Photo-induced charge-orbital switching in transition-metal compounds probed by photoemission spectroscopy

K Takubo¹, T Mizokawa¹, N Takubo², K Miyano³, N Matsumoto³, and S Nagata³

¹Department of Physics and Department of Complexity Science and Engineering, University of Tokyo, Kashiwa, Chiba 277-8561, Japan
²Research Center for Advanced Science and Technology (RCAST), University of Tokyo, Tokyo 153-8904, Japan
³Department of Materials Science and Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido, 050-8585 Japan

takubo@sces.k.u-tokyo.ac.jp

Abstract. Transition-metal compounds with spin, charge, and orbital degrees of freedom tend to have frustrated electronic states coupled with local lattice distortions and to show drastic response to external stimuli such as photo-excitation. We have studied the charge-orbital states in perovskite-type Pr₀.₅₅(Ca₁₋ySry)₀.₄₅MnO₃ thin films (PCSMO) and spinel-type CuIr₂S₄ using photoemission spectroscopy combined with additional laser illumination. PCSMO and CuIr₂S₄ are clear-cut examples of transition-metal compounds showing photo-induced metallic conductivities but the charge-orbital states in the two systems show contrasting responses to the photo-excitation. The charge-orbital states in PCSMO are stabilized by Jahn-Teller or Breathing-type lattice distortions and can be destroyed by photo-excitation. On the other hand, the charge-orbital states in CuIr₂S₄ are stabilized by dimer formation and tend to be robust against photo-excitation.

1. Introduction

In many transition-metal compounds, d-d transition and charge-transfer transition coexist in their optical excitation spectra, and the emission and excitation spectra show interesting interplay between the d-d and charge-transfer transitions. While local d-d excitations can couple with Jahn-Teller-type or anti-Jahn-Teller-type distortions, charge-transfer excitations tend to couple with breathing-type distortions or dimer formations. When the local lattice distortions stabilize the electronic states reached by the optical excitations and trigger successive d-d or charge-transfer transitions in the neighboring sites, global phase transitions can be induced. It is interesting and important to explore methods to control the spin, charge, and orbital states by the photo-excitation, but the detailed electronic structure changes by the photo-excitation have not been clarified yet. We have studied the charge-orbital states in perovskite-type Pr₀.₅₅(Ca₁₋ySry)₀.₄₅MnO₃ (PCSMO) and spinel-type CuIr₂S₄ by means of x-ray photoemission spectroscopy (XPS) and ultraviolet-ray photoemission spectroscopy (UPS) combined with visible laser illumination. PCSMO and CuIr₂S₄ show photo-induced metallic
conductivities but the charge-orbital states in the two systems show contrasting responses to the photo-excitation.

2. Experiments

Thin films of PCSMO \((y = 0.25, 0.40)\) and single crystals of CuIr\(_2\)S\(_4\) were grown by the pulsed laser deposition method and the bismuth solution method, respectively. The XPS measurements were performed using a JPS9200 spectrometer equipped with a monochromatized Al K\(\alpha\) x-ray source \((h\nu = 1486.6 \text{ eV})\). The total resolution was \(\sim 0.6 \text{ eV}\). The UPS measurements were conducted using a SCIENTA SES 100 electron-energy analyzer with a He I line \((h\nu = 21.2 \text{ eV})\). The resolution was set to 30 meV. The films of PCSMO were grown in the deposition chamber and were transferred to the XPS chamber within 12 hours after the growth. The films were exposed to the air during the transfer and no surface treatment was made prior to the XPS measurements. The amount of surface contamination was checked by the O 1s and C 1s core-level peaks and was found to be sufficiently small and have no temperature dependence. The single crystals of CuIr\(_2\)S\(_4\) were cleaved \textit{in situ} in order to obtain clean surfaces. A Nd:YAG pulsed laser provided optical excitation at energy of 2.3 eV (532 nm) with a pulse frequency of 30 Hz, and the pulse width is about 10 ns.

3. Results

3.1. XPS study of PCSMO thin film

Perovskite-type PCSMO shows competition between the ferromagnetic metallic (FM) state and the charge-orbital ordered insulating (COOI) state at low temperature. Recently, all optical control of FM and COOI state has been realized in PCSMO \((y = 0.25)\) thin films [1]. Figure 1(a) shows the lower energy tail of the Mn 2p\(_{3/2}\) XPS for the FM state \((y = 0.4)\) and COOI state \((y = 0.25)\). In Fig. 1(b), the integrated intensity of the well-screened structure is plotted as a function of temperature for \(y = 0.25\). While the integrated intensity is suppressed in the high temperature COOI phase, it is enhanced in the low temperature FM phase. To study the photo-induced change of the film, XPS data were taken before and after visible light irradiation from the Nd:YAG laser. In the cooling process, the COOI state can be changed into the FM state by the laser illumination below 80 K although it remains after

![Figure 1](https://via.placeholder.com/150)
the illumination above 80 K. Since the COOI state is stabilized by the Jahn-Teller distortion of the Mn$^{3+}$ site, the COOI state can be destroyed by the O 2p-to-Mn 3d charge-transfer excitation and the subsequent anti-Jahn-Teller distortion. Furthermore, the reverse phenomenon, persistent photo-induced metal-to-insulator transition is found on the same film above 80 K on the warming run [2]. These phenomena suggest that the relative stability of FM and COOI phases interchanges around 80 K.

3.2. XPS and UPS study of CuIr$_2$S$_4$

Spinel-type CuIr$_2$S$_4$ consists of edge-sharing IrS$_6$ octahedra and shows first order phase transition between the paramagnetic metallic (PM) state and the charge-orbital ordered insulating (COOI) state [3,4]. In the COOI state, the Ir$^{3+}$-Ir$^{3+}$-Ir$^{4+}$ charge ordering is stabilized by the xy orbital polarization of the Ir$^{3+}$ site and the subsequent Ir$^{4+}$-Ir$^{4+}$ dimer formation [5]. The Ir$^{3+}$-Ir$^{4+}$ charge disproportionation can be identified by the Ir 4f photoemission spectra as shown in Fig. 2 (a) [6]. Although the laser illumination of 532 nm to the COOI phase induces a reduction of resistivity, the Ir$^{3+}$-Ir$^{4+}$ charge disproportionation remains even after the illumination (Fig. 2). This result indicates that the Ir$^{4+}$-Ir$^{4+}$ dimer in the edge-sharing case is robust against the charge-transfer excitation in contrast to the fragile Mn$^{3+}$ Jahn-Teller polaron in the corner sharing case.

![Image](image.png)

Figure 2. (a) Ir 4f XPS of CuIr$_2$S$_4$ taken at 300 K and those taken at 50 K before and during the laser illumination. Dashed curves indicate the fitted results. (b) Resistance taken under the same condition as XPS measurements. (c) Valence band UPS of CuIr$_2$S$_4$ taken at 300 K and those taken at 20 K before and during the laser illumination.

4. Conclusion

We have studied the electronic structure and photo-induced effects in PCSMO ($y = 0.25, 0.40$) thin films and CuIr$_2$S$_4$ single crystals using XPS and UPS. The electronic structure changes through the metal-insulator transitions are obtained in the photoemission data of PCSMO and CuIr$_2$S$_4$. The temperature dependence of PCSMO for $y = 0.25$ shows a peculiar hysteresis curve between 50 K and 125 K, indicating the phase separation between the COOI and FM domains below 125 K. Ir 4f core-level spectra of CuIr$_2$S$_4$ support the Ir$^{3+}$-Ir$^{4+}$ charge-ordering model in the insulating phase. While no spectral change is obtained on the photoemission data of CuIr$_2$S$_4$ with edge-sharing octahedra against photo-excitation, the persistent photo-induced phase transition is observed on that of PCSMO for $y = 0.25$ with corner-sharing octahedra.

References

[1] Takubo N et al. 2005 Phys. Rev. Lett. 95 017404
[2] Takubo N et al. 2008 Phys. Rev. Lett. 101 177403
[3] Nagata S et al. 1994 Physica B (Amsterdam) 194-196 1077
[4] Radaelli P G et al. 2002 Nature (London) 416 155
[5] Khomskii D I and Mizokawa T 2005 Phys. Rev. Lett. 94 156402
[6] Takubo K et al. 2005 Phys. Rev. Lett. 95 246401