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X-ray Absorption Spectra of Delaffosite Oxides $CuCr_{1-x}Mg_xO_2$

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1 Introduction

Delaffosite oxides $CuMO_2$ (M = metal element) have various important physical properties both in fundamental and applicational terms. For example, $CuAlO_2$ is the first p-type transparent oxide semiconductor [1], and $CuFeO_2$ is a typical multiferroic compound [2]. This family have also potential for thermoelectric materials [3] because of its layered structure of edge-shared MO_6 octahedrons, being 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 a rapid change of density of states at the Fermi level (E_F) may be realized near the t_{2g} band edge in the hole-doped system $CuCr_{1-x}Mg_xO_2$, a high conductivity delaffosite [3]. However, whether the doped hole will go into the Cr $3d$ states or not is unknown. In order to observe valence changes of the Cu and Cr ion in this system, we performed x-ray absorption spectroscopic measurements.

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]. Soft x-ray absorption spectroscopy (XAS) measurements were performed at BL-2C of Photon Factory in KEK. The samples were fractured *in situ* right before measurements in ultrahigh vacuum (better than 1.2×10^{-7} Pa) at 300 K.

3 Results and Discussion

Figure 1 shows XAS spectra of $CuCr_{1-x}Mg_xO_2$ (x=0, 0.02, 0.03) at the Cr $L_{2,3}$ and Cu L_3 edges. The Cr $L_{2,3}$ spectra in Panel (a) are of the typical Cr^{3+} one [5] and show no observable change with x. By contrast, the Cu L_3 edge at x=0 is the typical Cu^+ spectrum and the prepeak at 926.5 eV, which is associated with the Cu^{2+} signal [6], systematically increases wih x. These facts are indicating that the hole is not doped into the Cr states but into the Cu states.

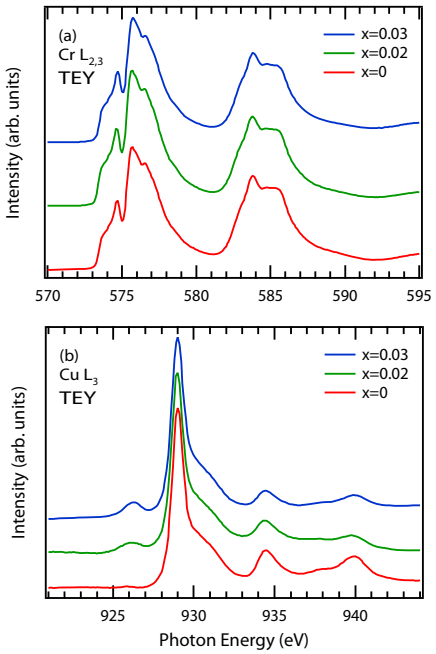

Fig. 1: XAS spectra of $CuCr_{1-x}Mg_xO_2$ (x=0, 0.02, 0.03) at (a) the Cr $L_{2,3}$ edge and (b) the Cu L_3 edge.

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