Spectral weight transfer in Pr$_{1-x}$Ca$_x$MnO$_3$ studied by photoemission spectroscopy

Kazuaki EBATA*, Hiroki WADATI, Masaru TAKIZAWA, Atsushi FUJIMORI
Akira CHIKAMATSU, Hiroshi KUMIGASHIRA, Masaharu OSHIMA
Yasuhide TOMIOKA, Yoshinori TOKURA
1Department of Complexity Science and Engineering and Department of Physics, University of Tokyo, Kashiwa, Chiba, 277-8561, Japan
2Department of Applied Chemistry, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8562, Japan
3Department of Applied Physics, University of Tokyo Bunkyo-ku, Tokyo 113-8656, Japan
4Spin Superstructure Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Corporation (JST), Tsukuba 305-8562, Japan

Introduction
In recent decades, manganites have been extensively studied because of their remarkable physical properties such as colossal magnetoresistance (CMR) and spin, charge and orbital ordering. The compound Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO), in which the band-width $W$ is small in comparison with other manganites, has a particularly stable charge ordered (CO) state [1]. Furthermore, CMR in the CO state of PCMO has been remarkable, amounting to several orders magnitude [1]. In this paper, we report on the composition dependence of the valence-band spectra in single crystals of PCMO.

Experimental
Single crystals of PCMO with the carrier concentrations of $x = 0.2, 0.25, 0.3, 0.45, 0.5$ and $0.65$ were grown by the floating-zone method. The photoemission spectroscopy (PES) measurements were performed at BL-2C of Photon Factory, High Energy Accelerators Research Organization (KEK) using photon energy of $h\nu = 600$ eV, 643.6 eV (Mn $2p$-3$d$ resonance), 930 eV (Pr $3d$-4$f$ resonance). Ultraviolet photoemission spectroscopy (UPS) was also performed using the photon energy $h\nu = 21.2$ eV. All the measurements were performed under the base pressure of $\sim 10^{-10}$ Torr at room temperature. Clean surfaces were obtained by repeated in situ scraping with a diamond file.

Results and Discussion
Valence-band spectra of PCMO taken at different photon energies are shown in Fig. 1(a). The spectra mainly consisted of structures as labeled A, A’, B, C, C’, C”, and D. The spectra taken at $h\nu = 930$ eV and 643.6 eV correspond to Pr $3d$-4$f$ and Mn $2p$-3$d$ on-resonant PES spectra, respectively. From the Mn $2p$-3$d$ resonance spectra, Mn 3$d$-derived features appeared as structures A’, C’, and D. Structures A’ and C’ are shifted slightly toward higher binding energies than A and C, respectively, due to the different matrix elements between normal PES and resonant PES. Also, the intensity of structure C” was strongly enhanced in the Pr $3d$-4$f$ resonance spectra. The UPS ($h\nu = 21.2$ eV) spectrum represents the O 2$p$ state due to the large relative photo-ionization cross-section of O 2$p$ at low photon energies. Therefore, structures A, B, C, and D in the UPS spectrum are assigned to the Mn 3$d$-O 2$p$ bonding state, the non-bonding O 2$p$ state, the Mn 3$d$ $t_{2g}$ plus the Pr 4$f$ states, and the Mn 3$d$ $e_g$ state, respectively, consistent with the cluster-model calculation for La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) [2].

Figure 1(b), 1(c) shows the valence-band spectra near Fermi level ($E_F$) for various hole concentrations taken at $h\nu = 21.2$ eV and 600 eV, respectively. The spectra have been normalized to the integrated intensity in the energy range from 1.5 eV to $\sim E_F$. Two features labeled D’ and D” were observed in these spectra. Spectral weight was transferred from D’ to D” with increasing hole concentration, that is, the valence-band spectra near $E_F$ exhibited highly non-rigid-band-like behavior, similar to that in the LSMO [2].

References
*ebata@wyvern.phys.s.u-tokyo.ac.jp