論文内容の要旨

論文題目　Photoemission studies of perovskite-type transition-metal oxides in epitaxial thin films

（エピタキシャル薄膜を用いたペロブスカイト型
遷移金属酸化物の光電子分光による研究）

氏　名　和達 大樹

Perovskite-type 3*d* transition-metal (TM) oxides have been attracting great interest in these decades because of their intriguing physical properties such as metal-insulator transition, colossal magnetoresistance (CMR), and ordering of spin, charge, and orbitals [1]. Photoemission spectroscopy has greatly contributed to the understanding of the electronic structures of these materials. Since the local electronic structure of 3*d* TM oxides has become basically established according to the cluster-model analyses, it has now become the most important issue to observe how the band structure is formed from the local electronic structure. Therefore, the determination of band dispersions by angle-resolved photoemission spectroscopy (ARPES) is highly required. High-quality samples are an essential part of the photoemission studies of the perovskite-type *3d* TM oxides especially for ARPES. However, bulk single crystals of these materials are sometimes difficult to grow, and even when single crystals are available, ARPES has rarely been performed because many of them do not have cleavage planes, which are required to perform ARPES measurements. Recently, high-quality single-crystal thin films grown by the pulsed laser deposition have become available for such materials, and a setup has been developed for their film growth followed by *in-situ* photoemission measurements [2].

Thin films have a lot of advantages which bulk samples do not have. The first

one is the availability of clean single-crystal surfaces. Owing to this advantage, we succeed in observing the detailed electronic structures of $La_{1-x}Sr_xFeO_3$ (LSFO), $Nd_{1-x}Sr_xMnO_3$ (NSMO), and $Pr_{1-x}Ca_xMnO_3$ (PCMO) by photoemission and x-ray absorption spectroscopy (XAS), and also in determining the electronic band dispersions by ARPES. The second advantage is the controllability of the electronic structures by the epitaxial strain effects from the substrates. One can control the electronic structures of these systems by growing their thin films on perovskite substrates with various lattice parameters, for example $SrTiO_3$ (STO), $(LaAlO_3)_{0.3}$-$(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT), and $LaAlO_3$ (LAO) [3]. The third advantage is the possibility to study the novel physical properties at the interfaces of heterostructures. For example, at the interface of a band insulator STO and a Mott insulator $LaTiO_3$ (LTO), metallic conductivity occurs due to the delocalization of Ti 3*d* electrons of LTO [4].

In the present thesis, by utilizing the above advantages of epitaxial thin films, we could address several important and unresolved issues in the electronic properties of TM oxides and their heterostructures. In Chapter 4, we discuss the origin of the wide insulating region in LSFO. In Chapter 5, we investigate the strain effects on the electronic structures in $R_{1-x}A_xMnO_3$ (R = La, Nd, Pr and A = Sr, Ca). In Chapter 6, we study the electronic reconstruction at the interface between a band insulator LAO and a Mott insulator $LaVO_3$ (LVO) by combining extremely bulk-sensitive hard x-ray and relatively surface-sensitive soft x-ray photoemission spectroscopy.

In-situ photoemission study of $La_{1-x}Sr_xFeO_3$ epitaxial thin films

LSFO has attracted much interest because it undergoes a pronounced charge disproportionation around x = 2/3. Another striking feature of LSFO is that the insulating phase is unusually wide in the phase diagram. We have performed an *in-situ* photoemission study of LSFO thin films grown on STO (001) substrates. From the valence-band photoemission and O 1*s* XAS studies, it has been found that the rigid-band model, in which the Fermi level (E_F) is shifted according to the band filling, does not work in the near-E_F region, that is, doped holes do not simply enter the top of the $e_g\uparrow$ band but enter localized states split off from the top of the $e_g\uparrow$ band. We have also measured the temperature dependence of the photoemission and XAS spectra, and observed gradual changes of the spectra with temperature not only for x = 0.67 but also for x = 0.2 and 0.4, suggesting that a local charge disproportionation occurs over a wider temperature and composition range. We have also determined its band structure by ARPES. Figure 1 shows the comparison of the ARPES spectra taken at the photon energy of 74 eV (a) and tight-binding (TB) band-structure calculation (b). By TB

band-structure calculations, the experimental results have been successfully reproduced. However, in experiment there is a downward energy shift of about 1 eV compared with calculation, which we attribute to a polaronic effect. Thus, we conclude that the insulating behavior of LSFO is caused by the strong localization of doped holes by electron-phonon interaction and/or short-range charge ordering.

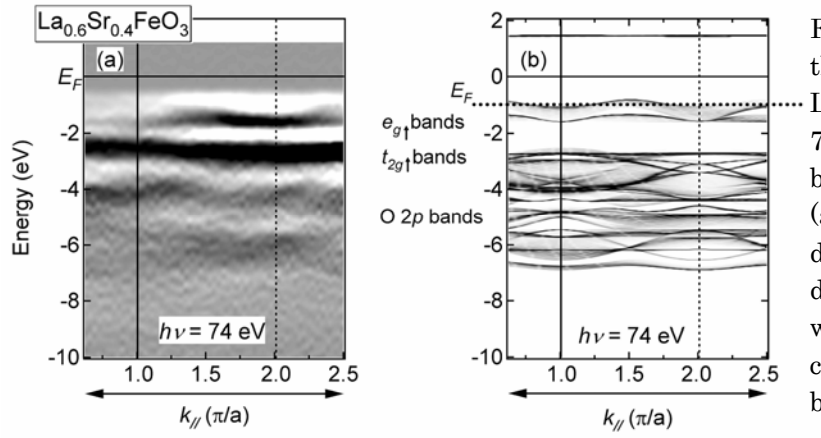


Fig. 1: Comparison of the ARPES spectra of $La_{0.6}Sr_{0.4}FeO_3$ taken at 74 eV (a) and tight-binding calculation (b). (a) is the plot of second derivatives of the energy distribution curves, where dark parts correspond to energy bands.

In-situ photoemission and x-ray absorption study of $R_{1-x}A_xMnO_3$ epitaxial thin films

Hole-doped perovskite manganese oxides $R_{1-x}A_xMnO_3$, where R is a rare-earth atom and A is an alkaline-earth atom, have attracted much attention because of their remarkable physical properties such as CMR and the ordering of spin, charge, and orbitals. PCMO, where the band width is the smallest, has a particularly stable charge-ordered state in a wide hole concentration range. We have performed an *in-situ* photoemission study of PCMO thin films grown on LAO (001) substrates. The present thin films were with compressive strain from the LAO substrates, which suppresses charge ordering. Figure 2 shows the valence-band photoemission spectra near E_F of PCMO thin films grown on LAO substrates. The line shapes were almost independent of x, and no new states appeared near E_F with hole doping. From the present spectra near E_F, we conclude that our PCMO thin films were complete insulators without any ferromagnetic fluctuations, in sharp

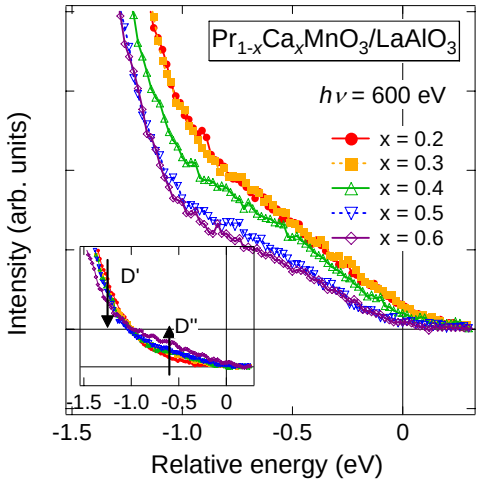
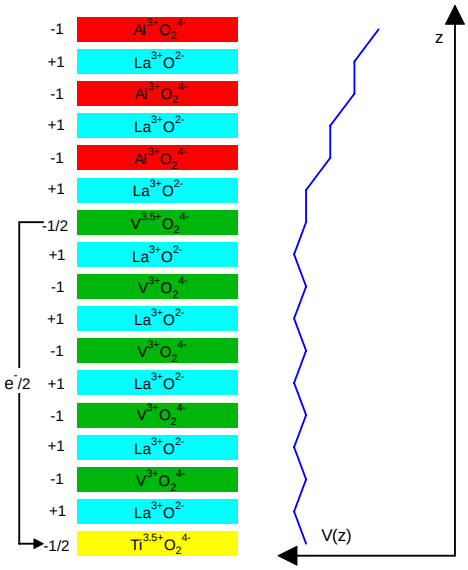


Fig. 2: Valence-band photoemission spectra near E_F of $Pr_{1-x}Ca_xMnO_3$ thin films grown on $LaAlO_3$ substrates. Energy positions have been shifted by considering the chemical potential shift. The inset shows the result of bulk samples taken from Ref. [5].

contrast to the bulk photoemission results by Ebata *et al.* [5]. These results are considered as the spectroscopic evidence for the suppression of charge ordering due to the compressive strain effects from the LAO substrates. We have also investigated the orbital states of $La_{1-x}Sr_xMnO_3$ thin films grown on STO, LSAT, and LAO substrates by measuring linear dichrosim (LD) in XAS. The present results showed that the O 1*s* LD spectra clearly reflect the change of orbital states under strain from the substrates.

Photoemission study of $LaAlO_3/LaVO_3$ interfaces

We investigated the electronic structure of superlattices consisting of a band insulator LAO and a Mott insulator LVO by combining hard x-ray and soft x-ray photoemission spectroscopy and observed how electrons behave if we confine electrons in the layers of Mott insulators. From the V 3*d* band photoemission spectra, a Mott-Hubbard gap of LVO has been found to remain open at the interface between LAO and LVO, indicating that this interface is insulating unlike the STO/LTO interfaces [4].



We have found that the valence of V in LVO was partially converted from V^{3+} to V^{4+} at the interface. We have constructed a model for the V valence distribution and succeeded in explaining the experimental results. We attribute this highly asymmetric valence change to the electronic reconstruction to eliminate polar catastrophe as shown in Fig. 3.

Fig. 3: Electronic reconstruction to eliminate polar catastrophe in the case of $LaAlO_3/LaVO_3/SrTiO_3$.

[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998). [2] K. Horiba *et al.*, Rev. Sci. Instr. **74**, 3406 (2003). [3] Y. Konishi *et al.*, J. Phys. Soc. Jpn. **68**, 3790 (1999). [4] A. Ohtomo *et al.*, Nature **419**, 378 (2002). [5] K. Ebata *et al.*, Phys. Rev. B **74**, 064419 (2006).