett. **95**, 246401 (2005).

17. D. I. Khomskii and T. Mizokawa, Phys. Rev. Lett. **94**, 156402 (2005).