In-situ photoemission study of La$_{1-x}$Sr$_x$FeO$_3$ epitaxial thin films

Master Thesis

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Chapter 1

Introduction

Since the discovery of high-$T_c$ superconductivity in the cuprates [1], great interest has revived in perovskite-type transition-metal oxides because of their intriguing properties, such as metal-insulator transition (MIT), colossal magnetoresistance (CMR), and ordering of spin, charge, and orbitals [2]. In most cases, hole doping plays a crucial role in realizing these interesting physical properties. However, there has been little consensus on how the electronic structure evolves with hole doping in these compounds, namely, whether new states are created in the gap or the chemical potential is simply shifted as in the rigid-band model, even in the most extensively studied case of the high-$T_c$ cuprates [3–5].

Among the perovskite-type transition-metal oxides, La$_{1-x}$Sr$_x$FeO$_3$ (LSFO) has attracted much interest because it undergoes a pronounced charge disproportionation and an associated MIT around $x \simeq 2/3$ [6]. One end member, LaFeO$_3$, is an antiferromagnetic insulator with a high Néel temperature ($T_N = 738$ K). The character of the band gap is of the charge-transfer (CT) type, and the optical gap is $\sim 2.1$ eV [7]. The other end member, SrFeO$_3$, is a helical antiferromagnetic metal with $T_N = 134$ K. In an early photoemission study, it was found that its ground state is dominated by the $d^5\mathbf{L}$ configuration, where $\mathbf{L}$ denotes a hole in the oxygen 2$p$ band, rather than the $d^4$ configuration [8], meaning that the system is a negative-charge-transfer-energy compound and that holes in the O 2$p$ band are responsible for the metallic behavior [9,10]. One striking feature of LSFO is that the insulating phase is unusually wide in the phase diagram (especially at low temperatures $0 < x < 0.9$, and even at room temperature $0 < x < 0.5$) [11]. The electrical resistivity and phase diagram of LSFO are shown in Fig. 1.1. The wide insulating phase may be related to charge disproportionation at $x \simeq 2/3$. The O 1$s$ x-ray absorption spectroscopy (XAS) study by Abbate et al. [12] (Fig. 1.2) has suggested that doped holes have the O 2$p$ character.
Figure 1.1: (a) Electrical resistivity of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$. (b) Phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$. The shaded zones represent the metal-insulator transition regions. [11]

Figure 1.2: X-ray absorption spectra of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ for various Sr concentrations. Left: O 1s spectra. Right: Fe 2p spectra. [12]
La$_{1-x}$Sr$_x$FeO$_3$ with $x \simeq 2/3$ exhibits charge disproportionation, a unique type of charge ordering, below 190 K [6], accompanied by both an MIT and antiferromagnetic ordering. Figure 1.3 shows a schematic structure of the charge- and spin-ordered state with charge disproportionation. This charge disproportionation has been studied by many experimental methods such as Mössbauer spectroscopy [6], neutron diffraction [13], and electron diffraction [14]. It was found to be described as $3d^5L^{0.67} \rightarrow 2d^5 + d^5L^2$ rather than $3d^{4.33} \rightarrow 2d^5 + d^3$ because of the negative effective charge transfer energy [8].

Recently, high-quality perovskite-type oxide single-crystal thin films grown by pulsed laser deposition (PLD) have become available [15,16], and a setup has been developed for their in-situ photoemission measurement [17,18]. By performing in-situ angle-resolved photoemission spectroscopy (ARPES) measurements, it became possible to determine the band structure of materials with no cleavage plane [18].

Therefore, the central questions of this system are as follows.

1. How does the electronic structure evolve from LaFeO$_3$ (charge-transfer-type insulator) to SrFeO$_3$ (oxygen-hole metal)?

2. How does the electronic structure change by charge disproportionation at $x = 0.67$?

3. What is the origin of the wide insulating phase of LSFO?

4. What is the band structure of LSFO?

To answer the above questions, we measured photoemission and x-ray absorption spectra of epitaxially-grown high-quality thin films of LSFO prepared in situ.
This thesis is organized as follows. In Chapter 2, we review the principles of photoemission spectroscopy and x-ray absorption spectroscopy. The experimental setup and procedure are described in Chapter 3. The hole-doping dependence of the electronic structure is discussed in Chapter 4 to answer the first question. Combining soft x-ray photoemission spectra and O 1s XAS spectra, we successfully obtain a picture of how the electronic structure evolves from a CT insulator to an oxygen-hole metal through the observation of the chemical potential shift and spectral weight transfer. The study of the charge disproportionation transition is presented in Chapter 5 as an answer to the second question. We observe spectral weight transfer not only in the $x = 0.67$ sample but also in the $x = 0.4$ and $x = 0.2$ samples. We propose an incomplete or local charge disproportionation around $x = 0.67$ as the origin of the wide insulating region of LSFO (an answer to the third question). In Chapter 6, an angle-resolved photoemission is studied to answer the final question. We succeed in determining the band structure of LSFO for the first time. The last chapter, Chapter 7 is devoted to conclusion.
Chapter 2

Principles of photoemission spectroscopy and x-ray absorption spectroscopy

In this chapter, we describe the principles of photoemission spectroscopy and x-ray absorption spectroscopy [19].

2.1 Principles of photoemission spectroscopy

2.1.1 General formulation of photoemission spectroscopy

Figure 2.1 illustrates a schematic diagram of the principle of photoemission spectroscopy (PES). When an electron in the solid absorbs a photon of sufficiently high energy $h\nu$, it is emitted as a photoelectron. From the energy conservation, the kinetic energy $E_{\text{kin}}^{\text{vac}}$ of the photoelectron is written as

$$E_{\text{kin}}^{\text{vac}} = h\nu - \phi - E_B,$$

(2.1)

where $E_{\text{kin}}^{\text{vac}}$ is measured from the vacuum level ($E_{\text{vac}}$), $\phi$ is the work function of the sample, and $E_B$ is the binding energy measured from the Fermi level ($E_F$). In real experiments the kinetic energy ($E_{\text{kin}}$) measured from $E_F$ rather than $E_{\text{kin}}^{\text{vac}}$ is directly observed. Then, it is convenient to use

$$E_{\text{kin}} = h\nu - E_B.$$

(2.2)

In the one-electron approximation, the binding energy is equal to the negative
Hartree-Fock orbital energy,

\[ E_B = -\epsilon_k. \]

This relationship is called Koopmans’ theorem [20]. This assumption is valid when the wave functions of both the initial and final states can be expressed by single Slater determinants of the \( N \)- and \( (N-1) \)-electron systems, respectively, and the one-electron wave functions do not change by the removal of the electron. If we apply this approximation, the photoemission spectrum \( I(E_B) \) can be expressed as

\[ I(E_B) \propto \sum_k \delta(E_B + \epsilon_k) \propto N(-E_B). \]

Thus, when the one-electron approximation is valid, the photoemission spectrum is proportional to the density of states of the occupied one-electron states \( N(E) \).

### 2.1.2 Principle of resonant photoemission spectroscopy

Through synchrotron radiation, we can use photons of continuously variable energy. A schematic diagram of resonant photoemission spectroscopy is depicted in Fig. 2.2. When the energy of the incident photon is equal to the energy difference between the \( p \) core level and the valence \( d \) states, besides the direct photoemission
process of a valence $d$ electron,

$$p^6d^N + h\nu \rightarrow p^6d^{N-1} + e^-,$$

the photoabsorption and subsequent Auger-type decay, called super Coster-Krönig decay,

$$p^6d^N + h\nu \rightarrow p^5d^{N+1} \rightarrow p^6d^{N-1} + e^-,$$

occur. The final states of these two processes have the same electron configuration, and therefore a quantum-mechanical interference occurs. The photoemission intensity is resonantly enhanced and shows a so-called Fano profile [21]. Since this enhancement takes place only for the $d$ orbitals, we can obtain the $d$ partial DOS in the compounds.

**2.1.3 Principle of angle-resolved photoemission spectroscopy**

Angle-resolved photoemission spectroscopy (ARPES) is the only experimental technique to determine the band structure of a material. In the photoexcitation by photons with low energy, the wave number of the incident photon can be neglected, and the wave number of the electron is conserved before and after the photoexcitation except for the reciprocal lattice vector. Therefore, the following relationship is satisfied between the wave vector of the initial state ($K_i$) and that of the final one ($K_f$)

$$K_f = K_i + G,$$

(2.5)
where $G$ is a reciprocal lattice vector.

Figure 2.3 shows schematically a diagram of the emission of an electron from a solid to vacuum. When the electron is emitted from a material, the wave vector perpendicular to the surface ($K_{f\perp}$) is modified by the potential barrier of the so-called inner potential ($V_0$), whereas the wave vector parallel to the surface ($K_{f\parallel}$) is conserved. Therefore, the following relationship is satisfied between the wave vector parallel to the surface of the emitted electron, $k_{f\parallel}$, and $K_{i\parallel}$,

$$ k_{f\parallel} = K_{f\parallel} = K_{i\parallel}. $$

(2.6)

Since $k_{f\parallel}$ is related to the polar emission angle $\theta$ and the photoelectron kinetic energy $E_k$ as

$$ k_{f\parallel} = \frac{\sqrt{2m}}{h} \sqrt{E_k \sin \theta} $$

$$ = 0.5123 \sqrt{h\nu - \phi - E_B \sin \theta} \ [\text{Å}^{-1}], $$

where $m$ is the free electron mass, $K_{i\parallel}$ is given by

$$ K_{i\parallel} = 0.5123 \sqrt{h\nu - \phi - E_B \sin \theta} \ [\text{Å}^{-1}], $$

(2.7)

and $K_{i\perp}$ is given by

$$ K_{i\perp} = 0.5123 \sqrt{(h\nu - \phi - E_B) \cos^2 \theta + V_0} \ [\text{Å}^{-1}]. $$

(2.8)

Consequently, when we set the analyzer at normal direction, $\theta$ becomes 0, and

$$ K_{i\parallel} = 0 $$

$$ K_{i\perp} = 0.5123 \sqrt{(h\nu - \phi - E_B) + V_0} \ [\text{Å}^{-1}]. $$

From this relationship, one can obtain information about the band dispersion along the surface normal by scanning the photon energy $h\nu$ using synchrotron radiation. The unknown value of $V_0$ can be estimated from the periodicity of the band dispersion.

2.2 X-ray absorption spectroscopy

The measurements of photo-absorption by excitation of a core-level electron into unoccupied states as a function of photon energy is called x-ray absorption spec-
Figure 2.3: Schematic diagram of the emission of an electron from a solid to vacuum.

troscopy (XAS). The photo-absorption intensity is given by

\[ I(\hbar \nu) = \sum_f \left| \langle f \mid T \mid i \rangle \right|^2 \delta(E_i - E_f - \hbar \nu), \]  

(2.9)

where \( T \) is the dipole transition operator. O 1s XAS spectra represent the unoccupied O 2p partial DOS. When other orbitals are hybridized with the O 2p orbitals, O 1s XAS can be used to investigate the unoccupied density of states. In the 3d transition-metal compounds, transition-metal 2p XAS spectra reflect the 3d states such as the valence, spin state and crystal-field splitting. Calculations of transition-metal 2p XAS spectra in a crystal field have been performed by Thole et al [22].

There are two measurement modes for XAS, the transmission mode and the total-yield mode. In the transmission mode, the intensity of the x-ray is measured before and after the sample and the ratio of the transmitted x-rays is counted. Transmission-mode experiments are standard for hard x-rays, while for soft x-rays, they are difficult to perform because of the strong interaction of soft x-rays with the sample. In our experiment, we adopted the total-yield mode.
Chapter 3

Experiment

The photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS) measurements were performed using a combined laser molecular beam epitaxy (laser MBE) and photoemission spectrometer system, at the soft x-ray undulator beamline BL-2C [23], and the bend magnet VUV beamline BL-1C [24] of Photon Factory, Institute of Materials Structure Science, High Energy Accelerators Research Organization (KEK),

Figure 3.1 illustrates a layout diagram of this apparatus. Roughly, it consists of a sample entry chamber, a laser MBE chamber, a sample preparation chamber, and a photoemission chamber. Epitaxial films of La$_{1-x}$Sr$_x$FeO$_3$ (LSFO) were fabricated by the laser MBE method. Laser MBE is the pulsed laser deposition (PLD) at a low background gas pressure with in situ reflection high-energy electron diffraction (RHEED) monitoring [25,26]. In situ RHEED monitoring is necessary to control the thickness of the deposited film. PLD is the method of transforming sintered targets into thin films by ablating the targets by pulsed laser and depositing on the substrates. Advantages of PLD are that it is possible to deposit under relatively high oxygen pressure, which is favorable for controlling volatile oxygen content in the film, and in the preservation of target composition in the film. Figure 3.2 illustrates this laser MBE method [27], though we used different lasers for heating substrates and ablating the target.

In our experiments, single crystals of Nb-doped SrTiO$_3$ were used as substrates. Nb-doping was necessary to avoid charging effects in 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$^\circ$C at an oxygen pressure of $\sim 1 \times 10^{-6}$ Torr to obtain an atomically flat TiO$_2$-terminated surface [28]. LSFO thin films of $\sim 100$ monolayers were deposited on the substrates at 950$^\circ$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 laser MBE chamber to the spectrometer under ultrahigh vacuum. Details of the experimental setup are described in Ref [18].

The surface morphology of the measured films was checked by ex-situ atomic force microscopy (AFM). Figure 3.3 shows an AFM image of a LaFeO$_3$ thin film. There we can see an atomically flat step-and-terrace structures. The crystal structure was characterized by four-circle X-ray diffraction, and coherent growth on the substrate was observed.

All the photoemission measurements were performed under ultrahigh vacuum of $\sim 10^{-10}$ Torr. The temperature was fixed at room temperature (Chapter 4), and at 150 K (Chapter 6), and was varied from room temperature down to 10 K (Chapter 5). The PES spectra were measured using a Scienta SES-100 electron-energy analyzer. The total energy resolution was about 200-500 meV at BL-2C, and about 30-300 meV at BL-1C, depending on photon energy. The Fermi level ($E_F$) position was determined by measuring gold spectra as a reference. The XAS spectra were measured using the total-electron-yield method.
Figure 3.2: Illustration of the laser molecular beam epitaxy (laser MBE) method [27].

Figure 3.3: AFM image of an epitaxially grown LaFeO$_3$ thin film. Image size is 1µm × 1µm.
Chapter 4

Hole-doping dependence of the electronic structure

4.1 Introduction

Among the perovskite-type transition-metal oxides, La$_{1-x}$Sr$_x$FeO$_3$ (LSFO) has attracted much interest because it undergoes a pronounced charge disproportionation and an associated metal-insulator transition around $x \simeq 2/3$ [6]. One end member, LaFeO$_3$, is an antiferromagnetic insulator with a high Néel temperature ($T_N = 738$ K). The other end member, SrFeO$_3$, is a helical antiferromagnetic metal with $T_N = 134$ K. Holes in the oxygen 2$p$ band are responsible for its metallic behavior [9,10]. In this chapter, we focus on the central question for this system of how does the electronic structure evolve from a charge-transfer-type insulator LaFeO$_3$ to the metallic oxygen holes of SrFeO$_3$ as a function of hole doping. A systematic x-ray photoemission study of scraped bulk LSFO samples has been reported by Chainani et al. [29]. Structures in the valence band, however, were not clearly resolved partly because of the limited energy resolution ($\sim 0.8$ eV) as shown in Fig. 4.1. In the present study, we have used soft x-rays with high-energy resolution ($\sim 200$ meV) and succeeded in resolving detailed spectral features and in directly obtaining more detailed information about the Fe 3$d$ states. We could determine the Fe 3$d$ contribution more clearly with better bulk sensitivity due to the longer photoelectron escape depth for the higher photoelectron kinetic energies [30]. We emphasize that in the present work the usefulness of bulk sensitivity is further enhanced by the use of high-quality epitaxial thin film samples [17]. Combining the soft x-ray photoemission spectra and O 1s XAS spectra, we have successfully obtained a picture of how the electronic structure evolves from a CT insulator to an oxygen-hole metal through the observation of
the chemical potential shift and spectral weight transfer.

4.2 Results and discussion

4.2.1 Electrical resistivities

Figure 4.2 shows the electrical resistivity of La$_{1-x}$Sr$_x$FeO$_3$ thin films samples which were made under the same condition as the samples for the photoemission measurements. The samples for the resistivity measurements were grown on Nb-free SrTiO$_3$ substrates to prevent the electric current from flowing through the conducting substrate. As for $x = 0.67$, there is a jump of resistivity, caused by charge disproportionation, almost at the same temperature as the bulk samples [11,31] ($T_{CD} = 190$ K).\footnote{This transition is often called “metal-insulator transition”, but the electrical resistivity satisfies $d\rho/dT < 0$ even above the transition temperature.} This can be naturally understood from the small lattice mismatch between La$_{1-x}$Sr$_x$FeO$_3$ and SrTiO$_3$.

4.2.2 LaFeO$_3$

Before proceeding to the composition dependence of LSFO, we first characterize the electronic structure of the La-end composition, LaFeO$_3$ (LFO). Figure
Figure 4.2: Electrical resistivity of La$_{1-x}$Sr$_x$FeO$_3$ thin films.

4.3 gives the Fe 2p PES spectrum, the valence-band PES spectrum, and the O 1s XAS spectrum of LFO. As the $E_F$ position for O 1s XAS cannot be determined unambiguously from the O 1s core-level PES and XAS data because of the unknown effect of the core-hole potential [32], the XAS spectrum has been aligned so that the gap magnitude agrees with that obtained from the optical measurements, 2.1 eV [7], as shown in Fig. 4.3 (b). In the main valence-band region $[-(0-10) \text{ eV}]$, we observe three structures denoted by A, B, and C and a satellite structure at $\sim -12 \text{ eV}$. The O 1s XAS spectrum shows empty Fe 3$d$ states within $\sim 5 \text{ eV}$ of $E_F$ and the La 5$d$ states above it. The empty Fe 3$d$ states are split into two peaks, D and E, due to the $e_g - t_{2g}$ crystal-field splitting.

In order to interpret those spectra quantitatively, we performed a configuration-interaction (CI) cluster-model calculation [8, 33]. We considered an [FeO$_6$]$^{9-}$ octahedral cluster. In this model, the ground state is described as

$$\Psi_g = \alpha_1|d^5\rangle + \alpha_2|d^6_L\rangle + \alpha_3|d^7L^2\rangle + \cdots$$  \hspace{1cm} (4.1)

Our model, in which $d$ electrons are assumed to be localized in the cluster, is considered to be a good approximation since LaFeO$_3$ is an insulator and the LDA+$U$ calculation has shown that the Fe 3$d$ states in LaFeO$_3$ have weak band dispersion, so the translational symmetry does not affect the angle-integrated photoemission spectra of the Fe 3$d$ band significantly. The final state for the
emission of an Fe $2p$ core electron is given by
\[ \Psi_f = \beta_1|c^5d^4\rangle + \beta_2|c^6d^5L\rangle + \beta_3|c^6d^7L^2\rangle + \cdots, \tag{4.2} \]
where $c$ denotes an Fe $2p$ core hole. The final state for the emission of an Fe $3d$ electron is given by
\[ \Psi_f = \gamma_1|d^4\rangle + \gamma_2|d^5L\rangle + \gamma_3|d^6L^2\rangle + \cdots, \tag{4.3} \]
and that for O $1s$ XAS by
\[ \Psi_f = \delta_1|d^6\rangle + \delta_2|d^7L\rangle + \delta_3|d^8L^2\rangle + \cdots. \tag{4.4} \]
The O $1s$ XAS spectrum represents the unoccupied O $2p$ partial DOS, and since other orbitals are strongly hybridized with the O $2p$ orbitals, O $1s$ XAS also reflects the empty Fe $3d$ and La $5d$ bands.

To calculate the valence-band PES spectrum, the O $2p$ emission spectrum has to be added to the Fe $3d$ spectrum. The line shape of the O $2p$ band was taken from the PES data of La$_{0.33}$Sr$_{0.67}$FeO$_3$, measured at $h\nu = 21.2$ eV [34]. In order to take into account the chemical potential shift between LaFeO$_3$ and La$_{0.33}$Sr$_{0.67}$FeO$_3$ (see Fig. 4.6), the $h\nu = 21.2$ eV spectrum has been shifted downward by 0.78 eV. The relative intensities of the Fe $3d$ - and O $2p$ - derived spectra have been determined from the atomic photoionization cross sections [35] with the O $2p$ intensity multiplied by a factor of $\sim 3$ [36]. Parameters to be fitted are the charge-transfer energy from the O $2p$ orbitals to the empty Fe $3d$ orbitals denoted by $\Delta$, the $3d - 3d$ on-site Coulomb interaction energy denoted by $U$, and the hybridization strength between the Fe $3d$ and O $2p$ orbitals denoted by Slater-Koster parameters $(pd\sigma)$ and $(pd\pi)$. The ratio $(pd\sigma)/(pd\pi) = -2.2$ has been assumed, as usual [8, 33]. The configuration dependence of the transfer integrals has been taken into account [37]. Racah parameters are fixed at the free ion values of Fe$^{3+}$ ($B = 0.126$ eV, $C = 0.595$ eV) [38]. We took into account the intra-atomic multiplet coupling for the valence-band spectrum, whereas it was not taken into account for the Fe $2p$ spectrum as in the case of [8].

The calculated Fe $2p$ core-level photoemission spectrum has been broadened with an energy-dependent Lorentzian with FWHM
\[ 2\Gamma = 2\Gamma_0(1 + \alpha\Delta E), \tag{4.5} \]
where $\Delta E$ denotes the energy separation from the main peak. We adopted the
values \( \alpha = 0.15 \) and \( \Gamma_0 = 1.2 \text{ eV} \). We then used a Gaussian broadening of 1.0 eV to simulate the instrumental resolution and broadening due to the core hole-3d multiplet coupling. The calculated valence-band spectrum has been broadened with a Gaussian of 1.6 eV FWHM and an energy-dependent Lorentzian (FWHM = 0.2|\( E - E_F \)| eV) [39] to account for the combined effects of the instrumental resolution and the d band dispersion, and the lifetime broadening of the photohole, respectively.

The best-fit results have been obtained setting \( \Delta = 2.0 \text{ eV}, U = 6.0 \text{ eV}, \) and \( \langle pd\sigma \rangle = -1.9 \text{ eV} \) as shown in Fig. 4.3. The \( e_g - t_{2g} \) crystal-field parameter of \( 10Dq = 0.41 \text{ eV} \) was assumed to reproduce the splitting in the O 1s XAS spectrum. These parameters are consistent with previously reported ones, which showed that LaFeO\(_3\) is a charge-transfer-type insulator, where \( \Delta < U \) [8]. However, the value of \( U \) had to be taken smaller than the previously reported value (\( U = 7.5 \text{ eV} \)) [8] in order to reproduce both the Fe 2p core level and valence-band spectra simultaneously. As we have succeeded in reproducing both the core level and the valence band using the same parameter set, the present results are more accurate than previous ones [8], although the PES spectrum calculated with this \( U \) value is still slightly too deep and the band gap is overestimated as shown in Fig. 4.3 (b). For the Fe 2p spectrum, we conclude that the main peaks mostly come from \( cd^6L \) and \( cd^7L_2 \) final states, while there is significant contribution of the \( cd^5 \) final states to the satellite. For the valence band, we conclude that the three main structures are derived from \( d^5L \) and \( d^6L_2 \) final states with admixture of the O 2p band, while the satellite has strong contribution from the \( d^4 \) final state. Due to the small value of \( \Delta \), final states with two holes at the ligand site are important for the interpretation of the PES spectra. As for the O 1s XAS spectrum, the final states have mostly \( d^6 \) character, and therefore one can interpret the data without significant contributions from charge-transfer (\( d^5L, d^6L_2, \cdots \)) final states.

We have also compared the spectra with the LDA +U band-structure calculation in Fig. 4.4. The full-potential linearized augmented-plane-wave (FLAPW) method was employed with an exchange-correlation potential of Vosko, Wilk and Nusair [40]. The effective Coulomb interaction parameter, \( U_{\text{eff}} \equiv U - J \), in the LDA +U scheme was set to 2 eV for all the Fe 3d orbitals [41]. A G-type antiferromagnetic state was assumed. The calculated DOS has been broadened with a Gaussian of 0.15 eV FWHM and an energy-dependent Lorentzian (FWHM = 0.2|\( E - E_F \)| eV) [39] to account for the instrumental resolution and the lifetime broadening of the photohole, respectively. Below \( E_F \), we have added the partial DOS of O p and Fe d, considering their cross sections at \( h\nu = 600 \)
Figure 4.3: Photoemission and XAS spectra of LaFeO$_3$ and their CI cluster-model analyses. In the bottom panels, final states are decomposed into contributions from different configurations. The dotted lines indicate the background due to secondary electrons. (a) Fe $2p$ core-level photoemission spectrum. (b) Valence-band photoemission and O $1s$ XAS spectra.
eV [35], with the multiplication factor of $\sim 3$ for the O $p$ partial DOS [36]. Above $E_F$, we have considered only the partial DOS of O $p$ because the O 1s XAS spectrum is due to the dipole-allowed transition from the O 1s core level. The three main structures, A, B, and C, were successfully reproduced (including a weak shoulder between B and C), consistent with a previous report [42]. However, the calculated band gap of 1.3 eV is too small compared with the optical gap of 2.1 eV [7], and the satellite structure could not be reproduced.

From this comparison, we conclude that the valence-band spectra of LFO can be explained well both by the CI cluster-model calculation and, except for the satellite structure, by the LDA +$U$ band-structure calculation. It is a reasonable result that both calculations can reproduce the Fe 3$d$ band region of LaFeO$_3$ equally well because there is one-to-one correspondence between the two calculations for the peak positions and the orbital character for the $e_g$ band (structure-A), $t_{2g}$ band (structure-B), and non-bonding state (structure-C).

### 4.2.3 La$_{1-x}$Sr$_x$FeO$_3$

Next, we go to the question of how the electronic structure of LFO changes upon hole doping. Figure 4.5 shows the core-level photoemission spectra of La$_{1-x}$Sr$_x$FeO$_3$. The “contamination” signal on the higher binding energy side
of the O 1s peak was weak enough, except for the $x = 0.67$ sample, indicating that the surface was reasonably clean. The line shape of the Fe 2p core level has almost no composition dependence, consistent with the picture that doped holes go into states of primarily O 2p character, and not of Fe 3d character [12].

All the core-level spectra, except for the Fe 2p core level, are shifted toward lower binding energies with $x$, as plotted in Fig. 4.6 (a). Here, the midpoint of the lower binding energy slope is taken as representing the shift of the peaks because this part is generally least affected by possible contamination [43,44].

The shift $\Delta E_B$ of a core-level binding energy measured from $\mu$ is given by

$$\Delta E_B = \Delta \mu + K \Delta Q + \Delta V_M + \Delta E_R,$$  \hspace{1cm} (4.6)
where $\Delta \mu$ is the change in the chemical potential, $\Delta Q$ is the change in the number of valence electrons on the atom considered, $\Delta V_M$ is the change in the Madelung potential, and $\Delta E_R$ is the change in the core-hole screening [19]. As seen in Fig. 4.6 (a) the Fe 2$p$ core level moves in a different way from the other core levels probably because the formal valence of Fe changes with hole doping, reflecting both the chemical potential shift and the “chemical shift”, which is due to the increase in the Fe valence with hole doping ($\propto -\Delta Q$), as in other transition-metal oxides [43–45]. The similar shifts of the O 1$s$, Sr 3$d$, and La 4$d$ core levels indicate that the change in the Madelung potential ($\Delta V_M$) is negligibly small because it would shift the core levels of anions and cations in different directions. Core-hole screening by conduction electrons is also considered to be negligibly small in transition-metal oxides [43–45]. Therefore, we take the average of the shifts of these three core levels as a measure of $\Delta \mu$ in LSFO. Figure 4.6 (b) shows $\Delta \mu$ thus determined plotted as a function of $x$. The shifts become slightly weaker above $x = 0.4$. We can consider two reasons for this weakening. The one reason is the increased DOS at $E_F$ with increasing $x$. This explanation is within the rigid band picture that $-\partial \mu / \partial x$ is inversely proportional to the DOS at $E_F$ [45]. The other reason is a pseudogap (depression of DOS at $E_F$, see also Fig. 4.7 (a)) and a charge disproportionation around $x = 0.67$, which is beyond the the rigid band picture. La$_{2-x}$Sr$_x$CuO$_4$ is a typical example in that the suppression of the chemical potential shift has been observed in the underdoped region, where there is a pseudogap at $E_F$ [43]. This phenomenon has been attributed to the formation of charge stripes, a kind of “microscopic phase separation” in which the distance between hole stripes decreases with hole concentration $x$. Further studies up to $x = 1$ are necessary to see whether the weakening of the shifts at large $x$’s is related to the charge disproportionation or not.

Figure 4.7 (a) shows the doping dependence of the combined valence-band photoemission and the O 1$s$ XAS spectra. Here, the Fermi levels of the XAS spectra for various $x$ have been determined by combining the Fermi level position in the LFO spectrum with the $x$-dependent shift of the O 1$s$ core-level peak for the sake of convenience. In the PES spectra, one can observe the three main structures A, B, and C and the satellite, as in the case of LFO. A gap (absence

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\[\text{It has been recognized for many years that XAS spectra, in particular O 1s XAS in transition-metal oxides, do not precisely represent unoccupied DOS and also that it is difficult to determine the exact } E_F \text{ position. For example, the BIS spectra (K. Morikawa et al., Phys. Rev. B 52, 13711 (1995)) and the O 1s XAS spectra (H. I. Inoue et al., Physica C 235-240 1007 (1994)) of CaVO}_3 \text{ and SrVO}_3 \text{ are different. The O 1s XAS spectra show a build-up of spectral weight at the leading edge, which is not present in the real DOS measured by BIS. Therefore, the tail of the XAS spectra of the doped samples does not necessarily mean that the DOS is finite at } E_F.\]
of finite DOS at $E_F$) or a pseudogap (depression of DOS at $E_F$) was seen for all values of $x$, as was observed for La$_{1-x}$Sr$_x$MnO$_3$ [32]. The sample of $x = 0.67$ undergoes a metal-insulator transition at 190 K, but there is little DOS at $E_F$ at room temperature. This may be related to the fact that the electrical resistivity satisfies $d\rho/dT < 0$ even above the transition temperature as shown in Fig. 4.2. The intensity of the satellite has almost no composition dependence. Figure 4.7 (b) shows the binding energy shifts of structures A, B, and C plotted against $x$. Structures A-C move toward $E_F$ upon hole doping up to $x = 0.4$. These shifts are in good agreement with the core level shifts, indicating the rigid-band shift occurs in the valence band. In addition, structure A, which is assigned to the “$e_g$ band”, becomes weaker with increasing $x$, indicating that holes are doped into the “$e_g$ band”, and is finally obscured at $x = 0.67$. The weakening of structure A with $x$ is more clearly seen in Fig. 4.7 (c), where the energy positions of structures B and C have been aligned. In the XAS spectra, a new peak F grows within the band gap of LFO upon hole doping, as seen in the previous study [12]. The combined PES and XAS spectra thus demonstrate that spectral weight is transferred from structure A below $E_F$ to structure F above $E_F$, and the band gap is filled by the new spectral weight F as holes are doped. Spectral weight of structures A and F is plotted as a function of Sr concentration $x$ in Fig. 4.7 (d). The weight of structure F is almost proportional to $x$, indicating that doped holes go into this structure. Also, $E_F$ is located within the gap or the pseudogap for all $x$’s, that is, the intensity at $E_F$ remains always small (more clearly in the PES spectrum), which may correspond to the wide insulating region in the LSFO phase diagram. This non-rigid-band behavior within $\sim 2$ eV of $E_F$ is apparently
in conflict with the monotonous chemical potential shift. We therefore conclude that in this system the effect of hole-doping can be described in the framework of the rigid-band model as far as the shifts of the spectral features are concerned, whereas the “$e_g$ band” shows highly non-rigid-band-like behavior with transfer of spectral weight from below $E_F$ to above it across the gap or pseudogap at $E_F$.

### 4.3 Conclusion

We have studied the composition-dependent electronic structures of LSFO using epitaxial thin films by *in-situ* PES and XAS measurements. By using soft x-rays of high energy resolution and high-quality sample surfaces, we succeeded in obtaining high-quality spectra with detailed spectral features of high bulk sensitivity. The Fe 2$p$ and valence-band PES spectra and the O 1$s$ XAS spectra of LaFeO$_3$ have been successfully reproduced by configuration-interaction cluster-model calculation and, except for the satellite structure, by band-structure calculation. From the shift of the binding energies of core levels, the chemical potential was found to be shifted downward as $x$ was increased. Among the three peaks in the valence-band spectra of La$_{1-x}$Sr$_x$FeO$_3$, the peak nearest to the Fermi level ($E_F$), due to the “$e_g$ band”, was found to move toward $E_F$ and became weaker as $x$ was increased, whereas the intensity of the peak just above $E_F$ in the O 1$s$ XAS spectra increased with $x$. The gap or pseudogap at $E_F$ was seen for all values of $x$, which is considered to be a natural consequence of the wide insulating phase of this material. These results indicate that the rigid-band model is applicable to the overall shifts of the electronic states (at least up to $x \sim 0.4$) but that changes in the spectral line shape around $E_F$ are dominated by spectral weight transfer from below to above $E_F$ across the gap and are therefore highly non-rigid-band-like.
Figure 4.7: PES and XAS spectra of La_{1-x}Sr_xFeO_3. (a) Combined PES and XAS spectra. (b) Shifts of structures in the valence band. (c) Valence-band photoemission spectra shifted so that structures A, B, and C are aligned. (d) Spectral weight of structures A and F as functions of x.
Chapter 5

Temperature-dependent studies of the charge disproportionation

5.1 Introduction

Carrier doping into a Mott insulator causes various intriguing properties. Recently, charge ordering (CO) and its associated metal-insulator transition (MIT) has attracted great interest in relation to charge stripes in high-$T_c$ cuprates [46] and giant magnetoresistance in manganites. La$_{1-x}$Sr$_x$FeO$_3$ (LSFO) with $x \simeq 0.7$ exhibits charge disproportionation (CD), a unique type of CO, below 190 K [6], accompanied by both an MIT and antiferromagnetic ordering. A neutron diffraction study by Battle et al. [13] 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 an apparent absence of structural distortion, whereas electron diffraction study by Li et al. [14] revealed a local structural distortion along the ⟨111⟩ direction. Optical spectra showed a splitting of the optical phonon modes due to the folding of the phonon dispersion branch, caused by lattice distortion at the CO transition [47]. The charge disproportionation was found to be described as $3d^5L^{0.67} \rightarrow 2d^5 + d^3L^2$, where $L$ denotes a hole in the O 2p band, rather than $3d^{4.33} \rightarrow 2d^5 + d^3$ because of the negative effective charge transfer energy [8].

Matsumo et al. studied detailed temperature dependent changes near the Fermi level ($E_F$) of LSFO ($x = 0.67$) [11], as shown in Fig. 5.1. The intensity at $E_F$ was found to change dramatically across the transition temperature. They also reported smaller but finite change at $x = 0.55$ and 0.80 (Fig. 5.1) and suggested an incomplete charge disproportionation even around $x = 0.67$. However, in their measurements, the O 2p contribution overwhelmed the Fe 3d contribu-
5.2 Results and discussion

5.2.1 La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.67$)

Figure 5.2 shows the temperature dependence of the valence-band photoemission spectra of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.67$) taken at $h\nu = 708$ eV (Fe $2p \to 3d$ resonance), 600 eV and 40 eV. From the atomic orbital photoionization cross-sections [35], the spectrum taken at 708 eV is considered to show the Fe $3d$ partial DOS (PDOS), whereas that of 40 eV is dominated by the O $2p$ PDOS and that of
600 eV is a mixture of the Fe 3d and O 2p PDOS. The spectra change gradually with temperature. The spectra for 708 eV and 600 eV clearly indicate transfer of the spectral weight from lower to higher binding energies within 2 eV below $E_F$ (within the $e_g$ band). The energy range at which spectral weight transfer occurs is about 2 eV, which is large compared with 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$_{1-x}$Ca$_x$MnO$_3$ [48], Nd$_{1-x}$Sr$_x$MnO$_3$ [49], Pr$_{1-x}$Sr$_x$MnO$_3$ [50] and Nd$_{1-x}$Sm$_x$NiO$_3$ [51, 52]. The area of the 600 eV spectrum from -3.0 eV to $E_F$ remains almost constant, whereas that of the 708 eV spectrum increases with decreasing temperature. The 40 eV spectrum does not appear to change in this wide energy region, but near $E_F$ spectral weight transfer is observed. From these results, the state near $E_F$ is considered to be O 2p dominant and the state around $-(1 - 2)$ eV below $E_F$ is considered to be Fe 3d dominant. Spectral weight is transferred from the former state to the latter state.

In order to describe this spectral weight transfer more precisely, we have plotted the spectral weight of the 708 eV spectrum (Fe 3d PDOS) integrated from $-2.0$ eV to $+0.4$ eV as a function of temperature in Fig. 5.3 (a). We have also plotted that of 40 eV (O 2p PDOS) integrated from $-0.3$ eV to $+0.1$ eV in Fig. 5.3 (b). A drastic change of spectral weight is observed across the transition temperature in both graphs. As for Fe 3d PDOS, spectral weight increases with decreasing temperature, whereas as for O 2p PDOS, spectral weight decreases with decreasing temperature. This behavior can be interpreted as follows. The degree of hybridization between Fe 3d and O 2p changes across the transition temperature. With decreasing temperature, Fe 3d character becomes stronger, and O 2p character becomes weaker near $E_F$.

Next, we measured the temperature dependence of XAS spectra. Figure 5.4 (a) shows the temperature dependence of the O 1s XAS spectra, and Fig. 5.4 (b) shows that of the Fe 2p XAS spectra. The Fe 2p spectra do not change appreciably with temperature, whereas there is a significant change in the O 1s spectra. The peaks in the Fe 3d region become sharp, and the first peak becomes intense upon cooling. This spectral change is opposite to the change of the photoemission spectra in the sense that with decreasing temperature the intensities near $E_F$ of the O 1s XAS spectra increases, whereas those of the photoemission spectra decreases.

In order to interpret these spectral changes, we considered that spectral weight transfer with decreasing temperature occurs as schematically shown in Fig. 5.5. Below $E_F$, spectral weight is transferred from the near-$E_F$ states of O 2p character
Figure 5.2: Temperature dependence of the valence-band photoemission spectra of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.67$). (a) 708 eV (Fe $2p \rightarrow 3d$ resonance) (b) 600 eV (c) 40 eV (d) 40 eV (near $E_F$)

Figure 5.3: (a) Spectral weight integrated from $-2.0$ eV to $+0.4$ eV for 708 eV (Fe $3d$ PDOS) as a function of temperature. (b) Spectral weight integrated from $-0.3$ eV to $+0.1$ eV for 40 eV (O $2p$ PDOS) as a function of temperature.
to the states of Fe 3d character well below $E_F$. This is spectral weight transfer within the $e_g$ band observed in the photoemission spectra. Above $E_F$, the spectral weight of O 2p character increases with decreasing temperature. This explains the change of the O 1s XAS spectra. Correspondingly, the spectral weight of Fe 3d character above $E_F$ should decrease, although we do not have direct experimental proof at present. 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 spectral weight transfer is a common phenomenon.
5.2.2 \textit{La}_{1-x}\textit{Sr}_x\textit{FeO}_3 \; (x = 0.4, 0.2)

We also measured $x = 0.4$ and 0.2 thin films. At $x = 0.4$ and 0.2, this system is insulating at all temperatures and does not exhibit any phase transition. Therefore, we considered these to be appropriate references for $x = 0.67$. We are also interested in seeing whether there are changes of the spectra even at $x = 0.4$ and 0.2 as a test to the scenario of incomplete charge disproportionation.

In Fig. 5.6, we show the temperature dependence of the valence-band photoemission spectra of \textit{La}_1-x\textit{Sr}_x\textit{FeO}_3 \; (x = 0.4) taken at $h\nu = 708$ eV ($2p \rightarrow 3d$ resonance) and 600 eV. The spectra change gradually with temperature as in the case of $x = 0.67$. The change in the spectra of $x = 0.4$ is similar to that of $x = 0.67$, that is, spectral weight transfers from lower to higher binding energies within 2 eV below $E_F$ ($e_g$ band). We also measured the temperature dependence of the XAS spectra. Figure 5.7 (a) shows the temperature dependence of the O 1s XAS spectra, and Fig. 5.7 (b) shows that of the Fe 2p XAS spectra. The Fe 2p spectra do not change appreciably with temperature as in the case of $x = 0.67$. There is a significant change in the O 1s XAS spectra as also in the case of $x = 0.67$. The change is as drastic as that of $x = 0.67$. Spectral weight is transferred to the first peak upon cooling.

As for $x = 0.2$, we show the temperature dependence of the valence-band photoemission spectra in Fig. 5.8, and that of the XAS spectra in Fig. 5.9. In Fig. 5.8, the spectra change gradually with temperature as in the case of $x = 0.67$ and 0.4, and spectral weight transfers within the $e_g$ band, which is a similar behavior to $x = 0.67$ and 0.4. As for the XAS spectra, the Fe 2p spectra do not
change appreciably with temperature as in the case of $x = 0.67$ and 0.4, whereas the O 1s spectra change a little, but not so drastically as those of $x = 0.67$ and 0.4.

Although the samples of $x = 0.4$ and 0.2 do not exhibit any phase transition, similar temperature dependence to $x = 0.67$ was observed both in the valence-band photoemission spectra and the O 1s XAS spectra. This result suggests an incomplete or local charge disproportionation even for $x = 0.4$ and 0.2. At $x = 0.67$, the charge disproportionation $\text{Fe}^{3+} : \text{Fe}^{5+} = 2 : 1$ is realized, and in a certain composition range around $x = 0.67$, the incomplete or local charge disproportionation may occur. This is consistent with the previous report on the photoemission study of $x = 0.55$ and 0.80 [11]. This also explains the result that
Figure 5.9: Temperature dependence of XAS spectra of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.2$). (a) O 1s (b) Fe 2p

the spectra of $x = 0.4$ change more drastically than those of $x = 0.2$ because this incomplete or local charge disproportionation is considered to occur more easily when $x$ is nearer to 0.67. As stated in Chapter 1, one striking feature of LSFO is that the insulating phase is unusually wide in the phase diagram (especially at low temperatures $0 < x < 0.9$, and even at room temperature $0 < x < 0.5$) [11]. In Chapter 4, we concluded that the fact that there is a gap or pseudogap at $E_F$ for all values of $x$ in the photoemission-XAS spectra is considered to be a natural consequence of the wide insulating phase of this material. From the results of this chapter, we conclude that the wide insulating region and the existence of a gap or pseudogap are due to incomplete or local charge disproportionation around $x = 0.67$.

5.3 Conclusion

We measured the temperature dependence of the photoemission and XAS spectra of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.67$) to study the spectral change across the transition temperature of charge disproportionation. We observed gradual changes of the spectra with decreasing temperature. Below $E_F$, spectral weight transfer was observed over an energy range of about 2 eV ($e_g$ band), which is large compared with the transition temperature. In order to interpret the changes of the spectra, we propose a schematic model of spectral weight transfer. Below $E_F$, spectral weight is transferred from the near-$E_F$ states of O 2p character to the states of Fe 3d character, and above $E_F$, the spectral weight of O 2p character increases with decreasing temperature. These observations suggest changes in the $p$-$d$ hybridization associated with charge disproportionation. We also measured the
temperature dependence of the photoemission and XAS spectra of \( \text{La}_{1-x}\text{Sr}_x\text{FeO}_3 \) \( (x = 0.4 \text{ and } 0.2) \) as references. Similar temperature dependence to \( x = 0.67 \) was observed, suggesting an incomplete or local charge disproportionation. This incomplete or local charge disproportionation is considered to be the origin of the wide insulating region of LSFO.
Chapter 6

Angle-resolved photoemission study

6.1 Introduction

Angle-resolved photoemission spectroscopy (ARPES) is a unique and powerful experimental technique by which one can determine the band structure of a material directly. ARPES has long played a central role in studying the electronic properties of strongly correlated electron materials with a layered perovskite structure. Especially for high-\(T_c\) cuprate superconductors, ARPES has revealed important features, such as the Fermi surface topology and the strong \(k\)-space anisotropy of the superconducting gap [53].

In contrast, there have been few studies on transition metal oxides with a three-dimensional perovskite structure such as \(\text{La}_{1-x}\text{Sr}_x\text{FeO}_3\) (LSFO) because they do not have any cleavage plane. In this work, we performed \textit{in-situ} ARPES measurements of single-crystal thin films of LSFO. \textit{Ex-situ} ARPES measurements were reported on thin films of \(\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3\) [54, 55] and \(\text{La}_{0.65}\text{Ba}_{0.33}\text{MnO}_3\) [56] with complicated surface cleaning procedures, but nearly flat bands were observed. By performing \textit{in-situ} studies, no cleaning procedures were necessary and we succeeded in determining the band structure of LSFO (\(x = 0.4\)).

6.2 Results and discussion

Before taking the ARPES spectra, we checked the surface cleanliness of our samples by measuring LEED patterns. A LEED pattern of the \(\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3\) thin film measured at an electron energy of 87 eV is shown in Fig. 6.1. \(1 \times 1\) spots are clearly observed, indicating that the surface of the fabricated LSFO thin film
Figure 6.1: LEED pattern of a La$_{0.6}$Sr$_{0.4}$FeO$_3$ thin film.

is clean enough.

Figure 6.2 (a) shows ARPES spectra of a La$_{0.6}$Sr$_{0.4}$FeO$_3$ thin film measured by changing the photon energy from 26 to 110 eV at normal emission. One can see from the figure that the ARPES spectra show considerable change with photon energy and exhibit some dispersive features. This spectral change represents the band structure of LSFO along the $\Gamma - X$ direction in the Brillouin zone of a cubic perovskite structure shown in Fig. 6.2 (b).

We have mapped out the band structure by converting the photon energy into the wave vector. At normal emission the wave number parallel to the crystal surface, $k_\parallel$ is always zero, and the wave number perpendicular to the crystal surface, $k_\perp$, is given by

$$k_\perp = 0.5123 \sqrt{\hbar \nu - \phi - E_B + V_0} \ [\text{Å}^{-1}],$$

where $\phi$ is the work function taken to be 5 eV, and $V_0$ is the inner potential. Figure 6.2 (c) shows the experimental band structure in the $\Gamma - X$ direction of La$_{0.6}$Sr$_{0.4}$FeO$_3$ obtained from the ARPES measurements. In order to map out the band structure, we took the second derivative of the ARPES spectra after smoothing and plotted the intensity in gray scale in the space of wave vector and binding energy. The inner potential is estimated to be 11 eV from the periodicity of the band dispersion. Dark parts correspond to energy bands. As the measurement was performed by changing the photon energy, the effect of varying cross-sections was substantial, and the interpretation is not straightforward. In
Figure 6.2: (a) ARPES spectra of a La$_{0.6}$Sr$_{0.4}$FeO$_3$ thin film. (b) Brillouin zone of a cubic perovskite structure. (c) Experimental band structure in the $\Gamma - X$ direction of La$_{0.6}$Sr$_{0.4}$FeO$_3$ obtained from the ARPES measurements of the thin film. Dark parts correspond to energy bands.
Figure 6.3: Trace in $k$-space by fixing photon energy.

particular, there is an Fe $3p \rightarrow 3d$ resonance near $h\nu = 60$ eV, which is responsible for the strong intensity modulation near X in Fig. 6.2 (c). Nevertheless, several highly-dispersive bands are observed in the binding energy region of $2-6$ eV.

As the change of the spectra at normal emission is difficult to interpret due to the effect of varying cross-sections, we fixed the photon energy and changed the emission angle from $-12^\circ$ to $32^\circ$. Figure 6.3 shows the trace in $k$-space obtained by fixing photon energy at certain values. The direction of $X - M$ corresponds to $h\nu = 58$ eV, whereas that of $\Gamma - X$ corresponds to $h\nu = 38$ eV and $88$ eV.

First, we fixed the photon energy at $58$ eV, and changed the emission angle to determine the band structure along the $X - M$ direction. This photon energy is in the range of the Fe $3p \rightarrow 3d$ resonance, and therefore we could obtain the dispersion of the Fe $3d$ bands. Figure 6.4 shows the ARPES spectra and experimental band structure. For converting the emission angle into wave vector, we used the following equation about the wave number parallel to the crystal surface, $k_\parallel$.

$$k_\parallel = 0.5123 \sqrt{h\nu - \phi - E_B \sin \theta} \ [\text{Å}^{-1}]$$

We assigned $e_g$ and $t_{2g}$ bands. One remarkable feature of this band structure is that the $e_g$ band which is located in the binding energy region of about $1.3$ eV shows significant dispersion while the $t_{2g}$ band does not.

Then we fixed the photon energy to $38$ eV, and changed the emission angle to determine the band structure along the $\Gamma - X$ direction, which is the same direction as the normal emission shown in Fig. 6.2. Figure 6.5 shows the ARPES
Figure 6.4: (a) ARPES spectra of a La$_{0.6}$Sr$_{0.4}$FeO$_3$ thin film at 58 eV. (b) Experimental band structure in the X – M direction of La$_{0.6}$Sr$_{0.4}$FeO$_3$ obtained from the ARPES measurements at 58 eV. Dark parts correspond to energy bands.
spectra and experimental band structure.

We also fixed the photon energy to 88 eV, and changed the emission angle to determine the band structure along the Γ – X direction. Figure 6.6 shows the ARPES spectra and experimental band structure. This is the same direction as in the case of 38 eV, but the Fe 3d contribution is observed more clearly considering the cross-section.

6.3 Conclusion

We have performed in-situ ARPES measurements on single-crystal thin films of La$_{1-x}$Sr$_x$FeO$_3$. As this material has the three-dimensional perovskite structure with no cleavage plane, this is the only photoemission method that can determine its band-structure experimentally. We observed several highly-dispersive bands in the binding energy region of 2 – 6 eV. Especially, at $h\nu = 58$ eV, we observed the dispersion of the $e_g$ band by making use of Fe 3p $\rightarrow$ 3d resonance.
Figure 6.5: (a) ARPES spectra of a La$_{0.6}$Sr$_{0.4}$FeO$_3$ thin film at 38 eV. (b) Experimental band structure in the $\Gamma$–X direction of La$_{0.6}$Sr$_{0.4}$FeO$_3$ obtained from the ARPES measurements at 38 eV. Dark parts correspond to energy bands.
Figure 6.6: (a) ARPES spectra of a La$_{0.6}$Sr$_{0.4}$FeO$_3$ thin film at 88 eV. (b) Experimental band structure in the Γ−X direction of La$_{0.6}$Sr$_{0.4}$FeO$_3$ obtained from the ARPES measurements at 88 eV. Dark parts correspond to the energy bands.
Chapter 7

Conclusion

In this thesis, we have studied the electronic structure of epitaxially grown thin films of perovskite-type transition-metal oxide \( \text{La}_{1-x}\text{Sr}_x\text{FeO}_3 \) (LSFO) by \textit{in-situ} photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS) measurements.

In Chapter 4, we investigated thin films of \( \text{La}_{1-x}\text{Sr}_x\text{FeO}_3 \) \((x = 0, 0.2, 0.4, 0.67)\) and discussed hole-doping dependence of the electronic structure. By using soft x-rays of high energy resolution and high-quality sample surfaces, we succeeded in obtaining high-quality spectra with detailed spectral features of high bulk sensitivity. The Fe 2\textit{p} and valence-band PES spectra and the O 1\textit{s} XAS spectra of \( \text{LaFeO}_3 \) are successfully reproduced by configuration-interaction cluster-model calculation and, except for the satellite structure, by band-structure calculation. From the shift of the binding energies of core levels, the chemical potential was found to be shifted downward as \( x \) was increased. Among the three peaks in the valence-band spectra of \( \text{La}_{1-x}\text{Sr}_x\text{FeO}_3 \), the peak nearest to the Fermi level \( (E_F) \), due to the “\( e_g \) band”, was found to move toward \( E_F \) and became weaker as \( x \) was increased, whereas the intensity of the peak just above \( E_F \) in the O 1\textit{s} XAS spectra increased with \( x \). The gap or pseudogap at \( E_F \) was seen for all values of \( x \). These results indicate the following: while the rigid-band model is applicable to the overall shifts of the electronic states (at least up to \( x \sim 0.4 \)), the changes in the spectral line shape around \( E_F \) are dominated by spectral weight transfer from below to above \( E_F \) across the gap and are therefore highly non-rigid-band-like. This is the picture of how the electronic structure evolves from \( \text{LaFeO}_3 \) (a charge-transfer-type insulator) to \( \text{SrFeO}_3 \) (an oxygen-hole metal), an answer to the first question in Chapter 1.

In Chapter 5, we studied the temperature-dependent metal-insulator transition. We measured the temperature dependence of the photoemission and XAS...
spectra of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.67$) to examine the spectral change across the metal-insulator transition. We observed gradual changes of the spectra with decreasing temperature. Below $E_F$, spectral weight transfer was observed over an energy range of about 2 eV ($e_g$ band), which is large compared with the transition temperature. In order to interpret the changes of the spectra, we proposed a schematic model of spectral weight transfer. Below $E_F$, spectral weight is transferred from the near-$E_F$ states of O $2p$ character to the states of Fe $3d$ character, and above $E_F$, the spectral weight of O $2p$ character increases with decreasing temperature. These observations suggest changes in the $p$-$d$ hybridization associated with charge disproportionation. The above results are an answer to the second question. It would be interesting to investigate other Fe oxides which undergoes charge ordering to see whether such a spectral weight transfer is a common phenomenon. We also measured the temperature dependence of the photoemission and XAS spectra of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.4$ and $x = 0.2$) as references. The similar temperature dependence to $x = 0.67$ was observed, suggesting an incomplete or local charge disproportionation. This incomplete or local charge disproportionation is considered to be the origin of the wide insulating region of LSFO (an answer to the third question).

In Chapter 6, we performed angle-resolved photoemission spectroscopy (ARPES) measurements on single-crystal thin films of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.4$) as an answer to the final question. As this material has the three-dimensional perovskite structure with no cleavage plane, this is the only photoemission method that can determine its band-structure experimentally. We observed several highly-dispersive bands in the binding energy region of $2 - 6$ eV. Especially, at $h\nu = 58$ eV, we observed the dispersion of the $e_g$ band by making use of Fe $3p \rightarrow 3d$ resonance.

In summary, we have obtained the following results. As for the hole-doping, the rigid-band model can describe the overall shifts of the electronic states. However, around $E_F$ there is a transfer of spectral weight from below to above $E_F$ across the gap, which is a highly non-rigid-band-like behavior. The fact that there exists a gap or pseudogap at $E_F$ for all values of $x$ in the photoemission-XAS spectra is considered to be a natural consequence of the wide insulating phase of this material. From the temperature dependence of the spectra, we conclude that the wide insulating region and the existence of a gap or pseudogap are due to incomplete or local charge disproportionation around $x = 0.67$. It should be interesting to investigate further this new viewpoint. Finally, from the ARPES measurements, we observed the band structure of this material for the first time.
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