Electronic structure reconstruction of $Ca_3Ru_2O_7$ induced by K adsorption

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1 Introduction

External perturbations to Mott insulators often result in dramatic changes in their electronic structure. For example, the Mott insulator Ca_2RuO_4 can be metallized by chemical substitutions [1,2], physical pressure [3], or electric current [4]. Change in the number of RuO_2 layers in a unit cell from one (Ca_2RuO_4) to two ($Ca_3Ru_2O_7$) also allows to maintain a metallic state [5]. Instead of a metal-insulator transition, $Ca_3Ru_2O_7$ exhibits a first-order phase transition involving lattice and spin degrees of freedom at $T = 48$ K [6], where the antiferromagnetically ordered spins change direction from the a-axis to the b-axis and the lattice is slightly compressed along the c-axis. This phase transition has a significant impact on transport properties such as resistivity, Hall effect, and Seebeck effect [7], suggesting a drastic change in the low-energy band structure. Indeed, our recent angle-resolved photoemission spectroscopy (ARPES) [8] has shown that cooling across 48 K reconstructs the band structure to the Dirac semimetallic state with extremely low carrier density.

Recently, alkali metal adsorption has been recognized as an efficient method of doping electrons onto solid surfaces. This method has been successfully applied to Mott insulators such as iridates [9] and cuprates [10] to demonstrate the occurrence of the metal-insulator transition by *in-situ* ARPES measurements. This technique allows electrons to be doped at the surface even when bulk electron doping by chemical substitution is not feasible; $Ca_3Ru_2O_7$ is such a case where electron doping has not been realized. Even though $Ca_3Ru_2O_7$ is not a Mott insulator, a large impact of electron doping is expected considering its small quasiparticle residue and low carrier density. We therefore attempted x-ray photoemission spectroscopy (XPS) measurements of $Ca_3Ru_2O_7$ dosed with potassium (K).

2 Experiment

High-quality single crystals of $Ca_3Ru_2O_7$ were grown by the floating zone technique. XPS measurements were performed at BL2A of Photon Factory at $T = 20$ K with an incident x-ray of $h\nu = 500$ eV. Pristine surface was obtained by cleaving the crystals *in-situ* using the top-post method. The photoemission angle was fixed at 45 degrees from the surface normal. K was evaporated with an incremental step (7.0 Ampere for 20 seconds) in the preparation chamber while samples are attached to a manipulator cooled to 90 K.

3 Results and Discussion

Figure 1 displays core-level and valence-band photoemission spectra of $Ca_3Ru_2O_7$. The K $2p$ peak develops by increasing the amount of dosing, but with a shift toward lower binding energies [Fig. 1(a)]. This is a standard behavior of adsorbed alkali metals as observed in previous studies [11], which results from gradual transition of the alkali-metal bonding nature from ionic to metallic. On the other hand, the Ca $2p$ peak is monotonically shifted to lower binding energies [Fig. 1(b)]. This is opposite to an expectation from a rigid-band shift caused by electron doping from alkali metals. The observation points toward electronic structure reconstruction occurring around the Fermi level to modulate the spectral function. As for the Ru $3d$ spectrum, a new peak emerges on the lower binding energy side upon K adsorption and develops with increasing dosing. A naive interpretation of this peak is Ru with lower valence (Ru^{2+}) created by electron doping. However, the weight of the new peak amounts to ~40 % of the total intensity and would mean 0.4 electrons doped per Ru. This is unrealistically large since alkali metals adsorbed on a transition-metal oxide typically dopes at most ~0.15 electrons per atom [9,10,12,13]. Instead, the lower energy peak would mainly arise from a final-state effect where core holes created by photoemission are screened by a coherent state near the Fermi level. This scenario has been proposed by a dynamical mean field approach to account for the ubiquitous two-peak structure in the Ru $3d$ spectra of metallic ruthenates. The evolution of the valence-band spectrum is in good agreement with this consideration; by alkali-metal dosing, the intensity around ~1.5 eV binding energy, corresponding to the remnant of the lower Hubbard band [3], is transferred to lower energies to condense near the Fermi level. All the observations suggest that, by alkali-metal dosing, an electronic reconstruction occurred to enhance the quasiparticle residue and produce electronic states with higher coherence around the Fermi level. Angle-resolved

measurements will further clarify the situation and help to reach a complete understanding on the nature of this electronic reconstruction.
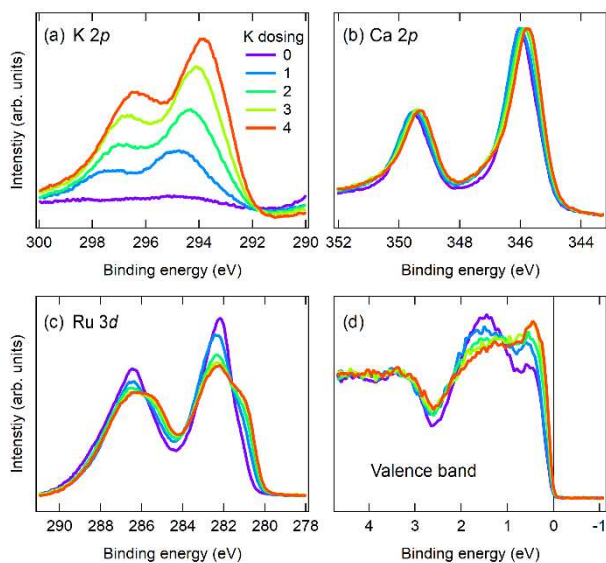

Fig. 1: XPS spectra of $Ca_3Ru_2O_7$ dosed with K. (a) K 2*p*. (b) Ca 2*p*. (c) Ru 3*d*. (d) Valence band. K was dosed in total four times, in increments of 20 seconds at 7.0 Ampere.

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