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Electronic Structure of Delaffosite Oxides $CuCr_{1-x}Mg_xO_2$

Takumi Yokobori,[1] Mario Okawa,[1] Kouta Konishi,[1] Ryota Takei,[1] Kazuya Katayama,[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, Shinjuku, Tokyo 162-8601, Japan
[2]Department of Electrical and Electronics Engineering, Kagoshima University, Korimoto, Kagoshima 890-0065, Japan
[3]Photon Factory, Tsukuba, Ibaraki 305-0801, Japan
[4]Department of Physics, Tokyo University of Science, Chiba 278-8510, Japan

1 Introduction

Delaffosite oxides $CuMO_2$ (M = metal element) have various interesting physical properties both in fundamental and applicational terms; $CuAlO_2$ is the first p-type transparent oxide semiconductor [1], for example, and $CuFeO_2$ is a typical multiferroic compound [2]. The delaffosite oxides have also considerable potential for thermoelectric materials [3] because of its layered structure of edge-shared MO_6 octahedrons, which is the same as thermoelectric $NaCoO_2$ [4]. Hole-doped $CuCr_{1-x}Mg_xO_2$ is one of such candidates; in $CuCrO_2$, $3d^3$ electrons of the Cr^{3+} ions under the O_h local symmetry fill up the narrow Cr 3d t_{2g} 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 $CuCr_{1-x}Mg_xO_2$ with one of the highest conductivity among delaffosite oxides [3]. In this paper, we briefly report our research on the valence-band electronic structure of this system.

2 Experiment

Polycrystalline samples of $CuCr_{1-x}Mg_xO_2$ (x=0, 0.02, 0.03) were prepared by the standard solid-state reaction [3]. Photoemission measurements were performed at BL-28A of Photon Factory in KEK. The samples were fractured *in situ* in the main chamber right before measurements in ultrahigh vaccum (better than 1.2×10^{-7} 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

Figure 1 shows the valence-band spectra of the x=0.02 sample taken with the photon energies around the Cr 3p-3d (Panel (a)) and the Cu 3p-3d (Panel (b)) resonance energies. The intensity of the near-E_F leading structures (the 1.4-eV shoulder and the 2.3-eV peak) systematically changes with increasing photon energy, as displayed in Fig. 1 (c) and (d). In Panel (c), the 1.4-eV shoulder shows a clear resonance-type behavior with the maximum at 50.0 eV, the Cr 3p-3d resonance energy, whereas the 2.3-eV peak shows a typical weak anti-resonance-type behavior with a dip at the Cu 3p-3d resonance energy of

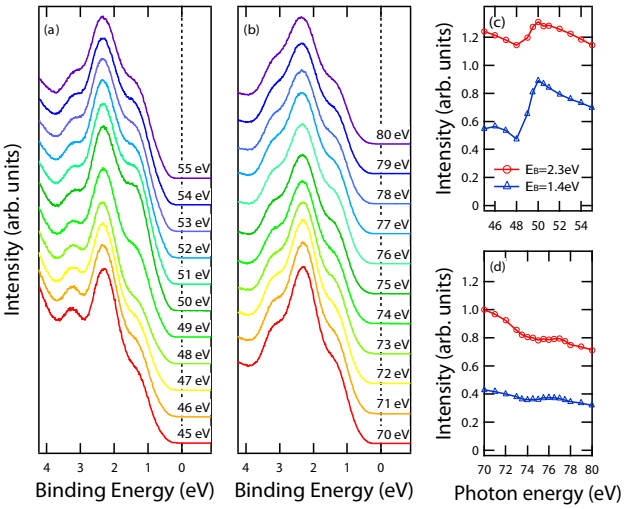

Fig. 1: Valence-band spectra of $CuCr_{0.98}Mg_{0.02}O_2$ taken with the photon energy around (a) the Cr 3p-3d resonance region and (b) the Cu 3p-3d resonance region. (c) and (d) show CIS spectra of the 1.4-eV and 2.3-eV structures.

74.0 eV in Panel (d). Therefore, the Cr 3d character is dominant in the 1.4-eV shoulder and the Cu 3d character is dominant in the 2.3-eV peak. However, one can also notice that a weak resonance of the 2.3-eV peak exists at 50.0 eV and a tiny anti resonance of the 1.4 eV at 74.0 eV does. This is demonstrating that there exists sizeable hybridization between the Cr 3d and Cu 3d states via O 2p states. Although the obtained energy diagram is somewhat different from previous works [5,6], it is in agreement with another previous work [7] and our band-structure calculations. It is also reasonable in terms of the difference between the O 2p-to-Cr 3d charge-transfer energy and the O 2p-to-Cu 3d charge-transfer energy [8].

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