Photoemission study of electron-doped high-$T_c$ superconductors

Master Thesis

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Chapter 1

Introduction

1.1 Introduction

Since the discovery of the high-$T_c$ superconductors (HTSCs) by Bednorz and Müller [1], a great number of experiments and theoretical studies have been performed to understand the mechanism of the HTSCs beyond the conventional BCS theory. The cuprate systems show not only high-$T_c$ superconductivity but also show various unusual behaviors certainly associated with their proximity to the Mott metal-insulator transition through filling control [2–4]. Intriguing behaviors in highly correlated electron systems have been extensively investigated in recent years [5]. However, due to the difficulties inherent in the many-body character of electron correlations, understanding the nature of the correlated electron systems has been the most challenging issue in condensed matter physics until now.

HTSCs are constituted by the layer structure in which the two-dimensional CuO$_2$ plane and the block layer lies, alternatively. The CuO$_2$ plane is the stage of superconductivity and related low-energy physics while the block layer supplies the CuO$_2$ plane with charge carriers. The roles of the CuO$_2$ plane and the block layer are common to all HTSCs. When the Cu $d_{x^2−y^2}$ orbitals of the CuO$_2$ plane are half-filled, the system is an antiferromagnetic Mott insulator because of the strong on-site Coulomb repulsion between electrons [2–4]. Removing (adding) electrons from (to) the insulating CuO$_2$ plane is regarded as hole (electron) doping into the Mott insulator. By the doping, the three-dimensional antiferromagnetic order is rapidly destroyed and the transition from the insulator to the superconductor takes place. With further doping, the superconducting critical temperature ($T_c$) reaches maximum, and then $T_c$ decreases and disappears. The doping level at the maximum $T_c$ is referred to as optimal doping, while lower and
higher doping level compared with optimal doping are referred to as underdoping and overdoping, respectively. In overdoped region, most of the HTSCs behave like a relatively conventional metal above $T_c$, while in underdoped region those behave as the anomalous metal which shows strong deviation from the standard Fermi-liquid behaviors.

The discovery of the electron-doped HTSCs clarified that not only holes but also electrons can become conductive carriers. This has had a great influence on theories on the mechanism of high-$T_c$ superconductivity based on the electron-hole symmetry [6–8]. The phase diagram is a remarkable example as shown in Fig. 1.1. In the hole-doped HTSCs, the antiferromagnetic order disappears for slight doping and the dome-shaped superconducting region appears. On the other hand, in the electron-doped ones, the antiferromagnetic order persists up to high doping level and the narrow superconducting region appears.

As discussed above, many studies of the electron-doped HTSCs have been performed in order to compare the behaviors of the electron-doped HTSCs and the hole-doped ones. However, electron-doped HTSCs possess interesting physics in their own rights, in addition to the comparison of them with the hole-doped ones.

The representative electron-doped HTSC is $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, which has the $T'$-type structure. Other electron-doped HTSCs are available by replacing $\text{Nd}^{3+}$ of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ by $\text{La}^{3+}$, $\text{Pr}^{3+}$, $\text{Sm}^{3+}$, or $\text{Eu}^{3+}$, that is, $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$) are the electron-doped HTSCs. They show systematic changes in $T_c$, lattice constant, chemical pressure, and so on, when a lanthanide ion is replaced with another lanthanide ion according to the atomic number of the lanthanide. Especially, the systematic variation of $T_c$ attracts much interest because we may elucidate the parameter which governs $T_c$ and the origin of superconductivity.

It is important to know the electronic structure of the CuO$_2$ plane in HTSCs in order to elucidate the mechanism of superconductivity. Photoemission spectroscopy (PES) is a powerful tool to directly investigate the electronic structure of solids. Recent development of PES techniques has enabled us to observe fine structures near the chemical potential. In PES, angle-resolved photoemission spectroscopy (ARPES) is the most powerful tool to probe the band dispersion directly.

This thesis is organized as follows. The present study of the electron-doped HTSCs is described in the next section. The principles of PES and the information which can be obtained from ARPES spectra are reviewed in Chapter 2. In Chapter 3, we discuss the pseudogap of the electron-doped HTSCs and the effect
of lanthanide substitution through angle-integrated photoemission spectroscopy. In Chapter 4, we discuss the ARPES measurements of Eu$_{2-x}$Ce$_x$CuO$_4$. In Chapter 5, the results of ARPES measurements of Sm$_{2-x}$Ce$_x$CuO$_4$ are presented.

1.2 Physical properties of electron-doped high-$T_c$ superconductors

So far, three kinds of electron-doped HTSCs have been discovered. The first is the HTSCs which have the $T'$-type structure. Representative materials are $Ln_{2-x}$Ce$_x$CuO$_4$ ($Ln =$La, Pr, Nd, Sm, and Eu) [9] and $Ln_{2-x}$Th$_x$CuO$_4$ ($Ln =$Pr, Nd) [10]. The crystal structure of the $T'$-type structure is shown in Fig. 1.2. The second is the infinite-layer superconductors [11]. The third is Li-intercalated superconductors [12], which are the first electron-doped HTSCs with apical anions. Hereafter, among three kinds of HTSCs, we pay attention to the HTSCs with $T'$-type structure, in which numerous theoretical studies and experiments have been performed.

1.2.1 Transport properties

The left panel in Fig. 1.3 shows the temperature dependence of the in-plane resistivity for Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO) with various doping levels [13]. The resistivity of undoped NCCO ($x = 0$) shows an insulating behavior, while that of NCCO
Figure 1.2: Schematic diagram of the $T'$-type structure. Red, blue, and green spheres represent copper, oxygen, and lanthanide, respectively.
with \( x = 0.15 \) represents an metallic behavior at high temperature. The right panel in Fig. 1.3 shows the temperature dependence of the resistivity for NCCO normalized by the value at 600 K [13]. Between 25 K and 200 K, the resistivity of NCCO \( (x = 0.15) \) is fitted by the relation

\[
\rho = \rho_0 + aT^2, \tag{1.1}
\]

although above 200 K the power becomes slightly lower than 2 \( (\sim 1.6) \). The resistivity for \( x = 0.10 \) and 0.125 shows an upturn at low temperatures (50 K-100 K), which may be due to weak localization effect [14, 15]. For NCCO with \( x = 0.10 \) and 0.125, the power in Eq.1.1 above 300 K is \( \sim 1.6 \), too. The resistivity for \( x = 0.05 \) and 0.075 tends to saturate toward higher temperatures. The resistivity for \( x = 0.025 \) above 430 K is no more metallic \((d\rho/dT \leq 0)\).

Importantly, the resistivity of NCCO with \( x = 0.025, 0.05, \) and 0.075 begins to decrease rapidly at temperatures marked with solid triangles although it shows an upturn at 100-150 K due to weak localization effect. The temperature marked with solid triangles also coincide with \( T^* \) below which the pseudogap begins to evolve in the optical spectra [16].

### 1.2.2 Neutron scattering

Neutron scattering studies have been performed on single crystals of NCCO and \( \text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4 \) (PCCO). Most of these single crystals are as-grown samples.

Undoped PCCO \( (x = 0) \) is an antiferromagnetic insulator and is described by the antiferromagnetic Heisenberg model. In the two-dimensional Heisenberg model, although antiferromagnetic correlation develops with decreasing temperature, antiferromagnetic long-range order does not exist at finite temperatures. However, actually weak interaction \( (J_\perp) \) between layers makes antiferromagnetic long-range order when antiferromagnetic correlation length \( (\xi) \) satisfies \( T < J_\perp \xi^2 \). Therefore, while antiferromagnetic correlation appears at high temperature as \( T \sim J_\perp \sim 1000 \text{ K}, \) Néel temperature \((T_N)\) is as low as about 250 K. Figure 1.4 shows the temperature dependence of the inverse antiferromagnetic correlation length [17]. Strong antiferromagnetic correlation is observed up to \( \sim 500 \text{ K} \). Figure 1.5 shows the temperature dependence of antiferromagnetic moment of as-grown PCCO with \( x = 0, 0.08, \) and 0.125 [17]. Antiferromagnetic moment increases below 250 K. Upon carrier doping, the antiferromagnetic ordering structure does not change while \( T_N \) and the magnetic moment of the antiferromagnetic order become small.
Figure 1.3: The left panel shows temperature dependence of the in-plane resistivity of NCCO with various $x$. The right panel shows the temperature dependence of the in-plane resistivity normalized to the value at 600 K [13].
Figure 1.4: Temperature dependence of the inverse correlation length [17]. The units are reciprocal lattice parameter (1 r.l.u. = $2\pi/a$).

Figure 1.5: Temperature dependence of three-dimensional ordered moment in PCCO ($x = 0$) [17]. The solid line represents the Cu$^{2+}$ moment, while the dashed lines represent fits to the $S = 1/2$ Brillouin functions.
1.2.3 Photoemission spectroscopy

PES has made great contributions to settle of various issues in high-$T_c$ superconductivity. Especially, the recent improvement of instrumental resolution has allowed us to detect fine electronic structures.

The superconducting gap symmetry of the hole-doped HTSCs is $d_{x^2-y^2}$ wave and is described with the gap function of the monotonic $d_{x^2-y^2}$ form $\Delta(k) \propto \cos(k_x a) - \cos(k_y a)$ [18, 19], where the maximum and zero-superconducting gaps are located in the $(\pi, 0)$ direction and the zone diagonal, respectively. Also it was believed that the superconducting gap of the electron-doped HTSCs is monotonic $d_{x^2-y^2}$ wave [20,21]. However, a recent study of the superconducting gap symmetry reports that in the electron-doped HTSCs the gap function deviates from the monotonic $d_{x^2-y^2}$ function [22]. Figure 1.6 shows the leading edge shift ($\Delta_{\text{shift}}$), which is about half of the superconducting gap, as a function of the Fermi-surface angle ($\phi$) for Pr$_{0.89}$LaCe$_{0.11}$CuO$_4$. For comparison, the monotonic $d_{x^2-y^2}$ gap function is also shown. The $\Delta_{\text{shift}}$ is about 2 meV at about $\phi = 0^\circ$, and gradually increases with increasing the Fermi-surface angle, reaching the maximum value of 2.5 meV at $\phi \sim 25^\circ$, which corresponds to the hot spot. After passing through the hot spot, $\Delta_{\text{shift}}$ rapidly decreases and becomes almost zero at the zone diagonal ($\phi = 0^\circ$). According to the fit of the nonmonotonic $d_{x^2-y^2}$ gap function to the $\Delta_{\text{shift}}$, the gap function is represented as

$$\Delta(\phi) = \Delta_0[1.43\cos(2\phi) - 0.43\cos(6\phi)],$$  \hspace{1cm} (1.2)

Therefore, the maximum gap is observed not at the zone boundary but at the hot spot.

Photoemission studies of the doping dependence for the electron-doped HTSCs were recently performed [23]. Figure 1.7 shows EDCs along the Fermi surface in NCCO. At low doping ($x = 0.04$), the spectra are gapped near $(\pi/2, \pi/2)$ over an energy scale of about 150 meV and exhibit a broad peak around 300 meV. Moving toward ($\pi, 0$), the 300 meV feature remains more or less at the same energy, and additional spectral weight develops near $E_F$. As the doping level is increased, the dispersive features become sharper and the peak at $(\pi/2, \pi/2)$ moves closer to $E_F$. At optimal doping ($x = 0.15$), the spectra are characterized by a sharp quasiparticle peak at $E_F$ both at $(\pi/2, \pi/2)$ and around $(\pi, 0)$. The momentum dependence of spectral weight near $E_F$ is shown in Fig. 1.8. At low doping ($x = 0.04$), the low energy weight is concentrated in a small pocket around $(\pi, 0)$, with a volume approximately consistent with the nominal doping level $x$. 

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Figure 1.6: Leading edge shift $\Delta_{\text{shift}}$ as a function of the Fermi surface angle ($\phi$) for Pr$_{0.89}$La$_{0.11}$CuO$_4$ [22]. The solid curve is the result of fitting the nonmonotonic $d_{x^2-y^2}$ gap function to $\Delta_{\text{shift}}$. The dotted curve is the monotonic $d_{x^2-y^2}$ gap function.
Figure 1.7: EDCs along the Fermi surface in NCCO [23]. Left, middle, and right panels correspond to $x = 0.04, 0.10,$ and $0.15$, respectively. Black vertical bars denote the peak positions. EDCs are arranged as denoted with arrows.

With increasing doping, one can observe both the modification of the electron pockets and the emergence of low-lying spectral weight around $(\pi/2, \pi/2)$. At optimal doping ($x = 0.15$), the intensity near $E_F$ evolves into the large hole-like Fermi surface centered at $(\pi, \pi)$ with a volume given by $\sim 1 + x$. 
Figure 1.8: Plot of the ARPES intensity around $E_F$ in NCCO taken from Ref. [23]. Left, middle, and right panels correspond to $x = 0.04, 0.10, \text{and } 0.15$, respectively. EDCs are integrated within a 60 meV window (-40 meV, 20 meV) around $E_F$. Data were taken in the upper octant and symmetrized with respect to the zone diagonal.
Chapter 2

Photoemission spectroscopy

The technique of photoemission spectroscopy has been widely used as one of the most suitable methods by which the electronic structure of solids can be revealed. In this Chapter, we will summarize the principles of photoemission spectroscopy, angle-resolved photoemission spectroscopy (ARPES), and information from ARPES spectra.

2.1 Photoemission spectroscopy

Photoemission spectroscopy (PES) is a powerful experimental method to directly investigate the electronic structure of solids. Figure 2.1 illustrates a schematic diagram of the principle of PES. When a photon of sufficiently high energy impinges on a solid, an electron in a solid is emitted as a photoelectron, according to photoelectric effect. By analyzing the kinetic energy of the photoelectron in the vacuum \( E_{\text{kin}} \), one can obtain PES spectra as shown in Fig. 2.1. In the one-electron approximation, the effect of electron correlation can be neglected and PES spectra represent the density of states (DOS) of energy bands in a solid [24]. \( E_{\text{kin}} \) also provides information about the strength to bind an electron to a solid. According to the energy conservation law,

\[
E_{\text{kin}} = h\nu - \Phi - E_B,
\]

(2.1)

where \( h\nu \) is the energy of the incident photon, \( E_B \) is the binding energy relative to the Fermi level \( E_F \) (chemical potential \( \mu \)) and \( \Phi \) is the work function of the solid under study. The work function \( \Phi \) is the energy required for an electron to escape from a solid through the surface and to reach the vacuum level \( E_{\text{vac}} \), that is,

\[
\Phi = E_{\text{vac}} - E_F.
\]

(2.2)
Because one cannot obtain $E_{\text{kin}}^\nu$ without measuring $\Phi$ but one can measure the kinetic energy of the photoelectron relative to $E_F$ ($E_{\text{kin}}$) directly, it is convenient to use $E_{\text{kin}}$. Then we obtain

$$E_{\text{kin}} = h\nu - E_B.$$  \hspace{1cm} (2.3)

In the one-electron approximation, $E_B$ is equal to the energy of an electron inside the solid before it is emitted. Therefore, the energy distribution of the electrons in the solids can be directly mapped from the distribution of the kinetic energy of the photoelectrons emitted by monochromatic incident photons. Figure 2.1 diagrammatically shows how the electronic DOS is mapped from the energy distribution curve (EDC). In this thesis, when photoemission spectra is displayed by the energy relative to $E_F$, $E \equiv -E_B$ is taken for the horizontal axis.

In real systems, photoemission spectra are influenced by the entire electron system in the solid, in addition to the one-electron energy (frozen-orbital approximation). In the photoemission process, holes are produced by removing electrons from the solid and the surrounding electrons tend to screen the holes to lower total energy of the system. Therefore, considering the entire electron system, the binding energy $E_B$ is given by the energy difference between the $N$-electron initial state $E_i^N$ and the $(N-1)$-electron final state $E_f^{N-1}$ as

$$E_B = E_f^{N-1} - E_i^N.$$  \hspace{1cm} (2.4)

In other words, $E_B$ is the energy of the hole produced by the photoemission process, including the relaxation energy of the total electron system. Hence, much information about the electron correlations is derived from the photoemission spectra.

### 2.2 Angle-resolved photoemission spectroscopy

Angle-resolved photoemission spectroscopy (ARPES) is the only experimental way to determine the band structure of the solid. In ARPES, one can probe not only the energy distribution but also the momentum distribution of electrons in the solid. In the photoexcitation by photons with low energy, the wave vector of an electron should be conserved before and after the photoexcitation except for the reciprocal lattice vector because the wave vector of the ultraviolet light, namely, $2\pi\nu/c$ is negligibly small compared with the size of the Brillouin zone.
Figure 2.1: Schematic diagram of the principle of photoemission spectroscopy. $h\nu$ is the energy of the incident photon and $\Phi$ is the work function. $E_{\text{kin}}^\text{v}$ is the kinetic energy of the photoelectron in the vacuum while $E_{\text{kin}}$ is the kinetic energy of the photoelectron relative to $E_F$. $E_B$ is the binding energy relative to the Fermi level $E_F$. 
Therefore, we obtain
\[ k_f = k_i + G, \tag{2.5} \]
where \( k_i \) and \( k_f \) are the wave vector of an electron in the initial and final states, respectively, and \( G = (2\pi/a, 2\pi/b, 2\pi/c) \) is an arbitrary reciprocal lattice vector.

Figure 2.2 shows a schematic diagram of the emission of a photoelectron from a solid to the vacuum. When a photoelectron is emitted from the solid to the vacuum, the wave vector perpendicular to the surface \( (k_f \perp) \) is modified because of the potential barrier of the inner potential, while the wave vector parallel to the surface \( (k_{f\parallel}) \) is conserved because of the translational symmetry along the surface. Therefore, we obtain,
\[ k_{f\parallel} = k_{f\parallel} + G'_{\parallel}, \tag{2.6} \]
where \( k_{f\parallel} \) is the wave vector of a photoexcited electron in the vacuum and, accordingly, \( k_{f\parallel} \) is the parallel component of \( k_f \).

In the ARPES measurement, the kinetic energy \( E_{\text{kin}} \) and the direction, \( \theta \) and \( \phi \), of the momentum of a photoelectron is measured by an electron energy analyzer. In Fig. 2.3, the geometry between the sample surface and the analyzer is shown. As shown in the schematic diagram of Fig. 2.3, \( k_{f\parallel} \) is resolved into the components, namely \( k_x \) and \( k_y \), and these components satisfy following relationship,
\[ k_x = \frac{\sqrt{2m_eE_{\text{kin}}^v}}{\hbar} \cos \phi \sin \theta, \tag{2.7} \]
\[ k_y = \frac{\sqrt{2m_eE_{\text{kin}}^v}}{\hbar} \sin \phi. \tag{2.8} \]

Summarizing the above equations, in the photoemission process, one can directly observe both the energy \( E \equiv -E_B \) and the parallel momentum \( k_{f\parallel}^v \) of the electron in the material as
\[ E = E_{\text{kin}} - h\nu, \tag{2.9} \]
\[ k_x = \frac{\sqrt{2m_eE_{\text{kin}}^v}}{\hbar} \cos \phi \sin \theta + \frac{2\pi n_x''}{a}, \tag{2.10} \]
\[ k_y = \frac{\sqrt{2m_eE_{\text{kin}}^v}}{\hbar} \sin \phi + \frac{2\pi n_y''}{b}, \tag{2.11} \]
where \( n_x'' \) and \( n_y'' \) are arbitrary integers.

Figure 2.4 schematically illustrates the procedure for mapping band dispersion from the ARPES spectra. If a material under study is a two-dimensional system
Figure 2.2: Schematic diagram of the emission of a photoelectron from a solid to the vacuum. A red arrow is decomposed into components of brown arrows.

such as high-$T_c$ superconductors, $E$ and $k^v_f$ are enough information to map the energy-momentum dispersion of the band structure.

### 2.3 Information from ARPES spectra

From the ARPES spectra, one can obtain useful information. In this section, we explain spectral weight mapping in energy ($E$)-momentum ($k$) space ($E$-$k$ plot), self-energy analysis, and analysis of electrical resistivity based on ARPES data.

#### 2.3.1 $E$-$k$ plot

In this thesis, we will often use EDCs and momentum distribution curves (MDCs) in order to illustrate ARPES spectra. Figure 2.5 shows a $E$-$k$ intensity plot, in which the spectral intensity is plotted in colors (high intensity in brown and low intensity in blue) in the $E$-$k$ plane.

In this plot, an EDC is a spectrum as a function of energy, which corresponds to a cut of constant momentum as described by red line in Fig. 2.5.

On the other hand, an MDC is a spectrum as a function of momentum, which corresponds to a cut of constant energy as described by blue line in Fig. 2.5. By fitting these MDCs to a Lorentzian, we can obtain full width at half maximum (FWHM) of MDCs.
Figure 2.3: Schematic diagram of the experimental geometry between a sample surface and an electron energy analyzer. We resolved the momentum of photoelectrons into $k_x$ and $k_y$. Red arrows represent the polarization vector of incident photons.
Figure 2.4: Schematic diagram of the procedure for mapping band dispersion from ARPES spectra.
Figure 2.5: An example of an $E$-$k$ intensity plot. A red line corresponds to a cut for an EDC, whereas a blue line corresponds to a cut for an MDC.
2.3.2 Self-energy analysis

Here, we describe the relationship between the photoemission spectra and the renormalization of the effective mass using the Green function formalism. First, the retarded Green function is given by

$$G(k, \omega) = \frac{1}{\omega - \epsilon_0^k - \Sigma(k, \omega)}.$$  \hspace{1cm} (2.12)

The photoemission spectrum is given by

$$A(k, \omega) = -\frac{1}{\pi} \text{Im} G(k, \omega) = -\frac{1}{\pi} \frac{\text{Im}\Sigma(k, \omega)}{(\omega - \epsilon_0^k - \text{Re}\Sigma(k, \omega))^2 + (\text{Im}\Sigma(k, \omega))^2}.  \hspace{1cm} (2.13)$$

The real part of the pole of $G(k, \omega)$, $\omega = E^*_k$ is determined by the equation

$$E^*_k - \epsilon_0^k - \text{Re}\Sigma(k, \omega) = 0,  \hspace{1cm} (2.14)$$

and the residue of the pole $Z_k$ is given by

$$Z_k = \left(1 - \left. \frac{\partial \text{Re}\Sigma(k, \omega)}{\partial \omega} \right|_{\omega=E^*_k} \right)^{-1}.  \hspace{1cm} (2.15)$$

Near $\omega = E^*_k$, we can expand Eq.(2.14) as follows,

$$\omega - \epsilon_0^k - \text{Re}\Sigma(k, \omega) \simeq \frac{1}{Z_k} (\omega - E^*_k).  \hspace{1cm} (2.16)$$

Therefore, Eq.(2.13) is written as

$$A(k, \omega) = -\frac{Z_k}{\pi} \frac{Z_k \text{Im}\Sigma(k, \omega)}{(\omega - E^*_k)^2 + (Z_k \text{Im}\Sigma(k, \omega))^2}.  \hspace{1cm} (2.17)$$

In the vicinity of $E_F$, $E^*_k$ can be written as $E^*_k = v_k^*(k-k_F)$, where $v_k^*(\equiv |\nabla E^*_k|)$ is the renormalized Fermi velocity and $k$ is taken perpendicular to the Fermi surface contour. Then, the MDCs at the Fermi level ($\omega = 0$) is given by

$$A(k, 0) = -\frac{Z_k}{\pi} \frac{Z_k \text{Im}\Sigma(k, 0) / v_k^*}{(k-k_F)^2 + (Z_k \text{Im}\Sigma(k, 0) / v_k^*)^2}.  \hspace{1cm} (2.18)$$
Thus, the MDC is given as a Lorentzian with a FWHM of \( \Delta k = 2|Z_k \text{Im} \Sigma/v_k^*| \), if the \( k \)-dependence of \( Z_k, \text{Im} \Sigma(k, 0) \) and \( v_k^* \) can be neglected. Since the inverse life time of the quasi-particle is given by \( 1/\tau_k = -2Z_k \text{Im} \Sigma \), \( 1/\Delta k \) represents the mean free path \( l_k \): \[
l_k = v_k^* \tau_k = \frac{1}{\Delta k} \tag{2.19}\]

The above relationship is used for the analysis in Chapter 4.

\subsection{2.3.3 Electrical resistivity}

Electrical resistivity is estimated from the measured ARPES spectra by using of Drude formula represented as \[
\rho = \frac{m^*}{n e^2 \tau}, \tag{2.20}\]

where \( m^*, n, \) and \( \tau \) are effective mass of an electron, carrier concentration, and the mean lifetime of electrons, respectively. Here, \( m^* \) and \( \tau \) satisfy following relation,

\[
m^* = \frac{\hbar k_F}{v_F}, \tag{2.21}\]

\[
\tau = \frac{l}{v_F} = \frac{1}{\Delta k v_F}, \tag{2.22}\]

where \( k_F \) and \( v_F \) are Fermi wave number and Fermi velocity, respectively.

Summarizing (2.20), (2.21), (2.22), we can obtain \[
\rho = \frac{m^*}{n e^2 \tau} = \frac{\hbar k_F \Delta k}{n e^2}. \tag{2.23}\]

In Eq.(2.23) , \( \Delta k \) is obtained from an MDC analysis. In case of high-\( T_c \) superconductors, \( k_F \) is obtained from the distance between “Fermi arc” and \((\pi, \pi)\) in the \( k \)-space, and \( n \) is obtained from the Fermi surface volume or the carrier concentration \( n \sim x \). As a result, one can estimate the electrical resistivity from the ARPES spectra.
Chapter 3

Angle-integrated photoemission spectroscopy of $Ln_{2-x}Ce_xCuO_4$ ($Ln =$ Pr, Nd, Sm)

In this Chapter, we present and discuss the results of the angle-integrated photoemission study of $Ln_{2-x}Ce_xCuO_4$ ($Ln =$ Pr, Nd, Sm)

3.1 Introduction

Since the discovery of the electron-doped high-$T_c$ superconductors (HTSCs) with the $T'$-type structure [9], their similarity or dissimilarity to the hole-doped HTSCs has been under dispute [6–8]. Above all, the pseudogap observed universally in HTSCs has been extensively studied in past years.

In the hole-doped HTSCs, there seem to be two kinds of pseudogaps in the energy scale. One is the high-energy-scale pseudogap phenomena appearing with a relatively high crossover temperature ($T^* = 200 \sim 500$ K). Below this temperature, Hall coefficient [25], magnetic susceptibility and NMR Knight shift [26,27] undergo considerable change. In the angle-integrated photoemission spectroscopy (AIPES) measurements, the high-energy pseudogap of 0.1 eV-0.2 eV was observed in $La_{2-x}Sr_xCuO_4$ (LSCO) [28] and that of 30-35 meV was observed in LSCO ($x = 0.15$) [29]. The other is the low-energy-scale pseudogap related to a low-lying crossover temperature. Below this temperature, the NMR relaxation rate is suppressed, the feature of the pseudogap in the tunneling spectroscopy is discerned [30], and the leading edge shift at around $(\pi,0)$ is observed in angle-resolved photoemission spectroscopy (ARPES) measurements [31,32]. In addition, the low-energy pseudogap seems to be smoothly connected to the
superconducting gap with the same $d_{x^2-y^2}$ symmetry.

Although the pseudogap behavior has been observed in the hole-doped HTSCs, the mechanism of its formation has not been known yet. Hence, it is important to investigate the pseudogap in the electron-doped HTSCs in order to elucidate the origin of the pseudogap and the factor which determines the magnitude of the pseudogap. Therefore, we performed AIPES measurements on $Ln_{2-x}Ce_xCuO_4$ ($Ln = Pr, Nd, Sm$), which are the electron-doped HTSCs.

Although it is interesting to compare the hole-doped HTSCs and the electron-doped HTSCs, the electron-doped HTSCs have interesting physics in their own right. The representative electron-doped HTSCs is $Nd_{2-x}Ce_xCuO_4$. The materials with replacing Nd$^{3+}$ of $Nd_{2-x}Ce_xCuO_4$ with La$^{3+}$, Pr$^{3+}$, Sm$^{3+}$, or Eu$^{3+}$ are also the electron-doped HTSCs with the $T'$-type structure. $Ln_{2-x}Ce_xCuO_4$ ($Ln = La, Pr, Nd, Sm, Eu$) shows systematic changes in $T_c$, lattice constant, chemical pressure, and so on, as a function of the ionic radius of lanthanide ion. Details are explained in the next section.

The pressure effect in the electron-doped HTSCs is mainly observed in the measurements of electrical resistivity. Photoemission spectroscopy (PES) is a powerful tool to observe directly the electronic structure. However, one cannot perform the PES measurements under pressure. Therefore, we make use of the effect of chemical pressure, which is able to be observed with PES. In $Ln_{2-x}Ce_xCuO_4$ ($Ln = La, Pr, Nd, Sm, Eu$), only $La_{2-x}Ce_xCuO_4$ shows superconductivity in thin films [33, 34] and single crystals of $Eu_{2-x}Ce_xCuO_4$ do not show superconductivity even after annealing. Therefore, we have performed AIPES measurements on the single crystals of $Ln_{2-x}Ce_xCuO_4$ ($Ln = Pr, Nd, Sm$) and examined systematic variation in the electronic structure.

### 3.2 Physical properties of $Ln_{2-x}Ce_xCuO_4$ ($Ln = La, Pr, Nd, Sm, Eu$)

Expecting the symmetry between the hole and the electron, the electron-doped HTSCs with the $T'$-phase were discovered [9]. The $T'$-type structure is shown in Fig. 1.2. It has no oxygen at the apical position of CuO$_2$ plane but has oxygen in a plane sandwiched between the lanthanide layers. The electron-doped HTSCs, namely, $Ln_{2-x}Ce_xCuO_4$ ($Ln = La, Pr, Nd, Sm, Eu$) is made from $Ln_2CuO_4$ ($Ln = La, Pr, Nd, Sm, Eu$) through doping carriers, namely, substituting Ce$^{4+}$ for part of La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, or Eu$^{3+}$. The lanthanide ion $Ln^{3+}$ has a great influence on the physical properties of $Ln_{2-x}Ce_xCuO_4$.
Table 3.1: Atomic number, ionic radius, and \( T_c \) of \( Ln_{2-x}Ce_xCuO_4 \) (\( Ln = \text{La, Pr, Nd, Sm, Eu} \)). As the atomic number increases, the ionic radius becomes smaller and the \( T_c \) of \( Ln_{2-x}Ce_xCuO_4 \) becomes lower.

<table>
<thead>
<tr>
<th>lanthanide (( Ln ))</th>
<th>La</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomic number</td>
<td>57</td>
<td>59</td>
<td>60</td>
<td>62</td>
<td>63</td>
</tr>
<tr>
<td>ionic radius (( \AA ))</td>
<td>1.160</td>
<td>1.126</td>
<td>1.109</td>
<td>1.079</td>
<td>1.066</td>
</tr>
<tr>
<td>( T_c ) of ( Ln_{2-x}Ce_xCuO_4 ) (K)</td>
<td>30</td>
<td>25</td>
<td>25</td>
<td>18</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3.1 shows the ionic radius of the lanthanide ion \( Ln^{3+} \). As the atomic number of the lanthanide ion increases, the ionic radius of it becomes small and, accordingly, the lattice constant of \( Ln_{2-x}Ce_xCuO_4 \) becomes small, as shown in Fig. 3.1 [35]. Hence, the chemical pressure of \( Ln_{2-x}Ce_xCuO_4 \) (\( Ln = \text{La, Pr, Nd, Sm, Eu} \)) becomes high, as the atomic number of the lanthanide ion increases. In addition, the \( T_c \) of \( Ln_{2-x}Ce_xCuO_4 \) (\( Ln = \text{La, Pr, Nd, Sm, Eu} \)) also takes a systematic variation as shown in Table 3.1. Figure 3.2 shows the phase diagram of \( Ln_{2-x}Ce_xCuO_4 \) (\( Ln = \text{La, Pr, Nd, Sm, Eu} \)) in thin films [36]. On the low doping side, superconductivity abruptly disappears in contrast to the phase diagram of the hole-doped HTSCs with its famous dome-shaped superconducting region. The range of the doping level for superconductivity decreases, as the ionic radius of the lanthanide ion becomes small. In \( \text{La}_{2-x}Ce_xCuO_4 \), the optimal doping level is around 0.10 as reported in Refs. [33, 34], while in \( Ln_{2-x}Ce_xCuO_4 \) (\( Ln = \text{Pr, Nd, Sm, Eu} \)) it is around 0.15.

Figure 3.3 shows the normalized electrical resistivity of \( Ln_{2-x}Ce_xCuO_4 \) (\( Ln = \text{Pr, Nd, Sm, Eu} \)) as a function of temperature [10]. Electrical resistivity \( \rho(T) \) is normalized to its maximum value. Considerable variation of the transition width and \( T_c \) is shown for the variation of the lanthanide ion. Figure 3.4 shows the electrical resistivity of the parent compounds \( Ln_2CuO_4 \) (\( Ln = \text{La, Pr, Nd, Sm, Eu} \)) [36]. \( Ln_2CuO_4 \) (\( Ln = \text{La, Pr, Nd, Sm, Eu} \)) shows “metallic” temperature dependence \( (d\rho/dT \geq 0) \) above \( \sim 150 \) K while it is insulating \( (d\rho/dT \leq 0) \) below \( \sim 150 \) K. Schematically, the electrical resistivity of \( Ln_2CuO_4 \) (\( Ln = \text{La, Pr, Nd, Sm, Eu} \)) increases, as the ionic radius of the lanthanide ion becomes smaller.

Figure 3.5 shows the effects of hydrostatic pressure on the resistivity for \( \text{Nd}_{2-x}Ce_xCuO_4 \) (NCCO) with \( x = 0.15 \) [37]. The qualitative temperature dependence of \( \rho_{ab}(T) \) and \( \rho_c(T) \) is not changed by the application of pressure. The resistivity of the normal state decreases when the hydrostatic pressure increases. The resistive transition width does not change by the application of pressure, namely, both the onset temperature and zero-resistivity temperature are inde-
Figure 3.1: Lattice constants of $Ln_{2-x}Ce_xCuO_4$ ($Ln =$ Pr, Nd, Sm, Eu, Gd) [35]. As the ionic radius of the lanthanide ion becomes smaller, the lattice constant of $Ln_{2-x}Ce_xCuO_4$ ($Ln =$ La, Pr, Nd, Sm, Eu) becomes smaller. The variation of the $c$-axis parameter is stronger than that of the $a$-axis.
Figure 3.2: Phase diagram of $Ln_{2-x}Ce_xCuO_4$ ($Ln = \text{La, Pr, Nd, Sm, Eu}$) [36]. The range of doping level for superconductivity decrease, as the ionic radius of the lanthanide ion becomes smaller.
Figure 3.3: Normalized electrical resistivity, $\rho(T)/\rho_{\text{max}}$, plotted as a function of temperature [10].
Figure 3.4: Electrical resistivity of $Ln_2CuO_4$ ($Ln = $ La, Pr, Nd, Sm, Eu) [36]. As the ionic radius of the lanthanide ion becomes smaller, the electrical resistivity of increases.
dependent of pressure. The pressure dependence of the resistivity in $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO) with $x = 0.15$ and $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_4$ (SCCO) with $x = 0.15$ is similar to that in NCCO ($x = 0.15$) except for the slight shift of the zero-resistivity temperature.

The upper panel of Fig. 3.6 shows the energy of the charge-transfer gap $\Delta$ of the parent compounds as a function of the Cu-O distance $d$ [38]. As the ionic radius of the lanthanide ion decreases, $\Delta$ becomes large. The lower panel of Fig. 3.6 shows the exchange energy $J$ as a function of Cu-O distance $d$. As the ionic radius of the lanthanide ion $Ln^{3+}$ decreases, $J$ becomes larger.

### 3.3 Experiment

High-quality single crystals of $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($Ln = \text{Pr, Nd, Sm}$) were grown by the traveling solvent floating zone method. The single crystals of NCCO ($x = 0.15$) and PCCO ($x = 0.15$) were annealed at 930 °C for 100 hours in Ar gas. The single crystals of SCCO ($x = 0.15$) were annealed at 920 °C for 100 hours in Ar gas and $T_c$ of SCCO ($x = 0.15$) was 16 K. These samples were crystals with multi-domains. The samples were provided by Mr. Unozawa, Mr. Kaga, Dr. Sasagawa, and Prof. Takagi, Department of Advanced Materials Science, University of Tokyo.

High-resolution AIPES measurements were performed using a Gammadata He I light source with the photon energy of 21.218 eV. The measurement system is shown in Fig. 3.7. We used a SCIENTA SES-100 spectrometer. The total energy resolution was set at $\sim$12 meV to obtain a reasonable count rate near $E_F$. The base pressure was $10^{-11}$ Torr. Samples were scraped every thirty minutes to expose a clean surface and measurements were performed at 9 K, 50 K, and 100 K. The photoemission spectra reflect the density of states (DOS) modulated by the photoionization cross-sections. The Fermi edge of gold was used to determine the $E_F$ position and the instrumental resolution before and after the AIPES measurements. We also performed X-ray photoemission spectroscopy (XPS) to confirm that the valence of Sm is trivalent. The XPS measurements were performed using the Mg $K\alpha$ line with the photon energy of 1253.6 eV. The base pressure was $10^{-10}$ Torr and measurements were performed at 100 K. The spectrum of Au $4f$ was used to determine the $E_F$ position.
Figure 3.5: Electrical resistivity of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ measured under hydrostatic pressure [37]. The upper panel shows the in-plane resistivity $\rho_{ab}(T)$ and the lower panel shows the out-of-plane resistivity $\rho_c(T)$. The resistivity of normal state decrease when the hydrostatic pressure increases.
Figure 3.6: (a) Log-log plot of charge-transfer gap $\Delta$ of the parent compounds $Ln_2CuO_4$ vs the Cu-O distance $d$. The dashed line is a least-squares fit to the $T'$-type structure data (solid squares), while the solid line is a fit to all the data including the $T$-type structure compounds (open circles). (b) Similar plot for the exchange energy $J$. The dashed line is a least-squares fit to the $T'$-type structure data (solid squares), while the solid line is a fit to all the data including the $T$-type structure compounds (open circles). The energy scales for both (a) and (b) are in $\log_{10}$ (cm$^{-1}$), and the distance scale is in $\log_{10}$ (Å) [38].
Figure 3.7: Overview of the measurement system for AIPES.
Figure 3.8: Overview of the measurement system for XPS.
3.4 Results and Discussion

3.4.1 Temperature dependence

Figures 3.9, 3.10, and 3.11 show photoemission spectra of PCCO \((x = 0.15)\), NCCO \((x = 0.15)\), and SCCO \((x = 0.15)\), respectively, taken at 9 K, 50 K, and 100 K. For comparison, the temperature dependence of AIPES spectra of LSCO \((x = 0.15)\) are shown in Fig. 3.12 [29] and the spectra of gold are shown in the inset of Fig. 3.12. While the spectra of gold intersect with each other the same point at \(E_F\) irrespective of temperature, the spectra of LSCO \((x = 0.15)\) do not intersect at \(E_F\) nor even at one point. This behavior of LSCO \((x = 0.15)\) is barely observed in PCCO \((x = 0.15)\), NCCO \((x = 0.15)\), and SCCO \((x = 0.15)\).

In order to see more directly the change of DOS near \(E_F\) at each temperature, we divided each spectrum by the Fermi Dirac function, convoluted with a Gaussian of the instrumental resolution. This procedure serves as a good approximation as long as we discuss the structure in the DOS larger than the energy resolution, as demonstrated in the previous studies [39, 40]. Figures 3.13, 3.14, and 3.15 show results of PCCO \((x = 0.15)\), NCCO \((x = 0.15)\), and SCCO \((x = 0.15)\), respectively. From these spectra, one can observe that the DOS near \(E_F\) was suppressed at low temperatures, suggesting that a pseudogap may open. The pseudogap had finite DOS and was gradually filled as the temperature increased. For comparison, the results of LSCO \((x = 0.15)\) are shown in Fig. 3.16. In LSCO \((x = 0.15)\), one can clearly observe the behavior discussed above. The size of the pseudogap is estimated as \(\sim 30\) meV for PCCO \((x = 0.15)\), NCCO \((x = 0.15)\), and SCCO \((x = 0.15)\), which is almost the same as that for LSCO \((x = 0.15)\).

3.4.2 Lanthanide dependence

We discuss the lanthanide dependence of the spectra of the electron-doped HTSCs with \(T'\)-type structure. Figure 3.17 shows photoemission spectra near \(E_F\) of PCCO \((x = 0.15)\), NCCO \((x = 0.15)\), and SCCO \((x = 0.15)\). From Fig. 3.17, spectral weight near \(E_F\) of SCCO \((x = 0.15)\) was the largest among the three. According to the scenario of van Hove singularity, materials with large DOS have the high \(T_c\). However, \(T_c\) of SCCO \((x = 0.15)\) is the smallest among the three. Here, we interpret this result as below.

First, we assume that the carrier concentration of \(Ln_{1.85}Ce_{0.15}CuO_4\) \((Ln = Pr,\) Nd, Sm) are the same. The lattice constant of SCCO \((x = 0.15)\) is the smallest among \(Ln_{1.85}Ce_{0.15}CuO_4\) \((Ln = Pr,\) Nd, Sm), as shown in Fig. 3.1. Therefore,
Figure 3.9: Temperature dependence of AIPES spectra for PCCO ($x = 0.15$).

Figure 3.10: Temperature dependence of AIPES spectra for NCCO ($x = 0.15$).
Figure 3.11: Temperature dependence of AIPES spectra for SCCO ($x = 0.15$).

Figure 3.12: Temperature dependence of AIPES spectra for LSCO ($x = 0.15$) taken from Ref. [29].
Figure 3.13: Temperature dependence of DOS in PCCO ($x = 0.15$).

Figure 3.14: Temperature dependence of DOS in NCCO ($x = 0.15$).
Figure 3.15: Temperature dependence of DOS in SCCO ($x = 0.15$).

Figure 3.16: Temperature dependence of DOS in LSCO ($x = 0.15$) taken from Ref. [29].
the chemical pressure of SCCO \((x = 0.15)\) is the largest of the three. The large chemical pressure results in a large band width \((W)\). Since the Coulomb energy \((U)\) should change little by the chemical pressure, the value of \(U/W\) in SCCO \((x = 0.15)\) is the smallest among the three. Therefore, in SCCO \((x = 0.15)\), spectral weight may be transferred from the incoherent part to the coherent part, compared with PCCO \((x = 0.15)\) and NCCO \((x = 0.15)\). This means that the effect of electron correlation in SCCO \((x = 0.15)\) is the weakest among the three. That is, we consider that the spectral weight near \(E_F\) reflects the variation of the effect of electron correlation. As for physical pressure, when hydrostatic pressure is applied, the electrical resistivity of the normal state decreases as shown in Fig. 3.5. Since the decrease of electrical resistivity means large spectral weight near \(E_F\), physical pressure brings about large spectral weight near \(E_F\). This scenario of physical pressure is consistent with that of chemical pressure effect observed in \(Ln_{1.85}Ce_{0.15}CuO_4 (Ln = Pr, Nd, Sm)\).

Finally, we discuss the possibility of overdoping in SCCO \((x = 0.15)\). According to the ARPES results of NCCO [23], the larger the doping level is, the stronger the spectral weight near \(E_F\) is. That is, it is possible that SCCO \((x = 0.15)\) is overdoped compared with PCCO \((x = 0.15)\) and NCCO \((x = 0.15)\). Here, we discuss the possible origin of this overdoped behavior of SCCO \((x = 0.15)\). First, we consider the variation of the valence of Sm in SCCO \((x = 0.15)\). To confirm the valence of Sm, we performed the core-level XPS measurements. Figure 3.18 shows the spectrum of the Sm 3\(d\) core level in SCCO \((x = 0.15)\). Figure 3.19 shows the spectrum of the Sm 3\(d\) core level in Sm(OH)\(_3\), whose valence number is trivalent [41]. Since the binding energy of the Sm 3\(d\) core level for SCCO \((x = 0.15)\) and Sm(OH)\(_3\) are almost the same, the valence of Sm in SCCO \((x = 0.15)\) is trivalent. Therefore, this can not cause overdoping in SCCO \((x = 0.15)\). Another possibility of overdoping in SCCO \((x = 0.15)\) is the oxygen defect. Since oxygen supplies CuO\(_2\) plane with holes, oxygen defects in the block layers may exist in SCCO \((x = 0.15)\), compared with PCCO \((x = 0.15)\) and NCCO \((x = 0.15)\). More experiment is needed to clarify whether the high spectral weight near \(E_F\) in SCCO \((x = 0.15)\) is due to the chemical pressure or overdoping.

3.5 Summary and Conclusion

In summary, we have performed AIPES measurements of \(Ln_{1.85}Ce_{0.15}CuO_4 (Ln = Pr, Nd, Sm)\). From the temperature dependence of the spectra, we observed that the pseudogap is gradually filled in \(Ln_{1.85}Ce_{0.15}CuO_4 (Ln = Pr, Nd, Sm)\) as the
Figure 3.17: Photoemission spectra near $E_F$ of PCCO ($x = 0.15$), NCCO ($x = 0.15$), and SCCO ($x = 0.15$) at 9 K. Similar behavior was observed at 50 K and 100 K.

Figure 3.18: Spectrum of the Sm 3$d$ core level in SCCO ($x = 0.15$).
Figure 3.19: Spectrum of the Sm 3d core level in Sm(OH)$_3$ taken from Ref. [41].
temperature increases, which is similar to LSCO \((x = 0.15)\). The size of the pseudogap in \(Ln_{1.85}Ce_{0.15}CuO_4\) \((Ln = \text{Pr, Nd, Sm})\) is also almost the same as that of LSCO \((x = 0.15)\).

From the lanthanide dependence of the spectra, we observed that the spectral weight near \(E_F\) increased as the ionic radius of \(Ln^{3+}\) in \(Ln_{1.85}Ce_{0.15}CuO_4\) \((Ln = \text{Pr, Nd, Sm})\) became small. As the first possibility, we assume that the carrier concentrations of \(Ln_{1.85}Ce_{0.15}CuO_4\) \((Ln = \text{Pr, Nd, Sm})\) were the same. Since the lattice constant of SCCO \((x = 0.15)\) is the smallest among the three, SCCO \((x = 0.15)\) has the largest chemical pressure and the largest band width. Hence, in SCCO \((x = 0.15)\), the value of \(U/W\) is the smallest among the three and the transfer of spectral weight from the incoherent part to the coherent part took place. This means that the effect of electron correlation in SCCO \((x = 0.15)\) is the smallest among the three. Also, this results are consistent with the results of physical pressure effect. As the second possibility, we consider overdoping in SCCO \((x = 0.15)\) compared with PCCO \((x = 0.15)\) and NCCO \((x = 0.15)\). As an origin of the overdoping in SCCO \((x = 0.15)\), we excluded the variation of the valence of Sm by the XPS measurements. Alternatively, we consider that overdoped behavior of SCCO \((x = 0.15)\) may result from the oxygen defects in the block layers.
In this Chapter, we present and discuss the results of an angle-resolved photoemission study of the electron-doped high-$T_c$ superconductor Eu$_{2-x}$Ce$_x$CuO$_4$.

4.1 Introduction

Since the discovery of the electron-doped high-$T_c$ superconductors (HTSCs) with the $T'$-type structure [9], their similarity or dissimilarity to the hole-doped HTSCs has been under dispute [6–8]. Angle-resolved photoemission spectroscopy (ARPES) measurements have played an important part in the studies of the HTSCs. The superconducting gap symmetry of the hole-doped HTSCs is $d_{x^2-y^2}$ like and is described by the gap function of $\Delta(k) \propto \cos(k_x a) - \cos(k_y a)$ [18,19], where the maximum and zero-superconducting gaps are located in the $(\pi, 0)$ direction and the zone diagonal, respectively. On the other hand, for the electron-doped HTSCs, it had been recognized that superconducting gap symmetry is monotonic $d_{x^2-y^2}$ wave [20, 21], which is similar to the hole-doped HTSCs. But it was found recently that the superconducting gap in Pr$_{1-x}$LaCe$_x$CuO$_4$ is nonmonotonic $d_{x^2-y^2}$ wave which have the maximum gap not in the $(\pi, 0)$ direction but around “the hot spot” [22]. Here, the hot spot is defined as an intersection of the Fermi surface and the antiferromagnetic Brillouin zone. In the hole-doped HTSCs, the hot spot is near $(\pi, 0)$. On the other hand, in the electron-doped HTSCs the hot spot is between $(\pi, 0)$ and the zone diagonal [42] and an electron pocket appears near $(\pi, 0)$ for low doping concentration.

As addressed above, many studies of the electron-doped HTSCs have been performed in order to compare the behavior of the electron-doped HTSCs and
the hole-doped ones. However, the electron-doped HTSCs possess interesting physics in their own rights, in addition to the comparison of them with the hole-doped ones. The representative electron-doped HTSC is Nd$_{2−x}$Ce$_x$CuO$_4$. If Nd$^{3+}$ of Nd$_{2−x}$Ce$_x$CuO$_4$ is replaced by La$^{3+}$, Pr$^{3+}$, Sm$^{3+}$, or Eu$^{3+}$, it remains an electron-doped HTSC with the $T'$-type structure. Ln$_{2−x}$Ce$_x$CuO$_4$ ($Ln=$La, Pr, Nd, Sm, Eu) exhibits systematic changes in $T_c$, lattice constant, chemical pressure, and so on, as a function of the atomic number of the lanthanide ion $Ln^{3+}$. Details are explained in the next section.

Eu$_{2−x}$Ce$_x$CuO$_4$ (ECCO) is interesting because it has an extremely low $T_c$ and has a small lattice constant compared with the other materials with the $T'$-type structure. Therefore, by ARPES measurements of ECCO we may be able to observe the effect of the lanthanide substitution. In addition, we may be able to obtain new information about the origin of the electron-doped HTSCs because in Ln$_{2−x}$Ce$_x$CuO$_4$ with $Ln=$ Gd, whose atomic number is next to Eu, does not show superconductivity. Hence, we have performed ARPES measurements of ECCO. Since it is hard to make single crystals of ECCO superconducting by annealing, we have performed ARPES measurements on as-grown samples and compared the present results with those of Ln$_{2−x}$Ce$_x$CuO$_4$ ($Ln=$Nd, Sm).

### 4.2 Physical properties of Eu$_{2−x}$Ce$_x$CuO$_4$

The crystal structure of ECCO is the $T'$-type structure, in which the CuO$_2$ plane and the (Eu,Ce)$_2$O$_2$ block layer are stacked alternatively. The CuO$_2$ plane contributes to the superconductivity while the (Eu,Ce)$_2$O$_2$ block layer supplies the CuO$_2$ plane with carriers. In ECCO, electrons are doped into the CuO$_2$ plane by substituting Ce$^{4+}$ for part of Eu$^{3+}$. Doping dependence of the length of the $a$-axis and the $c$-axis are shown in Fig. 4.1 [43]. As the doping level of Ce$^{4+}$ increases, the length of the $a$-axis increases and the length of the $c$-axis decreases. In addition, with the doping level of Ce$^{4+}$, the $T_c$ of ECCO also varies as shown in Fig. 3.2 of Chapter 3.

Among Ln$_{2−x}$Ce$_x$CuO$_4$ ($Ln=$La, Pr, Nd, Sm, Eu), ECCO has the narrowest range of doping level for superconductivity and the lowest $T_c$. Because the ionic radius of Eu$^{3+}$ is the smallest among the above $Ln^{3+}$, the lattice constant of ECCO is the smallest among Ln$_{2−x}$Ce$_x$CuO$_4$ ($Ln=$La, Pr, Nd, Sm, Eu). That is, the chemical pressure in ECCO is the largest among them. Details are shown in Chapter 3.

Superconductivity in Ln$_{2−x}$Ce$_x$CuO$_4$ ($Ln=$La, Pr, Nd, Sm, Eu) is achieved
through annealing. The sample before annealing is called as-grown sample, which has excess oxygen at the apical position of the CuO$_2$ plane, whereas the sample after annealing is called annealing sample, which has no apical oxygen. The thin films and polycrystals of ECCO become superconductors through annealing under appropriate conditions. However, the single crystals of ECCO do not become superconductors even if we anneal them with various condition, while the single crystals of $Ln_{2-x}Ce_xCuO_4$ ($Ln = \text{Pr, Nd, Sm}$) shows superconductivity through annealing. This behavior is the same as the small samples of granular ceramics [44].

4.3 Experiment

High-quality single crystals of ECCO ($x = 0.15$) were grown by the traveling solvent floating zone method. These samples were provided by Mr. Unozawa, Dr. Sasagawa, and Prof. Takagi, Department of Advanced Materials Science, University of Tokyo. Laue pattern of ECCO ($x = 0.15$) by X-ray diffraction is shown in Fig. 4.2. In single crystals of ECCO ($x = 0.15$), because it is difficult to make samples superconducting by annealing as stated in the preceding section, we performed ARPES measurements on the as-grown $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ (ag-ECCO).

ARPES measurements were performed at beamline 5-4 of Stanford Synchrotron Radiation Laboratory (SSRL), using incident photons with energy of 16.5 eV. The measurement system is shown in Fig. 4.3. We used a SCIENTA SES-200 spectrometer in the angle mode, where one can collect spectra over $\sim 14^\circ$, corresponding to a momentum width of $\sim 0.6\pi$ (in units of $1/a$, where $a = 3.9 \, \text{Å}$ is the lattice constant). The total energy resolution and angular (momentum) resolution were 15 meV and 0.2$^\circ$ (0.007$\pi$), respectively. Samples were cleaved in situ under an ultrahigh vacuum of $10^{-11}$ Torr to obtain a clean surface. The incident angle of photons was at approximately 45$^\circ$ to the sample surface with its polarization parallel to the Cu-O bond. The sample temperature was 10 K and was measured by a calibrated diode mounted near the measurement position. The temperature difference between the diode position and the actual measurement position was found to be negligible. The Fermi edge of gold was measured to determine the $E_F$ position and the instrumental resolution before and after the ARPES measurements. The spectral intensities have been normalized to the intensity above $E_F$, which arises from the second order light of the monochromator.
Figure 4.1: Lattice parameters of ECCO. The upper and lower panels show the lengths of the $a$-axes and the $c$-axes as functions of Ce$^{4+}$ concentration, respectively. For Ce$^{4+}$ doping, the variation of lattice constant in the $c$-axis is larger than that in the $a$-axis [43].
Figure 4.2: Laue pattern of as-grown Eu$_{1.85}$Ce$_{0.15}$CuO$_4$. The symmetry is clearly observed.

Figure 4.3: Overview of the ARPES measurement system on beamline 5-4 at SSRL.
4.4 Results and Discussion

Figure 4.4 shows EDCs in the nodal direction of as-grown Sm$_{1.85}$Ce$_{0.15}$CuO$_4$ (ag-SCCO) [45]. The red arrow in the inset shows the direction of the momentum cut. Figure 4.5 shows energy distribution curves (EDCs) across the nodal point of ag-ECCO. The red arrow in the inset shows the direction of the momentum cut. In the figure, a spectrum at the Fermi surface is denoted by a blue curve and the peak positions by black bars. From the black bars in Fig. 4.5, one can conclude that the high energy dispersive feature located about 0.3 eV below $E_F$ is symmetric with respect to ($\pi/2, \pi/2$), which shows the effect of antiferromagnetism. From comparison of Fig. 4.4 with Fig. 4.5, one can observe that the pseudogap in ag-ECCO is larger than that in ag-SCCO. This means that the effect of antiferromagnetism in ag-ECCO is stronger than that in ag-SCCO.

Figure 4.6 shows the plot of ARPES intensity near $E_F$ in ag-ECCO as a function of the two-dimensional wave vector to illustrate the Fermi surface of ag-ECCO. EDCs are integrated with a 60 meV window. Here, red parts correspond to high intensities. The highest ARPES intensity is seen near ($\pi, 0$), and low intensity is seen around ($\pi/2, \pi/2$).

The ARPES intensity is not observed near the hot spot, which is the intersection of the Fermi surface and the antiferromagnetic Brillouin zone boundary. A similar behavior of ARPES intensity has been reported for Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ [42], Nd$_{1.87}$Ce$_{0.13}$CuO$_4$ [46] and ag-SCCO [45], implying that the intensity suppression is an intrinsic effect.

Next, we compare the Fermi surface of ag-ECCO with that of annealed Nd$_{2-x}$Ce$_x$CuO$_4$ (an-NCCO). Figure 1.8 shows the plot of ARPES intensity near $E_F$ in an-NCCO [23]. Comparing Fig. 4.6 and Fig. 1.8, one can see that the Fermi surface of ag-ECCO is similar to that of underdoped an-NCCO.

Figure 4.7 shows the EDCs along the Fermi surface in ag-ECCO. EDCs are arranged as denoted by arrows. As one goes along the Fermi surface, as shown with a black arrow, the low energy dispersive feature appears near ($\pi, 0$). This dispersive feature leads to the formation of small Fermi surface around ($\pi, 0$).

Figure 1.7 shows the EDCs along the Fermi surface in an-NCCO [23]. The low energy dispersive feature ($\sim 0.4$ eV) and the high energy dispersive feature ($\sim 0.4$ eV) in underdoped an-NCCO is similar to those in ag-ECCO.

To confirm that ag-ECCO is in the underdoped region, we derived the doping level of carriers from the area of the Fermi surface in ag-ECCO. From the ratio between the part occupied by electrons and the part unoccupied by electrons in Fig. 4.6, we estimated doping level to be $0.08 \pm 0.03$. This shows that ag-ECCO
Figure 4.4: EDCs of ag-SCCO taken with $h\nu = 16.5$ eV taken from Ref. [45]. The direction of the cut in the Brillouin zone is denoted by a red arrow in the inset. Note that the direction of cut in this figure is different from Fig. 4.5.
Figure 4.5: EDCs of ag-ECCO. The direction of the cut in the Brillouin zone is denoted by a red arrow in the inset and EDCs are arranged as denoted by the arrows. A blue curve denotes a spectrum on the Fermi surface and black vertical bars denote the peak positions. Note that the direction of the cut in this figure is different from Fig. 4.4.
is in the underdoped region corresponding to the result of Fermi surface mapping and EDCs along the Fermi surface.

Here, we discuss the origin of the observed underdoped behavior of ag-ECCO. Since excess oxygen provides holes, we speculate that excess oxygen in apical position of the CuO$_2$ plane may reduce the electron doping level. In fact, it is said that this excess oxygen exists in the as-grown sample [48]. Also, there is a report that a large pseudogap in the optical spectra has been observed not in annealed samples but in as-grown samples [49]. Since the pseudogap is observed in the underdoped region, this also means that the as-grown samples are underdoped.

Next, we analyze momentum distribution curves (MDCs) of ag-ECCO. As shown in Chapter 2, the full width at half maximum (FWHM) of an MDC is equal to the inverse of the mean-free path ($l$). Figure 4.8 shows MDCs at the Fermi level. Each MDC in Fig. 4.8 corresponds to each black square in Fig. 4.6 and MDCs are arranged along the Fermi surface as denoted by a black arrow in Fig. 4.8 and Fig. 4.6. As one goes from near ($\pi, 0$) to near ($\pi/2, \pi/2$), the FWHMs of MDCs ($\Delta k$) increases. Then, the peak disappears near the hot spot and a small peak appears again near ($\pi/2, \pi/2$). The FWHM of each MDC in Fig. 4.8 is shown with a red square in Fig. 4.9. We could not estimate $\Delta k$ near the hot spot due to the strong peak broadening caused by the effect of

**Figure 4.6**: Plot of the ARPES intensity around $E_F$ in ag-ECCO as a function of the two-dimensional wave vector. EDCs are integrated with a 60 meV window. The data were taken over a Brillouin zone octant and symmetrized with respect to the $\Gamma$ to ($\pi, \pi$) line. The white dotted line is the antiferromagnetic Brillouin zone boundary. Black squares represent the position of peaks in momentum distribution curves (MDCs).
Figure 4.7: EDCs along the Fermi surface in ag-ECCO. Black vertical bars denote the peak positions. EDCs are arranged as denoted with black arrows.
Figure 4.8: MDCs at the Fermi level, which correspond to the black squares in Fig. 4.6.
Figure 4.9: FWHM of MDCs in Fig. 4.8 denoted with red squares. Blue squares represent \( \Delta k \) of an-NCCO \((x = 0.15)\) \[47\].
antiferromagnetism.

In Fig. 4.9, we compared $\Delta k$ of ag-ECCO with that of an-NCCO ($x = 0.15$) [47]. $\Delta k$ of ag-ECCO is larger than that of an-NCCO ($x = 0.15$), indicating that $l$ of ag-ECCO is smaller than that of an-NCCO ($x = 0.15$). This means that electron scattering in ag-ECCO is stronger than that of an-NCCO ($x = 0.15$). In addition, the value of $l$ in an-NCCO ($x = 0.15$) is twice as large as that in ag-ECCO. Since the uniformal shift is observed near the node and $(\pi, 0)$, this may show the effect of disorder.

To explain the difference between ag-ECCO and an-NCCO ($x = 0.15$), we have considered several effects. One is the effect of antiferromagnetism. Since ag-ECCO has excess oxygen, it becomes more underdoped than an-NCCO ($x = 0.15$). This means that additional electron scattering results from antiferromagnetism in ag-ECCO. Another effect is the disorder as addressed above. Since ag-ECCO may have apical oxygen, the distortion of electro-static potential may be caused by them. This means that the effect of disorder in ag-ECCO is stronger than that in an-NCCO ($x = 0.15$).

Next, we discuss the analysis of the electrical resistivity based on the ARPES spectra. From the carrier concentration ($n$), $\Delta k$, and the Fermi wave number ($k_F$), the electrical resistivity ($\rho$) can be expressed as

$$\rho = \frac{m^*}{ne^2\tau} = \frac{\hbar k_F \Delta k}{ne^2},$$

if a circular Fermi surface centered at $(\pi, \pi)$ is assumed. Details about Eq.(4.1) are shown in Chapter 2. From the analysis of the ARPES spectra, we obtain $\Delta k = 0.12 \ \text{Å}^{-1}$, $k_F = 0.76 \ \text{Å}^{-1}$, and $x = 0.08$, where $x$ is the doping level.

There are two ways to obtain $n$ from $x$. One is $n \sim x$, in which the small Fermi surface volume centered at $(\pi, 0)$ is considered as $n$. The other is $n \sim 1 \pm x$, in which large Fermi surface volume centered at $(\pi, \pi)$ is considered as $n$. In case of La$_{2-x}$Sr$_x$CuO$_4$, the former gives better agreement with transport data in the underdoped region and the latter is observed in the optimal region [50–52]. A similar behavior is also found in YBa$_2$Cu$_3$O$_{7+\delta}$ [51,53,54]. Therefore, we estimated $n$ in two ways. In case of $n \sim x$, we obtain $\rho = 8.4 \ \text{m\Omega cm}$. On the other hand, in case of $n \sim 1+x$, we obtain $\rho = 0.63 \ \text{m\Omega cm}$. Figure 4.10 shows the in-plane resistivity of both as-grown Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ and annealed Nd$_{1.85}$Ce$_{0.15}$CuO$_4$. A red circle in the figure represents electrical resistivity calculated from $n \sim 1+x$, which is in good agreement with the transport result. Therefore, we regard the behavior of ag-ECCO as $n \sim 1+x$ rather than $n \sim x$. This means that in ag-ECCO carriers are doped into the large Fermi surface although it shows underdoped behavior.
4.5 Summary and Conclusion

In summary, we have performed ARPES measurements of ag-ECCO. We observed that the high energy dispersive feature is symmetric with respect to $(\pi/2, \pi/2)$, indicating the effect of antiferromagnetism. From comparison of ag-ECCO with ag-SCCO, we conclude that the effect of antiferromagnetism in ag-ECCO is stronger than that in ag-SCCO. From the Fermi surface mapping and the dispersive feature of EDCs along the Fermi surface, the behavior of ag-ECCO is similar to that of underdoped an-NCCO. This underdoped behavior in ag-ECCO is confirmed by the estimation of the doping level from the area of Fermi surface. According to MDC analysis, the FWHM of MDCs of ag-ECCO is larger than that of an-NCCO ($x = 0.15$). This indicates strong effect of antiferromagnetism by underdoping or strong effect of disorder by apical oxygen. We have estimated the electrical resistivity from the ARPES spectra and have demonstrated that the behavior of ag-ECCO is $n \sim 1 + x$ rather than $n \sim x.$
Chapter 5

Angle-resolved photoemission spectroscopy of Sm$_{2-x}$Ce$_x$CuO$_4$

In this Chapter, we present and discuss the results of an angle-resolved photoemission study of the electron-doped high-$T_c$ superconductor Sm$_{2-x}$Ce$_x$CuO$_4$.

5.1 Introduction

Since the discovery of bosonic renormalization effects in high-$T_c$ superconductors (HTSCs) in the form of a kink structure in dispersive band for the nodal direction, a number of angle-resolved photoemission spectroscopy (ARPES) measurements in HTSCs have been performed in order to elucidate the origin of a kink structure [55–59]. The renormalization of dispersion of electrons near $E_F$ gives an enhanced mass and flatter $E$-$k$ dispersion. At a higher binding energy, the dispersion returns to the unrenormalized one, causing a kink structure. As for the origin of the kink structure, agreement has been reached that the renormalization is due to the coupling of the electron to a bosonic mode, thus the energy scale and the strength of the kink structure are related to the energy of the boson which coupled to the electron and the coupling strength between the electron and boson, respectively. On the other hand, disagreement has been left whether the boson is a phononic or an electronic mode. Recently, another kink structure has been observed for the antinodal electronic state near $(\pi, 0)$ [60–62]. In contrast to the renormalization in the nodal direction, which shows little change above and below $T_c$, that in the antinodal region has been clearly observed only below $T_c$. Also, the kink observed near $(\pi, 0)$ is stronger than that observed along the zone diagonal. Most of the studies of the kink structure mentioned above have been performed for the hole-doped HTSCs, although the symmetry between the
electron-doped HTSCs and the hole-doped ones is under dispute [6–8]. Hence, it is important to study the kink structure in the electron-doped HTSCs and, possibly, the investigation of electronic structure of the electron-doped HTSCs may be a key to elucidate the origin of the kink structure and its relation to superconductivity.

The electron-doped HTSC Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO) has been extensively studied by ARPES. Figure 5.1 shows an ARPES intensity plot of NCCO ($x = 0.15$) in the superconducting state [21]. The left and right panels in Fig. 5.1 show spectra near ($\pi$, 0) and in the nodal direction, respectively. In this figure, the strong kink structure was observed near ($\pi$, 0), while the kink structure was not observed in the nodal direction.

If Nd$^{3+}$ of NCCO is replaced by La$^{3+}$, Pr$^{3+}$, Sm$^{3+}$, or Eu$^{3+}$, it remains an electron-doped HTSC with the $T'$-type structure. These electron-doped HTSCs show systematic changes of $T_c$ as a function of the atomic number of the lanthanide ion as shown in Table 3.1. Hence, it is also important to probe the electronic structure of electron-doped HTSCs except for NCCO.

Therefore, we performed ARPES measurements of Sm$_{2-x}$Ce$_x$CuO$_4$ (SCCO) with $x = 0.15$ and investigated the electronic states in the nodal and antinodal directions in the normal state. In addition, we compare the results of SCCO ($x = 0.15$) with those of NCCO ($x = 0.15$).
5.2 Physical properties of Sm$_{2-x}$Ce$_x$CuO$_4$

The crystal structure of SCCO is the $T'$-type structure, in which the CuO$_2$ plane and the (Sm,Ce)$_2$O$_2$ block layer are stacked alternatively, as shown in Fig. 1.2. The CuO$_2$ plane contributes to the superconductivity while the (Sm,Ce)$_2$O$_2$ block layer supplies the CuO$_2$ plane with carriers. In SCCO, electrons are doped into the CuO$_2$ plane by substituting Ce$^{4+}$ for part of Sm$^{3+}$. Detailed physical properties of SCCO is shown in Chapter 3.

In this section, we will state the results of muon spin relaxation and rotation (μSR) measurements. Figure 5.2 shows the time spectra of μSR for SCCO ($x = 0$) [63]. At the temperature below 106 K, muon spin rotation is clearly observed, indicating the existence of the antiferromagnetic order. Hence, the Néel temperature is defined as about 106 K. By determining the Néel temperature for various doping level of SCCO, the magnetic phase diagram is obtained as shown in Fig. 5.3 [63]. In SCCO, although the Néel temperature of the parent compounds is small, the antiferromagnetic phase persists to the overdoping level. Figure 5.4 shows magnetic phase diagram for NCCO and Pr$_{1-x}$LaCe$_x$CuO$_4$ (PLCCO) [64].

![Figure 5.2: Time spectra of μSR for SCCO ($x = 0$) [63].](image)
From Fig. 5.3 and Fig. 5.4, we can see the systematic change of antiferromagnetic phase. That is, as the ionic radius of the lanthanide ion for substitution becomes small, the range of doping level for antiferromagnetism becomes large.

5.3 Experiment

High-quality single crystals of SCCO were grown by the traveling solvent floating zone method. The single crystals of SCCO \( (x = 0.15) \) were annealed at 920 °C for 100 hours in Ar gas and \( T_c \) of SCCO \( (x = 0.15) \) was \( \sim 16 \) K. These samples were provided by Mr. Unozawa, Dr. Sasagawa, and Prof. Takagi, Department of Advanced Materials Science, University of Tokyo.

ARPES measurements were performed at beamline 28 of Photon Factory (PF), Institute of Materials Structure Science, High Energy Accelerators Research Organization (KEK), using incident photons with energy of 55 eV. The measurement system is shown in Fig. 5.5. We used a SCIENTA SES-2002
Figure 5.4: Antiferromagnetic phase diagram for NCCO and PLCCO [64]. $T_{N1}$ is the Néel temperature determined by neutron scattering measurements while $T_{N2}$ is the Néel temperature determined by µSR measurements.
electron-energy analyzer in the angle mode, where one can collect spectra over \( \sim 14^\circ \), corresponding to a momentum width of \( \sim 1.1\pi \) (in units of \( 1/a \), where \( a = 3.9 \) Å is the lattice constant). The total energy resolution and angular (momentum) resolution were 15 meV and 0.2\(^\circ\) (0.01\(\pi\)), respectively. Samples were cleaved \textit{in situ} under an ultrahigh vacuum of \( 10^{-11} \) Torr to obtain clean surfaces. The incident photon beam angle was at approximately 45\(^\circ\) to the sample surface with circularly polarized. The sample temperature was measured by a calibrated diode mounted near the measurement position and was \( \sim 18 \) K. The temperature difference between the diode position and the actual measurement position was found to be negligible. The Fermi edge of gold was used to determine the \( E_F \) position and the instrumental resolution before and after the ARPES measurements. The spectral intensity has been normalized to the intensity above \( E_F \), which arises from the second order light of the monochromator.

### 5.4 Results and Discussion

Figure 5.6 shows the plot of ARPES intensity near \( E_F \) in SCCO \( (x = 0.15) \) as a function of the two-dimensional wave vector to illustrate the Fermi surface. Energy distribution curves (EDCs) are integrated with a 60 meV window. The largest ARPES intensity is seen near \((\pi, 0)\), and finite intensity is seen near \((\pi/2, \pi/2)\). Also, the ARPES intensity is not observed near the hot spot, which is the intersection of the Fermi surface and the antiferromagnetic Brillouin zone.
boundary (see Fig. 5.6). A similar behavior of the ARPES intensity has been observed for as-grown Eu$_{1.85}$Ce$_{0.15}$CuO$_4$ as shown in Chapter 4.

We calculated the doping level of carriers from the area of the Fermi surface. From the ratio between the area occupied with electrons and the area unoccupied with electrons in Fig. 5.6, we estimated the doping level to be 0.04 ± 0.02. In case of NCCO ($x = 0.15$), it was reported that the doping level is 0.12 ± 0.05 from the area of the Fermi surface [23]. This implies that SCCO ($x = 0.15$) shows underdoped behavior compared with NCCO ($x = 0.15$). Therefore, the small $T_c$ of SCCO ($x = 0.15$), compared with NCCO ($x = 0.15$), may result from the underdoping.

Figure 5.7 shows EDCs in the nodal direction of SCCO ($x = 0.15$) in the normal state. A blue curve denotes a spectrum on the Fermi surface. Near the Fermi surface, the characteristic peak-dip-hump structure was clearly observed. The energy position of the dip was about 60 meV below $E_F$. Also, one can observe the energy gap. From the leading edge midpoint, we estimated the gap size to be $\sim 15$ meV. This may show that SCCO ($x = 0.15$) is indeed underdoped. Actually, the energy gap in the nodal direction was observed in underdoped NCCO [23]. However, in the underdoped NCCO, clear quasiparticle peak was not observed, different from SCCO ($x = 0.15$). Possibly, in SCCO ($x = 0.15$),
the antiferromagnetic phase and superconducting phase overlap and both effects may be observed in the form of the energy gap and quasiparticle peak. But the clear reason why the energy gap opens in the nodal direction with quasiparticle peak is not understood now. This extraordinary phenomenon has to be resolved in the future studies.

Figure 5.8 shows an ARPES intensity plot in $E$-$k$ space derived from Fig. 5.7. Near $E_F$, one can observe a clear band dispersion with a kink structure, while in NCCO ($x = 0.15$) a clear kink structure was not observed in this direction as shown in the right panel of Fig. 5.1.

Figure 5.9 shows EDCs near $(\pi,0)$ of SCCO ($x = 0.15$) in the normal state. Near the Fermi surface, a weak peak-dip-hump structure was observed compared with that in the nodal direction.

Figure 5.10 shows an ARPES intensity plot derived from Fig. 5.9. From Figs. 5.8 and 5.10, the kink structure near $(\pi,0)$ was weak compared with that in the nodal direction. In NCCO ($x = 0.15$), the clear kink structure is observed in the superconducting state as shown in the left panel of Fig. 5.1.

Figure 5.11 shows EDCs along the Fermi surface from $(\pi/2,\pi/2)$ to $(\pi,0)$ as shown in the inset. Consistent with the intensity map in Fig. 5.6, a clear and intense peak appears near $E_F$ in $(\pi/2,\pi/2)$ and $(\pi,0)$. As one goes from $(\pi/2,\pi/2)$ to $(\pi,0)$, the peak in the low energy region moves to the higher binding energy $\sim 0.2$ eV. Then, near the hot spot, another peak appears in the low energy region. This low energy peak becomes intense as one closes to $(\pi,0)$. These spectra also prove that the suppression of intensity seen in Fig. 5.6 is not due to the matrix elements, which will not change the shape of the spectra drastically.

The behavior of the spectra near the hot spot indicates the transfer of spectral weight from the low energy region to the high energy region as reported in NCCO ($x = 0.15$) [42]. Qualitatively, the full width at half maximum (FWHM) of EDCs, which is regarded as the scattering rate of electrons, is the largest near the hot spot.

5.5 Summary and Conclusion

In summary, we have performed ARPES measurements of SCCO ($x = 0.15$) in the normal state. From the Fermi surface mapping, we observed that the intensity near the hot spot was suppressed like NCCO ($x = 0.15$) and ag-ECCO in Chapter 4. From the area of the Fermi surface, we estimated the doping level to be 0.04±0.02. Therefore, the small $T_c$ of SCCO ($x = 0.15$), compared with NCCO
Figure 5.7: EDCs of SCCO ($x = 0.15$) in the nodal direction. EDCs are arranged as denoted by the arrows. The blue curve denotes a spectrum on the Fermi surface. The direction of the cut is shown in the inset.
Figure 5.8: ARPES intensity plot in SCCO ($x = 0.15$) as a function of the binding energy and the momentum. The Fermi level is denoted by the black line. The direction of the cut is shown in the inset.
Figure 5.9: EDCs of SCCO (x = 0.15) near (π, 0). EDCs are arranged as denoted by the arrows. The blue curve denotes a spectrum on the Fermi surface. The direction of the cut is represented in the inset.
Figure 5.10: ARPES intensity plot in SCCO ($x = 0.15$) as a function of the binding energy and the momentum. The Fermi level is denoted by the black line. The direction of the cut is denoted in the inset.
Energy relative to $E_F$ (eV)

$\sim(\pi,0)$

$\sim(\pi/2,\pi/2)$

Figure 5.11: EDCs along the Fermi surface in SCCO ($x = 0.15$). Black vertical bars denote the peak positions. EDCs are arranged as denoted with black arrows.
$(x = 0.15)$, may result from the underdoping. The EDCs in the nodal direction shows the characteristic peak-dip-hump structure. Accordingly, the strong kink structure was observed in the ARPES intensity plot while in NCCO $(x = 0.15)$ the clear kink structure was not observed. Also, the energy gap $\sim 15$ meV was observed in the nodal direction with quasiparticle peak. Hence, possibly, in SCCO $(x = 0.15)$, the antiferromagnetic phase and superconducting phase overlap and both effects may be observed in the form of the energy gap and quasiparticle peak. In the region near $(\pi, 0)$, the weak kink structure was observed in SCCO $(x = 0.15)$, while in NCCO $(x = 0.15)$ the strong kink structure had been observed in the superconducting state. In the EDCs along the Fermi surface, we recognized that two bands exist and the electron scattering frequently occurs near the hot spot, which is consistent with the results of the Fermi surface mapping.
Chapter 6

Summary and Conclusion

In this thesis, we have studied the electronic structure of the electron-doped high-
$T_c$ superconductors (HTSCs) with $T'$-type structure by angle-integrated photo-
emission spectroscopy (AIPES) and angle-resolved photoemission spectroscopy
(ARPES).

In Chapter 3, we have performed AIPES measurements of $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($\text{Ln} = \text{Pr, Nd, Sm}$) and examined systematic variation in the electronic structure. We observed that the pseudogap is gradually filled in $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($\text{Ln} = \text{Pr, Nd, Sm}$) as the temperature increases, which is similar to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) with $x = 0.15$. The size of the pseudogap in $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($\text{Ln} = \text{Pr, Nd, Sm}$) was also almost the same as that of LSCO ($x = 0.15$). We also observed that the spectral weight near $E_F$ increased as the ionic radius of $\text{Ln}^{3+}$ in $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($\text{Ln} = \text{Pr, Nd, Sm}$) became small. We interpreted this results as below. As the first possibility, we assume that the carrier concentrations of $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($\text{Ln} = \text{Pr, Nd, Sm}$) were the same. Then, we considered that the effect of electron correlation became small, as the ionic radius of $\text{Ln}^{3+}$ in $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($\text{Ln} = \text{Pr, Nd, Sm}$) became small. As the second possibility, we consider overdoping in $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_4$ (SCCO) with $x = 0.15$ compared with $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO) with $x = 0.15$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (NCCO) with $x = 0.15$. Then, we considered that overdoped behavior of SCCO ($x = 0.15$) may result from the oxygen defects in the block layers.

In Chapter 4, we have performed ARPES measurements of as-grown $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ (ag-ECCO) and compared the present results with those of $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{Ln} = \text{Nd, Sm}$). In ag-ECCO, the effect of antiferromagnetism was observed. Also, we observed that the effect of antiferromagnetism in ag-ECCO is stronger than that in as-grown $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$. From the Fermi surface mapping and the dispersive feature of EDCs along the Fermi surface, the behavior of ag-ECCO is
similar to that of underdoped NCCO. This underdoped behavior in ag-ECCO was confirmed by the estimation of the doping level from the area of the Fermi surface. The full width at half maximum of momentum distribution curves of ag-ECCO is larger than that of NCCO ($x = 0.15$). This indicates strong effect of antiferromagnetism by underdoping or strong effect of disorder by apical oxygen. From the ARPES spectra, we have demonstrated that the behavior of ag-ECCO is $n \sim 1 + x$ rather than $n \sim x$.

In Chapter 5, we have performed ARPES measurements of SCCO ($x = 0.15$) in the normal state and compared the present results with those of NCCO ($x = 0.15$). From the Fermi surface mapping in SCCO ($x = 0.15$), we observed that the intensity near the hot spot was suppressed like NCCO ($x = 0.15$). From the area of the Fermi surface, we estimated the doping level to be $0.04 \pm 0.02$, which is underdoping compared with NCCO ($x = 0.15$). Therefore, the small $T_c$ of SCCO ($x = 0.15$), compared with NCCO ($x = 0.15$), may result from the underdoping. In SCCO ($x = 0.15$), the strong kink structure was observed in the ARPES intensity plot while in NCCO ($x = 0.15$) the clear kink structure was not observed. Also, the energy gap $\sim 15$ meV was observed in the nodal direction with quasiparticle peak. This may indicate that SCCO ($x = 0.15$) is in the boundary between antiferromagnetic phase and superconducting phase. In the region near $(\pi, 0)$, the weak kink structure was observed in SCCO ($x = 0.15$), while in NCCO ($x = 0.15$) the strong kink structure had been observed in the superconducting state. In the EDCs along the Fermi surface, we recognized that two bands exist and the electron scattering frequently occurs near the hot spot.

In conclusion, we have elucidated the difference of electronic structure among $Ln_{1.85}Ce_{0.15}CuO_4$ ($Ln = Pr, Nd, Sm, Eu$), which is the electron-doped HTSCs. Especially, the difference between ag-ECCO and NCCO ($x = 0.15$) was revealed in detail. We demonstrated that the effects of antiferromagnetism and disorder have a great influence on the variation of the electronic structure. However, how these effects contribute to the magnitude of $T_c$ will be resolved in the future study. Also, we found the clear kink structure and the energy gap in the nodal direction in the electron-doped HTSCs for the first time.
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