Temperature-dependent soft x-ray photoemission and absorption studies of charge disproportionation in La$_{1-x}$Sr$_x$FeO$_3$

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We have measured the temperature dependence of the photoemission and x-ray absorption spectra of La$_{1-x}$Sr$_x$FeO$_3$ (LSFO) epitaxial thin films with $x = 0.67$, where charge disproportionation ($3\text{Fe}^{3.67+} \rightarrow 2\text{Fe}^{3+} + \text{Fe}^{5+}$) resulting in long-range spin and charge ordering is known to occur below $T_{CD} = 190$ K. With decreasing temperature we observed gradual changes of the spectra with spectral weight transfer over a wide energy range of ~5 eV. Above $T_{CD}$ the intensity at the Fermi level ($E_F$) was relatively high compared to that below $T_{CD}$ but still much lower than that in conventional metals. We also found a similar temperature dependence for $x = 0.4$, and to a lesser extent for $x = 0.2$. These observations suggest that a local charge disproportionation occurs not only in the $x = 0.67$ sample below $T_{CD}$ but also over a wider temperature and composition range in LSFO. This implies that the tendency toward charge disproportionation may be the origin of the unusually wide insulating region of the LSFO phase diagram.

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I. INTRODUCTION

It has been well known that carrier doping into Mott insulators causes various intriguing physical phenomena 1,2. Among them, charge ordering (CO) and associated metal-insulator transition (MIT) have attracted particular interest in relation to charge stripes in high-$T_c$ cuprates 2 and spin-charge-orbital ordering in 'colossal' magnetoresistive manganites. La$_{1-x}$Sr$_x$FeO$_3$ (LSFO) with $x \approx 0.3$ exhibits a charge disproportionation (CD) from the average valence state of Fe$^{3.67+}$($d^{8.33}$) into 2Fe$^{3+}$($d^5$) + Fe$^{5+}$($d^3$), a unique type of CO, below $T_{CD} = 190$ K 6, accompanied by both a resistivity jump by an order of magnitude and antiferromagnetic ordering. A neutron diffraction study by Battle et al. 7 revealed a spin-density wave (SDW) of sixfold periodicity and a charge-density wave (CDW) of threefold periodicity along the (111) direction. They also reported the apparent absence of structural distortion in the charge ordered state, whereas electron diffraction study by Li et al. 8 revealed superspots corresponding to a local structural distortion along the (111) direction for the sample of $x = 0.7$. Optical conductivity spectra showed a splitting of optical phonon modes due to the folding of the phonon dispersion branch, caused by the lattice distortion below $T_{CD}$ 6. Cluster-model analyses of photoemission spectra revealed that the charge disproportionation is better described as $3d^5L^{0.67} \rightarrow 2d^5 + d^5L^2$, where $L$ denotes a hole in the O 2$p$ band, rather than $3d^{4.33} \rightarrow 2d^5 + d^3$, because of the oxygen $p$ character of holes doped into the charge-transfer insulator LaFeO$_3$ 7. Matsuno et al. 8 studied temperature dependent changes near the Fermi level ($E_F$) in the photoemission spectra of LSFO with $x = 0.67$ and found that the intensity at $E_F$ clearly changed across the transition temperature. They also reported smaller but finite changes for $x = 0.55$ and 0.80 and suggested that a local charge disproportionation may occur even away from $x = 0.67$. It was recently reported that Mössbauer spectra of LSFO with $x = 0.5$ 9 show temperature-dependent valence changes similar to $x = 0.67$.

In the previous work, we have performed soft x-ray photoemission and absorption measurements of high-quality La$_{1-x}$Sr$_x$FeO$_3$ single crystals epitaxially grown by the pulsed laser deposition (PLD) method in situ 10. Owing to the atomically flat, well-defined surfaces of the single-crystal thin films and the use of high energy soft x-rays ($h\nu = 600 - 710$ eV) compared to the previous work ($h\nu = 21.2 - 100$ eV) 8, the photoemission spectra, especially of the valence band, revealed well-resolved structures directly related to the Fe 3$d$ states, enabling detailed electronic structure studies of this material. In the present work, we address the questions of how the electronic structure of LSFO changes when the CD occurs as a function of temperature, using soft x-ray photoemission and absorption. We have also utilized Fe 2$p$ $\rightarrow$ 3$d$ res-
onant photoemission effect to further enhance the Fe 3d contribution. We have investigated LSFO with $x = 0.67$ to observe the change of the electronic structure accompanied by charge disproportionation, as well as $x = 0$, 0.2, and 0.4 samples.

II. EXPERIMENT

The experiment was performed at BL-2C and BL-1C of Photon Factory (PF), High Energy Accelerators Research Organization (KEK), using a combined laser molecular beam epitaxy (MBE) photoemission spectrometer system. The experimental setup is the same as that in Ref. [10] and described in detail in Ref. [11]. Epitaxial thin films of LSFO were fabricated from ceramic targets of desired chemical compositions by the PLD method. Single crystals of Nb-doped SrTiO$_3$ were used as substrates. Nb doping was necessary to avoid charging effects during the PES measurements. A Nd:YAG laser was used for ablation in its frequency-tripled mode ($\lambda = 355$ nm) at a repetition rate of 0.33 Hz. The substrates were annealed at 1050°C at an oxygen pressure of $\sim 1 \times 10^{-6}$ Torr to obtain an atomically flat TiO$_2$-terminated surface [12]. LSFO thin films of $\sim 100$ monolayers were deposited on the substrates at 950°C at an oxygen pressure of $\sim 1 \times 10^{-4}$ Torr. The films were post-annealed at 400°C at an atmospheric pressure of oxygen to remove oxygen vacancies. The samples were then transferred from the MBE chamber to the spectrometer under an ultrahigh vacuum. The surface morphology of the measured films was checked by ex-situ atomic force microscopy. The electrical resistivity of $x = 0.67$ sample showed a jump at 190 K ($= T_{C,D}$), whereas the other samples showed insulating behaviors in the whole temperature range, as shown in Fig. 1.

Photoemission measurements were performed under an ultrahigh vacuum of $\sim 10^{-10}$ Torr from room temperature down to 10 K. The PES spectra were measured using a Scienta SES-100 electron-energy analyzer. The total energy resolution was about 200 meV at the photon energy of 600 eV, about 250 meV at that of 710 eV (on Fe 2p $\rightarrow$ 3d resonance), and about 35 meV at that of 40 eV. The $E_F$ position was determined by measuring gold spectra. The XAS spectra were measured in the total-electron-yield mode. The stoichiometry of the thin films was characterized by analyzing the relative intensities of relevant core levels, confirming that the compositions of the samples were nearly those of the ceramic targets [10].

III. RESULTS AND DISCUSSION

A. La$_{0.33}$Sr$_{0.67}$FeO$_3$

Figures 2 and 3 show the temperature dependence of the valence-band photoemission spectra of La$_{0.33}$Sr$_{0.67}$FeO$_3$ taken at $h\nu = 710$ eV (on Fe 2p $\rightarrow$ 3d resonance), 600 eV and 40 eV. The spectra taken at $h\nu = 710$ eV are considered to represent the Fe 3d partial DOS (PDOS) with extra enhancement of the satellite around $-11$ eV, whereas those taken at $h\nu = 40$ eV are dominated by the O 2p PDOS and those taken at
$h \nu = 600$ eV are mixtures of the Fe 3$d$ and O 2$p$ PDOS according to the corresponding atomic orbital photoionization cross-sections [13]. In Fig. 2, the spectra have been normalized to the area from 1 eV to $-14$ eV. One can observe four structures, namely, A ($e_{g1}$ band), B ($t_{2g1}$ band), C (Fe 3$d$–O 2$p$ bonding states), and the satellite structure. The intensity at $E_F$ is considerably low without a clear Fermi-level cutoff even at room temperature. A similar observation was reported for Fe$_3$O$_4$ [14, 15, 16], which also shows charge ordering below $\sim 120$ K. The spectra change gradually with temperature. With decreasing temperature, spectral weight is transferred from the vicinity of $E_F$ to structure A ($e_{g1}$ band) while the height of structure B ($t_{2g1}$ band) remains almost unchanged. In Fig. 3 (a) (b) and thereafter we have normalized the spectra to the height of structure B, and concentrate on the spectra within $\sim 3$ eV of $E_F$. The spectra for 710 eV and 600 eV clearly indicate a transfer of spectral weight from the vicinity of $E_F$ to structure A, that is, within the $e_{g1}$ band region with decreasing temperature. The energy range in which spectral weight transfer occurs is two orders of magnitude larger than the transition temperature $T_{CD} = 190$ K ($\sim 22$ meV). Spectral weight transfer over such a wide energy range was also reported in other transition-metal oxides such as La$_{1-x}$Sr$_x$MnO$_3$ [17], La$_{1-x}$Ca$_x$MnO$_3$ [18], Nd$_{1-x}$Sr$_x$MnO$_3$ [19], Pr$_{1-x}$Sr$_x$MnO$_3$ [20] and Nd$_{1-x}$Sm$_x$NiO$_3$ [21, 22]. The 40 eV spectrum [Fig. 3 (c)] does not show appreciable changes on the same energy and intensity scales, but near $E_F$ a clear spectral weight transfer is observed [Fig. 3 (d)]. From those photon energy dependences, we conclude that the temperature-dependent part of O 2$p$ states are distributed within $\sim 0.8$ eV of $E_F$ and the temperature-dependent part of Fe 3$d$ states within $\sim 2$ eV of $E_F$.

In order to characterize the spectral weight transfer more clearly, we have plotted the spectral weight of the 710 eV spectrum (Fe 3$d$ PDOS) integrated from $-2.0$ eV to $+0.3$ eV and that of the 40 eV spectrum (O 2$p$ PDOS) integrated from $-1.0$ eV to $+0.3$ eV as a function of temperature in Fig. 4 (a). We have also plotted the spectral weight integrated from $-0.3$ eV to $+0.3$ eV for the same photon energies in Fig. 4 (b). A dramatic but gradual change of spectral weight is observed across the transition temperature in both plots. While the spectral weight within $\sim 2$ eV of $E_F$ increases with decreasing temperature, reflecting the spectral weight transfer from $-(4-5)$ eV to structure A, spectral weight in the vicinity of $E_F$ decreases with decreasing temperature, reflecting the spectral weight transfer from near $E_F$ to structure A.

Next, Fig. 5 shows the temperature dependence of the Fe 2$p$ and O 1$s$ XAS spectra. One cannot observe any changes in the Fe 2$p$ XAS spectra within experimental errors, whereas there is a significant change in the O 1$s$ XAS spectra. Upon cooling, the peaks in the empty Fe 3$d$ band region become sharp, and the first peak corresponding to the doping-induced $e_{g1}$ band becomes more intense. This spectral change is opposite to the change of the photoemission spectra in the vicinity of $E_F$ but is the same as the increase of structure A. At the same time, spectral weight on the higher energy side of the first peak decreases upon cooling, resulting in the overall shift of the first peak toward lower energies. In addition, the structure at $\sim 530$ eV changes its lineshape and is shifted to lower energies.
To summarize those spectral changes, we show a schematic picture in Fig. 6. Below $E_F$, upon cooling, spectral weight is transferred from the near-$E_F$ states as well as from the states at $-(4 - 5)$ eV of Fe 3$d$ character to the states of Fe 3$d$ character and O 2$p$ character at $\sim -2$ eV and $\sim -1$ eV, respectively (composing structure A). Correspondingly, there is an increase in the O 2$p$ DOS at $\sim +1$ eV above $E_F$ upon cooling. We believe that the DOS in the vicinity of $E_F$ decreases above $E_F$, too, since a gap should open at $E_F$, but the change associated with the gap opening may be too small to be observed with the resolution of O 1$s$ XAS.

The gradual temperature dependence indicates that CD does not occur abruptly at $T_{CD}$ but occurs gradually from well above $T_{CD}$, namely, that a local CD occurs well above $T_{CD}$ and continues to develop below $T_{CD}$, too. It would be interesting to investigate other Fe oxides which undergoes charge ordering such as CaFeO$_3$ and Fe$_3$O$_4$ to see whether such a temperature-dependent spectral weight transfer is a common phenomenon or not.

**B. La$_{1-x}$Sr$_x$FeO$_3$ with x = 0, 0.2, 0.4**

We have also measured LSFO thin films with $x = 0$, 0.2, and 0.4 by photoemission and O 1$s$ XAS to see whether the temperature dependence seen for $x = 0.67$ is unique to this composition or not. For $x = 0$, 0.2, and 0.4, the system is insulating at all temperatures without any abrupt change in the resistivity as shown in Fig. 1 and exhibits only antiferromagnetic transitions above room temperature (at about 740 K, 320 K, and 320 K, respectively).

In Fig. 7 we show the temperature dependence of the valence-band photoemission spectra of LSFO with $x = 0$, 0.2, and 0.4 taken at $h\nu = 710$ eV, i.e., Fe 2$p$ $\rightarrow$ 3$d$ resonance. The intensity of peak A increases with decreasing $x$ due to the increase in the $e_g$ band filling, as reported in the previous paper [10]. There was only very weak temperature dependence for $x = 0$, as expected. As for $x = 0.2$ and 0.4, however, the spectra change gradually with temperature as in the case of $x = 0.67$, that is, the intensity of peak A increases and that in the vicinity of $E_F$ decreases with decreasing temperature. Surprisingly, the magnitude of the changes for $x = 0.4$ is comparable to that of $x = 0.67$.

We also measured the temperature dependence of the O 1$s$ XAS spectra, as shown in Fig. 8. The spectra for all $x$'s show appreciable temperature dependence. Particularly for $x = 0.4$, the change is as dramatic as in the case of $x = 0.67$. From Figs. 7 and 8, we conclude that the temperature dependence becomes stronger with increasing $x$ until $x = 0.67$ but that $x = 0.4$ shows as strong temperature dependence as $x = 0.67$.

Although there is no long-range charge ordering in the $x = 0.4$ sample, the temperature dependence comparable to $x = 0.67$ suggests that a local charge disproportionation occurs at low temperatures for $x = 0.4$. 

**FIG. 5:** (Color) Temperature dependence of XAS spectra of La$_{0.33}$Sr$_{0.67}$FeO$_3$. (a) Fe 2$p$ (b) O 1$s$.

**FIG. 6:** Schematic picture of the spectral changes with decreasing temperature in La$_{0.33}$Sr$_{0.67}$FeO$_3$.

**FIG. 7:** (Color) Temperature dependence of the valence-band photoemission spectra of La$_{1-x}$Sr$_x$FeO$_3$ taken at $h\nu = 710$ eV, i.e., Fe 2$p$ $\rightarrow$ 3$d$ resonance. (a) $x = 0$ (b) $x = 0.2$ (c) $x = 0.4$. 

FIG. 8: (Color) Temperature dependence of the O 1s XAS spectra of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$. (a) $x = 0$ (b) $x = 0.2$ (c) $x = 0.4$.

is naturally related to the wide insulating phase of this material. From the present work, we propose that the wide insulating region with the gap or pseudogap are due to the local charge disproportionation. Search for, e.g., diffuse scattering corresponding to the local charge disproportionation in samples with $x \neq 0.67$ is desired to test our proposal.

IV. CONCLUSION

We have measured the temperature dependence of the photoemission and XAS spectra of $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_3$ to study the spectral change across the transition temperature of charge disproportionation. We observed gradual changes of the spectra with temperature. Above $T_{CD}$ the intensity at the Fermi level ($E_F$) becomes relatively high compared to that below $T_{CD}$ but shows no clear Fermi-level cutoff and still remains much lower than that in conventional metals. Below $E_F$, spectral weight transfer was observed. Spectral weight is transferred from the near-$$E_F$$ states of mixed Fe 3$d$–O 2$p$ character to the states of both Fe 3$d$ and O 2$p$ character well below $E_F$ primarily within the $e_{g7}$ band. Strong temperature dependence was also observed above $E_F$ in the O 1s XAS spectra. We also measured the temperature dependence of the photoemission and XAS spectra of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ with $x = 0, 0.2, 0.4$. For $x = 0.4$, temperature dependence comparable to $x = 0.67$ was observed. Those observations suggest that a local charge disproportionation occurs not only in the $x = 0.67$ sample below 190 K but over a wider temperature and composition range. We propose that this local charge disproportionation is the origin of the wide insulating region of the LSFO phase diagram.

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