BL-28A/ 2012G146, 2010G655, 2009S2-005; HiSOR BL-1/12-A-33

Angle-resolved Photoemission Study of a Delafossite Oxide $CuCrO_2$

Kouta Konishi,[1] Mario Okawa,[1] Takumi Yokobori,[1] Satoshi Oozono,[2] Takashi Shinmura,[2] Tetsuji Okuda,[2] Kanta Ono,[3] Noriaki Hamada,[4] and Tomohiko Saitoh[1,*]

[1]Department of Applied Physics, Tokyo University of Science, Katsushika, Tokyo 125-8585, Japan
[2]Department of Electrical and Electronics Engineering, Kagoshima University, Kagoshima, Kagoshima 890-0065, Japan
[3]Photon Factory, Tsukuba, Ibaraki 305-0801, Japan
[4]Department of Physics, Tokyo University of Science, Noda, Chiba 278-8510, Japan

1 Introduction

Delafossite oxides $CuMO_2$ (M = metal element) have interesting and useful physical properties both from fundamental and applicational points of view. For example, $CuAlO_2$ is the first p-type transparent oxide semiconductor [1], while $CuFeO_2$ is a typical multiferroic compound [2]. Moreover, it has recently been noticed that these delafossite oxides have also considerable potential for thermoelectric materials [3] as an analogue of the thermoelectric Na_xCoO_2 [4] because of its layered structure of edge-shared MO_6 octahedrons. Hole-doped $CuCr_{1-x}Mg_xO_2$ is a candidate for such thermoelectrodes; $CuCrO_2$ has three 3d electrons at the Cr^{3+} ions under the O_h local symmetry which completely fill up the narrow Cr 3d t_{2g} (majority spin) band and thus steep density of states (DOS) at the Fermi level (E_F) may be realized near the t_{2g} band edge in the hole-doped system $CuCr_{1-x}Mg_xO_2$, which has one of the highest conductivity among delafossite oxides [3]. In terms of the k-resolved electronic structure, this should correspond to the pudding-mold band structure that is predicted to govern a large thermoelectric power in Na_xCoO_2 [5]. We have recently published a comprehensive study on the electronic structure of $CuCr_{1-x}Mg_xO_2$ [6]. In this report, we briefly report our research on the k-resolved valence-band electronic structure of this system by angle-resolved photoemission spectroscopy (ARPES) as a continuation of the previous angle-integrated study.

2 Experiment

Single crystals of $CuCrO_2$ were prepared by the standard solid-state reaction [3]. ARPES measurements in the range of the Cr/Cu 3p-3d resonance ($h\nu$=40–90 eV) were performed at BL-28A of Photon Factory in KEK, and BL-1 at HiSOR as well. The samples were fractured *in situ* in the main chamber right before measurements in ultrahigh vaccum (better than 2.0×10^{-8} Pa) at 300 K. The intensity of the spectra was normalized using photon current of the exit mirror. The energy resolution of about 30 meV and the E_F location were both determined by Gold Fermi edge.

3 Results and Discussion

The right panel of Figure 1 shows the second-derivative plot of ARPES spectra of $CuCrO_2$ along the Γ–M symmetry line taken with 70-eV photons. The overall experimental dispersion relation fairly matches the first-principles band-structure calculations with GGA scheme [7] shown in the left panel. However, there exist important differences between the experiment and the theory; the experimental lowest-energy electronic bands (red dots) are located far below E_F compared with the theory. This results in the situation that the lowest- and the second lowest-bands (blue dots) almost merge together while these two are well separated at the Γ point in the theory shown in the middle panel. Since it is established that the lowest-energy bands mainly have the Cr 3d character [6], the deep location of this band would be caused by a large Coulomb repulsion U in the Cr 3d states. Also, the lowest-energy bands are very flat compared with the theory, which probably comes from the same reason.

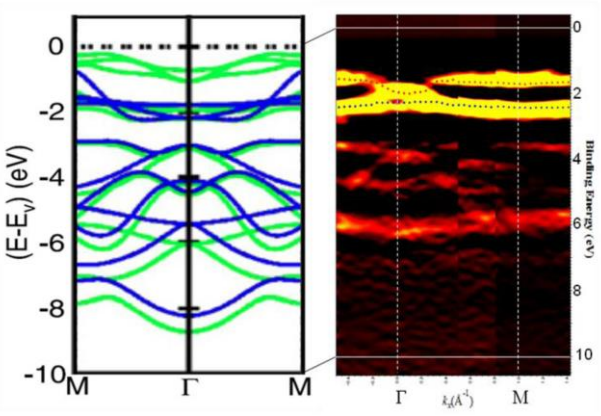

Fig. 1: Right Panel: Second-derivative plot of ARPES spectra of $CuCrO_2$ along the Γ–M symmetry line taken with 70-eV photons. Left Panel: First-principles band-structure calculations of $CuCrO_2$ with GGA scheme [7].

References

[1] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, Nature **389**, 939 (1997).

[2] T. Kimura, J. C. Lashley, and A. P. Ramirez, Phys. Rev. B **73**, 220401(R) (2006).

[3] T. Okuda, N. Jufuku, S. Hidaka, and N. Terada, Phys. Rev. B **72**, 144403 (2005).

[4] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56**, R12685 (1997).

[5] H. Hiraga, T. Makino, T. Fukumura, H. Weng, and M. Kawasaki, Phys. Rev. B **84**, 041411(R) (2011).

[6] T. Yokobori, M. Okawa, K. Konishi, R. Takei, K. Katayama, S. Oozono, T. Shinmura, T. Okuda, H. Wadati, E. Sakai, K. Ono, H. Kumigashira, M. Oshima, T. Sugiyama, E. Ikenaga, N. Hamada, and T. Saitoh, Phys. Rev. B **87**, 195124 (2013).

[7] A. Maignan, C. Martin, R. Fresard, V. Evert, E. Guilmeau, S. Hebert, M. Poienar, and D. Pelloquin, Solid State Commun. **149** (2009) 962.

[8] H. Iwasawa, K. Yamakawa, T. Saitoh, J. Inaba, T. Katsufuji, M. Higashiguchi, K. Shimada, H. Namatame, and M. Taniguchi, Phys. Rev. Lett. **96** (2006) 067203.

[6] T. Arnold, D. J. Payne, A. Bourlange, J. P. Hu, R. G. Egdell, L. F. J. Piper, L. Colakerol, A. De Masi, P.-A. Glans, T. Learmonth, K. E. Smith, J. Guo, D. O. Scanlon, A. Walsh, B. J. Morgan, and G. W. Watson, Phys. Rev. B **79**, 075102 (2009).

* t-saitoh@rs.kagu.tus.ac.jp