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 Cu$_M$O$_2$ ($M$ = 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$_x$CoO$_2$ [4] because of its layered structure of edge-shared $MO_6$ octahedrons. Hole-doped CuCr$_{1-x}$Mg$_x$O$_2$ is a candidate for such thermoelectrodes; CuCrO$_2$ has three 3$d$ electrons at the Cr$^{3+}$ ions under the $O_h$ local symmetry which completely fill up the narrow Cr 3$d_{t_2g}$ (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$_x$O$_2$, 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$_x$CoO$_2$ [5]. We have recently published a comprehensive study on the electronic structure of CuCr$_{1-x}$Mg$_x$O$_2$ [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 3$p$-3$d$ 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 $2.0 \times 10^{-8}$ 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 $\Gamma$–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 $\Gamma$ point in the theory shown in the middle panel. Since it is established that the lowest-energy bands mainly have the Cr 3$d$ character [6], the deep location of this band would be caused by a large Coulomb repulsion $U$ in the Cr 3$d$ 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 $\Gamma$–M symmetry line taken with 70-eV photons. Left Panel: First-principles band-structure calculations of CuCrO$_2$ with GGA scheme [7].
References

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