One Gap. Two Gaps. Universality in High Temperature Superconductors

ΒY

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THESIS

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LIST OF ABBREVIATIONS

HTSC	High Temperature Superconductor
T _c	Critical temperature
BCS	Bardeen Copper Schrieffer
FL	Fermi Liquid
ARPES	Angle Resolved Photoemission Spectroscopy
PES	Photoemission Spectroscopy
UHV	Ultra High Vacuum
Bi2212	${\rm Bi_2Sr_2CaCu_2O_{8+\delta}}$
Bi	Bismuth
Sr	Strontium
Cu	Cooper
0	Oxygen
Dy	Dysprosium
La	Lanthanum
\mathbf{FS}	Fermi Surface
SC	Superconducting
PG	Pseudogap

LIST OF ABBREVIATIONS (Continued)

TSFZ	Travelling Solvent Floating Zone
EDC	Energy Distribution Curve
MDC	Momentum Distribution Curve
XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
EDS	Energy Dispersive X-ray Spectroscopy

SUMMARY

One of the goals in contemporary condensed matter physics, is to understand various emergent properties of matter due to many body interactions — e.g. superfluidity, superconductivity, colossal magnetoresistance and so on. Superconductors, discovered more than a century ago, have the remarkable property of zero resistance to electrical current below certain temperatures, commonly known as critical temperatures (T_c 's). The T_c value for conventional superconductor is relatively low, less than 30K, while it could be as high as 150K for a new class of materials, known as high temperature superconductors (HTSCs). The mechanism behind superconductivity in conventional superconductors can be well understood under the framework of the famous BCS (Bardeen, Cooper, Schrieffer) theory, while for HTSCs, it is still a mystery. Angle Resolved Photoemission Spectroscopy (ARPES), which directly probes the momentum space structure of a physical system, has been instrumental to provide new insights in understanding various strongly correlated systems — particularly the HTSC materials.

In this thesis, I will present and discuss our recent research on various Bi2212 HTSCs using ARPES. For the first time, we provided the spectroscopic evidence for the three distinct phases in the normal state of Bi2212 HTSC. By comparing the systematic ARPES data of pure Bi2212 and cation-doped Bi2212 HTSCs, we found that introducing different elements would not only change the carrier concentration, but also create additional disorders inside the system, which is responsible for the different spectroscopic properties. In additon, we found that the deviation

SUMMARY (Continued)

from d-wave gap anisotropy in cation-doped Bi2212 is correlated to the lack of coherent spectral peaks.

I will also give an overview of the synthesis of La-doped Bi2212 single crystals by using floating zone technique. Even though the La content varies along the crystal growth direction, our crystals are of the pure Bi2212 crystal structure, and their carrier concentrations are in the underdoped side of the superconducting dome.

CHAPTER 1

INTRODUCTION

Principle of reductionism, that is all the matter around us is governed by the same fundamental laws, is widely accepted among physicists. One might think that if we know the physical properties of each of the constituents in a system as well as the laws governing them, then the understanding the physical properties of the whole system would follow quite trivially. However, the ability to reduce everything to the fundamental laws governing the elementary particles does not imply the ability to start from those laws and reconstruct the universe [13]!

In a macroscopic system consisting of a large number of particles, the collective behaviors of the system could not be extracted only by understanding the physics of the individual elements. For example, gold wires are made of a substantial number of gold atoms. Even thoug single gold atoms do not conduct electrically, gold wires are very good conductors. Therefore, to understand the collective behaviors of a macroscopic system, we need to study the interactions between the particles inside the system — we need many-body physics.

In reality, many-body interactions in solids are responsible for a large variety of properties of the solids, such as the dynamics of chemical reactions and catalytic processes on surface, carrier transpot properties, and superconductivity, etc. In this thesis, we will focus our discussions only on superconductivity.

1.1 Superconductivity

When metals are cooled to low temperatures, usually the resistivity decreases because of the reduction of inelastic scattering of electrons by phonons. The temperature dependence of the resistivity in a metal is given by $\rho(t) = \rho_0 + cT^5$ where ρ_0 is the residual resistivity due to lattice imperfections and impurities and T is temperature. Now the question is what happens as temperature approaches absolute zero? In 1911, Dutch physicist Heike Kamerlingh Onnes and his collaborators, Cornelis Dorsman, Gerrit Jan Flim and Gilles Holst discovered that the resistivity of mercury became absolute zero below 4.1K (Figure 1)[14, 15]. It took quite a while for both Host and Onnes to realize that the zero resistivity property of mercury below 4.1K was not an experimental artifact but the manifestation of a new electronic phase, namely superconductivity.

However, a superconductor is not just a perfect conductor, it is a perfect diamagnet as well — magnetic field lines get completely expelled from the interior of a superconductors, commonly known as Meissener effect, discovered by Meissner and Ochsenfeld in 1933 (Figure 2). Perfect conductivity together with perfect diamagnetism makes superconductor truly a new state of matter! Since the discovery of superconductivity, many different superconductors have been discoverd, and one can think of different criteria to classify them. Some of them are as follows:

(1) By their response to a magnetic field: they can be Type I, meaning there is a single critical field, H_c, above which superconductivity is completely destroyed; or they can be Type II, such that there is partial penetration of the magnetic field between two critical fields, H_{c1} and H_{c2}.



Figure 1. Resistivity versus temperature plot for mercury. Superconducting phase transistion happens at \sim 4.2 K.



Figure 2. Meissner effect. Upper panel: Magnetic field lines are excluded from a superconductor when it is below it T_c ; lower panel: a magnet levitating above a superconductor cooled by liquid nitrogen.

- (2) By the theory to explain them: they can be conventional (if they are explained by the BCS theory or its extensions) or unconventional (if not).
- (3) By their critical temperature: they can be high temperature (generally considered high if their T_c 's are >30 K), or low temperature.
- (4) By material: they can be chemical elements (as mercury or lead), alloys (as niobiumtitanium or germanium-niobium or niobium nitride), ceramics (as YBCO or the magnesium diboride), or organic superconductors (as fullerenes or carbon nanotubes, though these examples technically might be included among the chemical elements as they are composed entirely of carbon).

1.2 BCS theory of superconductivity

Conventional superconductors are materials that display superconductivity as described by BCS theory or its extensitions. Those superconductor are mostly elemental metals and alloys, and their T_c 's are usually relatively low.

Over the next several decades after superconductivity was discovered, theorists stuggled to find a microscopic theory for superconductivity. Major advances were made with the London theory [16] in 1935 and then by Ginzburu-Landau theory [17] in 1950. But it was not until 1957, 46 years since the discovery of superconductivity, that a universally accepted microscopic theory of the phenomenon was put forth by Bardeen, Cooper, and Schrieffer [18] — BCS theory.

The underlying points of the theory are that the Fermi surface is unstable to infinitesimal attractive forces [19], and electron phonon coupling provides such an attractive force[20]. Therefore, the total energy of the system can be reduced by allowing electrons to pair, which causes an increase in kinetic energy but a much larger decrease in potential energy. The paired electrons have euqal and opposite momentum, and must scatter in tandem, so the total momentum of the electrons in the system (i.e. the current) is conserved by scattering, thus the superconductivity. According to this theory, an energy gap E(T) is formed near the Fermi energy, at temperature T, approximately given by

$$E = 3.52 k_B T_c \sqrt{1 - (T/T_c)},$$

where k_B is Boltzmann constant and T_c the critical temperature; the superconducting transition temperature in terms of the electron-phonon coupling potential and the Debye cutoff energy is given by

$$k_B T_c = 1.14 E_D e^{-1/N(0)V},$$

where N(0) is the electronic density of state at the Fermi energy, and V is interaction potential. From these two formula, one can see: (a) the superconducting gap at T = 0 is directly proportional to T_c , and (b) as $T \to T_c$ the superconducting gap approaches zero in a meanfield fashion (Figure 3).

Two of the key experimental facts that led to the BCS uderstanding were:

(1) The density of states is gapped at the Fermi surface. This was determined experimentally first by the measurement of an exponential specific heat [21, 22]. This led to the realization that some kind of pairing is occurring. The gap was later confirmed by electromagnetic absorption in aluminum [23] and lead [24, 25].



Figure 3. Temperature dependence of superconducting gap in BCS theory.

(2) Phonons are involved. This was shown experimentally by the isotope effect [26, 27]: the critical temperature T_c was found to vary as the inverse square root of the nuclear mass. Since the phonon frequency varies as √k/M, the discovery of the isotope effect led to the realization that phonons are involved.

1.3 High Temperature Superconductor

Since the discovery of superconductivity in 1911, many efforts have been put into seeking superconducting materials with high T_c . However, several decades later, the highest T_c 's had been found was only around 20K, and the field was considered by many people to be at a dead end (Figure 4). It was until 1986 that the research field of superconductivity got reopened, when Alex Müller and Georg Bednorz, two researcheres at the IBM Research Laboratory, created a brittle ceramic compound $La_{2-x}Ba_xCuO_4$ that superconducted at the highest temperature then



Figure 4. A roadmap for the discovery of higher T_c superconductor materials

known: 30K[28]. This discovery triggered a flurry of activity in the field of superconductivity. In the following year, the liquid nitrogen temperature barrier (77K) was broken with the discovery of YBa₂Cu₃O_{7- δ}, superconducting at 90K [29]. Soon a whole host of related were found, e.g., Bi₂Sr₂Ca_nCu_{n+1}O_{6+2n+ δ}, Tl₂Ba₂Ca_nCu_{n+1}O_{6+2n+ δ}, and HgBa₂Ca_nCu_{n+1}O_{2n+4+ δ}. Since all of these new high temperature superconductors have a CuO₂ plane, these materials are referred to as the "cuprates". Recently, a new "family" of superconductors was discovered in iron-based compounds, which are called "pnictides" [30]. All of these new class of materials are called High Temperature Superconductors (HTSC) because their T_c 's are much higher compared to conventional superconductors. In this thesis, we are going to focus only on the high temperature cuprate superconductors, or HTSC for abbreviation.

The discovery of superconductivity in the cuprates was surprising because: (1) no previous superconductor had been found in ceramics, which are normally very good insulators; (2) in their stoichiometric form (with no additional oxygen or other dopant atoms added), these materials are antiferromagnetic Mott insulators. It is conventional wisdom that magnetism cannot coexist with superconductivity. For example, Abrikosov and Gor'kov showed that magnetic impurities disrupt superconductivity and depress T_c in conventional superconductors[31, 32]. The obvious difference between HTSC cuprates and conventional superconductors inspired enormous research in this field during the last several decades, but even today the physics of superconductivity in HTSC is still lack of understanding.

1.3.1 Common features in HTSC cuprates

There is a wide variety of materials which are high temperature cuprate superconductors, e.g., $La_{2-x}Sr_xCuO_4$ (LSCO), $YBa_2Cu_3O_{7-\delta}$ (YBCO), and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) and so on. Even though these families have different chemical compositions, they share certain common features:

(1) They have layered peroskite crystal structure containing one or more CuO₂ planes — that is why they are called cuprates. It is commonly believed that the physical mechanism behind superconductivity in cuprate superconductors are related to the CuO₂ planes.



Figure 5. Crystal structures of three high temperature superconductor families: (a)La_{2-x}Sr_xCuO₄, (b) YBa₂Cu₃O_{7- δ}, and (c) Bi₂Sr₂CaCu₂O_{8+ δ}.

- (2) They have similar phase diagram.
- (3) The generic features of their electronic structure are similar.

Crystal Structure As shown in Figure 5, CuO₂ layers in HTSCs are separated from each other by the so-called charge reservoirs — the insulating block layers. Typically in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO, or Bi2212) system (Figure 5 c), the bonding between two Bi-O layers is caused by Van-der-Waals interaction, which is very weak, and therefore it is easy to cleave Bi2212 samples between the two layer. In Figure 5c we can see that the orthorhombic unit cell of Bi2212 has lattice constant a=b=5.4Å, and c=30.7Å. However, in the real structure, there is a super-lattice with an incommensurate wave vector directed along the b direction. The periodicity along the b-direction is about 27Å.

Electronic Structure The HTSCs exhibit a quasi-2D electronic structure with weak out-ofplane band dispersion. So the electronic structure can be discussed in two dimensional k-space and the 3D Brillouin zone can also be projected into a square. In a parent compound like Bi₂Sr₂CaCu₂O₈, Cu atom is surrounded by six oxygen atoms which form an octahedral environment. Due to the octahedral crystal field, the 3d states will split into degenerate e_g and t_{2g} states. The distortion due to the shift of the apical oxygens make those states split further e_g splits into $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$, and t_{2g} splits into $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ states. Cu is divalent with $3d^9$ electronic configuration, so all the states will be fully occupied except the topmost $3d_{x^2-y^2}$, which is half filled. According to band theory, this system should be metal, but in reality it is a very good insulator — Mott insulator, which is fundamentally different from a conventional band insulator. In a band insulator, conductivity of electron is inhibited by a large energy gap between conduction and valence bands, while for a Mott insulator, conductivity is inhibited by coulomb repulsion between electrons: Coulomb repusion energy is much stronger than the nearest hopping energy. Therefore, a Mott insulator is a direct consequence of local correlations between electrons in the system.

Doping Evolution and Phase Diagram Parent compounds of the high- T_c cuprate superconductors are antiferromagnetic Mott insulators. Upon removal of some of the electrons (or creating holes), the antiferromagnetic phase is suppressed rapidly, and the system enters different phases depending on how much electrons get removed (or holes get created). The dynamic process of changing carrier concentration in a system is known as doping. Operationally, there are two ways to change doping values: (1) altering oxygen content through annealing; (2) replacing some of the trivalent ions in the charge reservoir layers with divalent ions. Some of the high- T_c materials can be doped with electrons as well, known as electron doped high T_c s'. In this thesis, we will focus only on hole doped materials.

Figure 6 shows a schematic phase diagram of hole-doped HTSCs. Parent compounds ($\delta = 0$) are antiferromagnetic insulators with Néel temperature about 300K. The antiferromagnetic phase is suppressed rapidly as doping increases. With further hole doping, antiferromagnetic phase is completely suppressed at doping (δ) = 0.03 ~ 0.05 and superconductivity appears for 0.06 < δ < 0.30. The superconducting region has a typical dome shape. The doping level corresponding to the highest value of T_c is called the optimally doping δ ~ 0.16. The doping values below the optimal doping is called underdopings, while the ones above are called overdoping. In the underdoping side, above T_c, it is called "pseudogap" phase, which is rather



Figure 6. Schematic of the temperature-doping phase diagram of hole-doped high-T $_c$ cuprates.

poorly understood. Close to the optimal doping, above T_c there is a "strange metal" phase where resistivity shows linear temperature dependence. In the overdoping side, the normal state behaves more normally in the sense that the T-dependence of resistivity has some T^2 component.

Superconducting gap The symmetry of the superconducting order parameter is important to understand superconductivity. For conventional superconductors, the order parameter is isotropic s-wave, while for high-T_c cuprate superconductors, it has a $d_{x^2-y^2}$ symmetry. The superconducting gap for HTSCs $\Delta_k = \Delta_{max}(cos(k_x) - cos(k_y))$, where $k = (k_x, k_y)$. In ARPES experiments one can only measure the absolute value of the order parameter, which means one cannot see the change of sign of Δ_k , but one can readily observe that in Josephson Junction experiments. In Figure 7, we are showing ARPES data on one Bi2212 sample, whose T_c is about 83K — its energy gap anisotropy follows d-wave pattern [1]. For samples in the optimal and overdoping region, their gap symmetry is d-wave like, and Δ_{max} becomes smaller with the increase of doping; while for samples in the underdoping side, whether their gap deviates from a simple d-wave symmetry or not is still questionable.

Pseudogap Normal state of the HTSCs is rather poorly understood — especially in the pseudogap (PG) state and in the strange metal state (Figure 6) [33, 34, 35]. Here we are going to discuss only about the PG state. Unlike in the superconducting state, there is no hard gap in the PG state and therefore this energy gap is called pseudogap. A pseudogap can be seen with several different experimental methods. In the spin excitation spectrum, it was first observed in nuclear magnetic resonance (NMR) experiments [36], and then found in



Figure 7. Superconducting gap versus Fermi surface angle (Φ) with fits to a d-wave form (solid curve)[1].

transport measurments, like in-plane resistivity [37], in-plance optical conductivity [38], specific heat measurement [39], and so on. However, the most direct evidence comes from the ARPES experiments. In the ARPES data, the lineshape of antinodal spectrum in the pseudogap state is broad and incoherent. As T goes higher, pseudogap will be filled in at some temperature, which is denoted by T^{*} (see Figure 8). Unlike T_c , T^{*} does not identify a well defined phase transition, rather it is associated with a crossover. T^{*} increases alomost linearly as doping value is decreased, but the origin of pseudogap and how it is related to superconductivity are still not clear. Two scenarios have been proposed as the origin of PG: (1) pseudogap is a precursor to superconducting gap without phase coherence; (2) pseudogap is not related to the pairing gap and is a competing phase. However, whether PG phase is precursor or competing phase to superconductivity is still under debate.

1.3.2 Organization of the thesis

In this thesis, I will present our recent ARPES results on high temperature cuprate superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$. I will also explain briefly about sample synthesis using floating zone. The organization of the thesis is as follows:

In chapter 2, I will briefly discuss ARPES measurements as well as how to represent ARPES data in general. I will also describe a little bit about image furnaces for crystal growth.

In chapter 3, I will present our recent ARPES data investigating the anisotropy of energy gap on $Bi_2Sr_2CaCu_2O_{8+\delta}$. I will show the ARPES spectra as well as energy gap as a function of carrier concentration over the entire superconducting dome, including one insulating sample,



Figure 8. Spectra in the pseudogap state for two samples (broken lines are reference Pt spectra): (a)T_c=83K with T^{*}=170K. (b) T_c=10K with T^{*} higher than 301K [2].

which is alreavy beyond the superconducting dome. The results to be explained in this chapter will be mostly based on our publication in *Nature Physics*[40].

In chapter 4, I will discuss the electronic phase diagram of Bi₂Sr₂CaCu₂O_{8+ δ} HTSCs based on our ARPES data. I will show the evolution of antinodal ARPES spectrum with both carrier concentration (or doping) and temperature. By plotting the doping-dependent curves of both T^{*} (above which antinodal spectra are gapless) and T_{coh} (above which antinodal spectra do not change with temperature), I will show the three distinct regions in the normal state of HTSC cuprate. This part will be mostly based on our recent publication in *Proceedings of the National Academy of Sciences* [41].

In chapter 5, I will show the ARPES data on Dy-doped Bi2212 (Bi₂Sr₂Ca_{1-x}Dy_xCu₂O_{8+ δ}), and compare it with that on pure Bi2212 (Bi₂Sr₂CaCu₂O_{8+ δ}) and Ca-doped Bi2212 samples (Bi₂Sr_{2-x}Ca_xCaCu₂O_{8+ δ}). We found that by introducing Dy, the sharp peaks of ARPES spectrum at antinode got suppressed and the gap anisotropy along Fermi surface does not follow the simple d-wave anymore, even for the moderately underdoped samples.

In chapter 6, I will describe the procedure for synthesizing $Bi_2Sr_{2-x}La_xCaCu_2O_{8+\delta}$ single crystals via floating zone. I will also show the results of XRD, SEM-EDX, and SQUID measurements.
CHAPTER 2

EXPERIMENTAL TECHNIQUES

For all the work presented in this thesis, we have done Angle Resolved Photoemission Spectroscopy(ARPES) study on high temperature superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212), and most of the samples were single crystals grown via Travelling Solvent Floating Zone (TSFZ, or floating zone) method. In this chapter we will firstly describe working principle of ARPES, and then we will briefly talk about the floating zone technique.

2.1 Angle Resolved Photoemission Spectroscopy

2.1.1 Principles of Photoemission Spectroscopy

When light of sufficiently high energy shines on a solid, electrons are emitted out of the solid as photoelectrons. This is the so-called photoelectric effect, and was discovered by Hertz in 1887. Einstein explained this phenomenon in 1905 by invoking quantization of light and the notion of the work function:

$$E_{kin}^{v} = h\nu - \Phi - E_B, \qquad (2.1)$$

where E_{kin}^{v} is the kinetic energy of photo-electrons in the vacuum, $h\nu$ is the photon energy, E_B is the binding energy relative to the Fermi level E_F (chemical potential μ) and Φ is the work function of the solid under study. The work function Φ is the energy required for an electron to escape from a solid through the surface and to reach the vacuum level (E_{vac}) , that is,

$$\Phi = E_{vac} - E_F. \tag{2.2}$$

Even though one cannot measure E_{kin}^v or E_{vac} directly, one can obtain E_B easily by measuring the the kinetic energy of the photoelectron:

$$E_B = h\nu + E_F - E_{kin}.\tag{2.3}$$

In the one-electron approximation, E_B is equal to the energy of a 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 9 diagrammatically shows how the electronic DOS is mapped from the photoemission spectrum.

Photoemission process is a single coherent process which can be rigorous and more accurately described by the one-step model [42] — a electron is excited from the Bloch initial state into a state that is composed of a free propagating part outside the crystal and a damped part inside the crystal, the damping taking account of the limited mean free path of the photoelectrons. However the one-step model is very complex, because photoemission involves many body processes which are in general very difficult to handle quantum mechanically[43, 44, 45, 46, 47].



Figure 9. Schematics of Photoemission Spectroscopy. The left figure represents the electronic structure of the solid, and the right one represents the photoemission spectrum.

One can take some phenomenological approach, known as *three step model*, in which the whole process is decomposed into three sequential steps:

- (1) Photoexcitation of an electron in solid due to light-matter interaction.
- (2) Propagation of the excited electron to the surface.
- (3) Escape of the photoelectron into vacuum.



Figure 10. Pictorial representations for one step and three step process[3].

From now on, we will deal with the photoemission using the *three step model*.

Step One— **photon excitation process** An electron in the solid absorbs one photon and enters an unoccupied state. This can be described by the Fermi golden rule:

$$w_{fi} = \frac{2\pi}{\hbar} |\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu)$$
(2.4)

where w_{fi} is the transition probability from the N-electron initial state Ψ_i^N to N-electron final state Ψ_f^N , and the interaction H_{int} is described with the dipole approximation:

$$H_{int} = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} \tag{2.5}$$

Where **A** is the electromagnetic vector potential with gauge $\Phi = 0$ and **p** is the electronic momentum operator.

The photoexcitation process in general can be very complex, due to the interaction between the emitted electron and the remaining (N-1) ones. However, one can ignore such interactions when the kinetic energy of emitted electrons are high. This is often called *sudden approximation*.Under the sudden approximation, the final state Ψ_f can be written as a product of wave function of the photoelectron $\phi_f^{\mathbf{k}}$ and that of the system with the remaining (N-1) electrons Ψ_f^{N-1} :

$$\Psi_f = \mathcal{A}\phi_f^{\mathbf{k}}\Psi_f^{N-1} \tag{2.6}$$

Where \mathcal{A} is the operator that antisymmetrizes the wavefunction. Let us assume the initial state Ψ_i^N is a single Slater determinant, and write it as:

$$\Psi_i = \mathcal{A}\phi_i^{\mathbf{k}}\Psi_i^{N-1} \tag{2.7}$$

where $\phi_i^{\mathbf{k}}$ is the orbital from which the electron is excited and Ψ_i^{N-1} is the wave function of the remaining (N-1) electrons. Now we can simply write the transition probability as:

$$\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle = \langle \phi_f^{\mathbf{k}} | H_{int} | \phi_i^{\mathbf{k}} \rangle \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle$$
(2.8)

$$w_{fi} = \frac{2\pi}{\hbar} |\langle \phi_f^{\mathbf{k}} | H_{int} | \phi_i^{\mathbf{k}} \rangle|^2 |\langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle|^2 \delta(E_f^N - E_i^N - h\nu)$$
(2.9)

where $\langle \phi_f^{\mathbf{k}} | H_{int} | \phi_i^{\mathbf{k}} \rangle = M_{f,i}^{\mathbf{k}}$ is the one electron dipole matrix element, and the second term is the (N-1) electron overlap integral. After excitation of the electron from orbital \mathbf{k} , the remaining (N-1) electrons are at excited states and will relax to minimize their energy. Assuming that the final state with (N-1) electrons has m excited states with the wave function Ψ_m^{N-1} and energy E_m^{N-1} , the total photoemission intensity measured as a function of E_{kin} at a momentum \mathbf{k} is proportional to

$$\sum_{f,i} |M_{f,i}^{\mathbf{k}}|^2 \sum_m |c_{m,i}|^2 \delta(E_{kin} + E_m^{N-1} - E_i^N - h\nu)$$
(2.10)

where $c_{m,i} = \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle$ such that $|c_{m,i}|^2$ is the probability that after removal an electron from orbital $\phi_i^{\mathbf{k}}$ from N electron state and the remaining (N-1) electrons will be in excited state m.

Step two — the propagation of the excited electron to the surface of solids During this process, photoelectron can be scattered by electrons and phonons. This can be described in terms of mean free path which is inverse proportional to the probability of scattering. In most

cases electron-electron interaction has a strong influence on the mean free path. Even though the property of materials can be very different, an universal mean free path curve can be drawn for various kinetic energies, because the photoelectrons inside solids can be approximated as free electrons. Figure 11 shows the universal curve for the mean free path of photoelectrons at different kinetic energies, characterized by a minimum about a few anstroms at $20 \sim 100$ eV, which is the typical energy range widely used in ARPES. This makes ARPES a surface sensitive technique, probing the electronic states within a few layers from the surface. Therefore ARPES experiments have to be performed on atomically clean and well ordered system, implying that fresh and flat surfaces have to be prepared immediately prior to the experiment in the ultra-high vacuum (UHV) condition.

Step three — escape of photoelectrons into the vacuum There is a potential barrier between the solid surface and the vacuum. The potential is usually called the work function ϕ , which is the minimum energy needed for an electron at Fermi energy to escape into vacuum. Only those photoelectrons whose kinetic energies are higher than the work function ϕ can escape into vacuum. The work function ϕ (a few eVs) can be different from material to material.

2.1.2 Energetics of Angle-Resolved Photoemission Spectroscopy

Angle Resolved Photoemission Spectroscopy (ARPES) takes the technique of Photoemission Spectroscoy (PES) one step further. In ARPES, not only the energy but also the momentum of emitted electrons are measured. Momentum of electrons is obtained by measuring the angles of emission. In order to perform angle or equivalently momentum resolved measurements, electrons are characterized in vacuum by energy analyzers having finite acceptance angle. Once



Figure 11. The variation of the inelastic mean free path with electron kinetic energy "universal curve". Based on Briggs and Seah[4].

the kinetic energy E_{kin} of the electrons and angles of emission (polar angle θ , azimuthal angle ϕ) of the electron with respect to the sample surface are known, the momentum (**p**) or wave vector (**K**) of the photoelectron can be determined. Quite generally, **K** can be written as $\mathbf{K} = (\mathbf{K}_{||}, \mathbf{K}_{\perp})$, where $\mathbf{K}_{||} = (\mathbf{K}_x, \mathbf{K}_y)$ and $\mathbf{K}_{\perp} = \mathbf{K}_z$ correspond to the components of wave vector parallel and perpendicular to the sample surface respectively. A typical geometry of an ARPES experiment is shown in Figure 12 and for this geometry one could write:

$$K_z = \sqrt{\frac{2mE_{kin}}{\hbar^2}}\cos(\theta) \tag{2.11}$$



Figure 12. A typical cartoon showing the schematics of ARPES experiment

$$K_x = \sqrt{\frac{2mE_{kin}}{\hbar^2}} \sin(\theta)\cos(\phi) \tag{2.12}$$

$$K_y = \sqrt{\frac{2mE_{kin}}{\hbar^2}} sin(\theta) sin(\phi)$$
(2.13)

This in turn gives the direct relation between energy and momentum of electrons in the system, provided we know how to relate the momentum and energy of the photoemitted electron to those of the electronic state inside the solid. For most experiments ultraviolet light is used as the impinging radiation and hence one can neglect the momentum associated with the electromagnetic radiation. For a real three dimensional system it is quite non trivial to relate momentum of the photoemitted electron (**K**) to the one (**k**) for a state inside the system, as \mathbf{k}_z is not conserved at the surface because the system differs from the bulk at the surface. But for translationally invariant quasi two dimensional system \mathbf{k}_z is irrelevant and $\mathbf{k}_{||} = (\mathbf{k}_x, \mathbf{k}_y)$ is conserved and for such systems one could simply relate $E = -E_B$ and \mathbf{k} , i.e., the attributes of the electronic state inside the system with E_{kin} and **K** which are measured kinetic energy and momentum of photoelectron, as follows:

$$E = E_{kin} - h\nu \tag{2.14}$$

$$k_x = K_x = \sqrt{\frac{2mE_{kin}}{\hbar^2}} \sin(\theta)\cos(\phi)$$
(2.15)

$$k_y = K_y = \sqrt{\frac{2mE_{kin}}{\hbar^2}} \sin(\theta)\sin(\phi)$$
(2.16)

Hence ARPES gives direct information about the relation between E and \mathbf{k} for electronic states inside the system. We have mostly studied high temperature superconductors which are translationally invariant quasi two dimensional systems. Therefore, the above simple minded formulation would be sufficient for the analysis presented in this thesis.

2.1.3 Spectral Function formalism of ARPES data

In the context of discussions related to many body system, Green's function $G(\mathbf{k}, t)$ formalism[48] is useful. $G(\mathbf{k}, t)$ can be thought as the probability amplitude that an electron having momentum \mathbf{k} added to the system, and will still be in the same state after time t. Fourier transform of $G(\mathbf{k}, t)$ is $G(\mathbf{k}, \omega)$. One can write $G(\mathbf{k}, \omega) = G^+(\mathbf{k}, \omega) + G^-(\mathbf{k}, \omega)$. Now let us consider creation $(c_{\mathbf{k}}^+)$ and annihilation operators $(c_{\mathbf{k}})$ such that $\Psi_i^{N-1} = c_{\mathbf{k}} \Psi_i^N$. In zero temperature limit Green's function can be written as:

$$G^{\pm}(\mathbf{k},\omega) = \frac{\sum_{m} |\langle \Psi_{m}^{N\pm1} | c_{\mathbf{k}}^{\pm} | \Psi_{i}^{N} \rangle|^{2}}{\omega - E_{m}^{N\pm1} + E_{i}^{N} \pm i\eta}$$
(2.17)

One can define single particle spectral function $A(\mathbf{k}, \omega) = -\frac{1}{\pi} Im G(\mathbf{k}, \omega)$, then:

$$A(\mathbf{k},\omega) = A^{+}(\mathbf{k},\omega) + A^{-}(\mathbf{k},\omega) = -\frac{1}{\pi}(G^{+}(\mathbf{k},\omega) + G^{-}(\mathbf{k},\omega))$$
(2.18)

with

$$A^{\pm}(\mathbf{k},\omega) = \sum_{m} \left| \langle \Psi_{m}^{N\pm 1} | c_{\mathbf{k}}^{\pm} | \Psi_{i}^{N} \rangle \right|^{2} \delta(\omega - E_{m}^{N\pm 1} - E_{i}^{N})$$
(2.19)

Now if we compare Equation 2.19 and Equation 2.10, it is easy to see that ARPES intensity can be related to $A^{-}(\mathbf{k}, \omega)$ if we identify ω as the energy of the electron in the system with respect to the Fermi energy E_F . Hence one could finally write

$$I(\mathbf{k},\omega) = M(\mathbf{k},\omega,h\nu)f(\omega)A(\mathbf{k},\omega)$$
(2.20)

where

(1) $M(\mathbf{k}, \omega, h\nu) = |M_{f,i}^{\mathbf{k}}|^2$, dipole matrix element which is general a function of \mathbf{k} , ω and photon energy $h\nu$

- (2) \mathbf{k} is electronic momentum parallel to the sample surface
- (3) ω is the energy of the electron with respect to the Fermi level E_F
- (4) $f(\omega)$ is fermi function which makes sure that photoemission intensity is related to only $A^{-}(\mathbf{k}, \omega)$

2.1.4 Different Representations of ARPES Data

Figure 13 shows a typical ARPES data, for which x-axis is momentum (**k**) and y-axis is energy (ω), and z-axis is intensity, i.e., the number of photoelectrons with energy ω and momentum **k**. There are two ways to view an ARPES spectrum. One can represent ARPES data as:

- (1) a function of ω for a fixed **k**, known as Energy Distribution Curve(EDC)
- (2) a function of **k** for a fixed ω , known as Momentum Distribution Curve(MDC)

For a non-interacting system, EDC and MDC should be equivalent, while for an interacting system, as for example High Temperature Superconductor, they are not equivalent.

2.2 Crystal Growth By Using Floating Zone Method with Image Furnaces

For studies of physics and chemistry of condensed phases, it is crucial to obtain good quality single crystals, because for polycrystalline materials, the properties of the grain boundaries are often manifested stronger than those of the material itself. For the synthesis of oxide single crystals, methods of crystallization from high temperature solutions ("solvent") are usually applied. These are especially useful for materials with incongruent melting points, having high vapor pressure upon melting or undergoing a phase transition under cooling.



Figure 13. EDC and MDC representation of ARPES data



Figure 14. Traveling Solvent Floating Zone (TSFZ). Panel(a) is a sketch showing the principle of floating zone technique. Panel (b) is a real picture og a solvent zone taken during crystal growth: the bright yellow part in the middle is the image of filaments. The lower shiny rod is newly grown crystal, and the upper rod is called feed rod, which is polycrystalline. These two rods are connected by the solvent zone. Panel (c) shows an open mirror furnace.

The floating zone technique is based on the zone melting principle and its main advantage is crucible free, which reduces possible contaminations. A molten zone is established and held by the surface tension between the seed crystalline rod and the raw material rod (feed rod). In Figure 14 we show image furnaces consisting of two ellipsoidal mirrors to focus the light onto a small part of the sample to create a molten zone — this is the place where temperature is highest. This molten zone is moved along the rod by the motion of the rod itself. A single crystal can be generated by spontaneous nucleaion or by using a single-crystalline seed crystal as the initial part of the rod. The driving force of the crystal growth is the temperature gradient in the molten zone. In image furnaces, the sample is protected from air by a large diameter, clear quartz tube which both prevents any evaporant settling on the mirror and allows control of the growth atmosphere and gas pressure around the growing crystal. The positions of the feed and seed rods may be reversed for growth process in the opposite direction.

A comprehensive review of the literature has identified the most important experimental variables during crystal growth: the nature of the feed rod, the growth rate, the growth atmosphere and gas pressure, the temperature gradient within the sample, the molten zone temperature and the rotation rate [49]. Optimizing these parameters is the key to achieving growth stability, and consequently, good crystals.

CHAPTER 3

UNIVERSAL *D*-WAVE GAP IN HTSC $Bi_2Sr_2CaCu_2O_{8+\delta}$

In this chapter, we will present our ARPES data investigating the anisotropy of energy gap in momentum space as a function of carrier concentration over the entire superconducting dome. These discussion will be mostly based on our published work, in Nature Physics [40].

3.1 Introduction

As mentioned in chapter one, high temperature superconductivity in the cuprates occurs by doping a Mott insulator with carriers. By adding carriers, the parent insulator turns into a superconductor for dopings that exceed 0.05 holes per CuO₂ plane. The *d*-wave nature of the superconducting ground state and its low-lying excitations are more or less understood[50, 51]. However, between these phases lies the pseudogap state which is a complete mystery, and it is from this state the superconductivity emerges for all but the most highly doped samples. Consequently, the nature of this phase holds the key to the origin of high-temperature superconductivity. Whereas the electronic excitations in the pseudogap regin have been studied extensively, there is little spectroscopic data at low temperatures, as there is only a very narrow window of dopings where neither superconducting nor antiferromagnetic order occurs. Here, we present ARPES data on single crystals and thin films [52] with doping levels that range all the way from the insulator to the over-doped superconductor. We focus in particular on



Figure 15. Phase diagram of $Bi_2Sr_2CaCu_2O_{8+\delta}$ in the hole-doping (δ), temperature (T) plane (the arrow indicates δ for the insulator). AFM: antiferromagnet.

non-superconducting thin films, just to the left of the superconducting transition temperature T_c dome (see Figure 15), with an estimated hole doping ~ 0.04 [52].

3.2 Symmetrization

As discussed in the first chapter, the spectra obtained from ARPES measurements can be described by $I(\omega) = \sum_k I_0 f(\omega) A(k, \omega)$ (with the sum over a small window about the Fermi momentum k_F), where $f(\omega)$ is the Fermi function, and $A(k, \omega)$ is the spectral function. Making the reasonable assumption of particle-hole symmetry for a small range of ω and ϵ_k , we have $A(\epsilon_k, \omega) = A(-\epsilon_k, -\omega)$ for $|\omega|$, $|\epsilon_k|$ less than few tens of meV (where ϵ_k are the bare energies).



Figure 16. Elimination of the influence of Fermi fuction from raw ARPES spectra via the division by resolution-broadened Fermi function (green curves) and symmetrization (black curves). (a) Symmetrized and resolution-broadened Fermi function divided ARPES spectra which do not show energ gap. (b) Same as (a), but show energy gap. Gap value is determined by the peak position.



Figure 17. Fermi surface of $\text{Bi}_2\text{Sr}_2\text{Ca}\text{Cu}_2\text{O}_{8+\delta}$ in the first Brillouin zone. Nodes, which are indicated by green dots, are the Fermi momenta $k_{\rm F}$, where there are no energy gap. Antinodes, which are indicated by blue dots, are the Fermi momenta having maximum energy gap. The angle Φ is called Fermi surface angle.

It then follows, using the identity $f(-\omega) = 1 - f(\omega)$, that $I(\omega) + I(-\omega) = \sum_k I_0 A(k, \omega)$. This procedure is called symmetrization [53]. To eliminate the effect of Fermi function, we can also divide the ARPES spectra by a resolution-broadened Fermi function. In Figure 16, we show the resluts of one gapless (panel (a)) and one gapped spectra (panel (b)) after performing both procedures, and it turn out that they give consistent result at least in the occupied side.

3.3 Fermi surface of $Bi_2Sr_2CaCu_2O_{8+\delta}$

The red curves shown in Figure 17 show the Fermi surface of a Bi2212 HTSCs in the first Brillouin zone. On the Fermi surface, any point can be defined by two momentum components k_x and k_y , and equivalently, it can be indicated by the Fermi surface angle, Φ . The intersections of the Brillouin zone edge and Fermi surface are known as the antinode (blue dots, $\Phi=0^\circ$), where the energy gaps are maximum; on the other hand, the intersection of the Fermi surface and the diagonal lines are known as the node (green dots, $\Phi=45^\circ$), where there is no energ gap.

3.4 Insulator Sample

It is normally difficult to span the insulator-superconductor transistion in Bi₂Sr₂CaCu₂O_{8+ δ} single crystals. However, it is possible to obtain very underdoped thin films by removing oxygen without film decomposition, as their large suface/volume ratio allows much lower annealing temperatures than those required for crystals. The integrity of the insulating film was confirmed by re-oxygenating them checking their resistivity R(T) and X-ray diffraction spectra[52].

Once sufficient oxygen is removed, the samples have an insulating upturn in resistance R(T) with decreasing temperature, shown in Figure 18a, that is well described by two-dimensionalvariable range hopping [54, 55] (see Figure 18b). We have measured the diamagnetic susceptibility down to 1.5K, finding no trace of superconductivity (sensitivity: 1% of volume fraction).

Figure 19a shows the EDCs at different \mathbf{k}_F . Despite the low temperature, no sharp, coherent features are discernible in the spectra. This is not supersing, because earlier work had found a strong suppression of coherent spectral weight in the superconducting state with underdoping



Figure 18. Transport property of the non-superconductor sample. (a) Resistance versus T plot. (b) Plot of the logarithm of the resistance verus $(1/T)^{1/3}$, showing that the sample is in the variable range hopping regime.

[56]. In contrast, the MDCs in Figure 19b at zero energy show clearly visible peaks. Thus, the excitations are much better defined in **k**-space than they are in energy, and are sharper in the nodal region than antinodal region. Remarkably, despite the insulating-like nature of the resistivity, the MDC peaks indicate a locus of minimum energy excitations similar to that of the superconductors, visible in the ARPES intensity map in Figure 19c. Those MDC peaks are taken as 'Fermi momentum' (\mathbf{k}_F), which were used to generate the EDCs in Figure 19a. Figure 19d shows the ARPES intensity as a function of energy and k for another sample at the same doping, which shows that there is a well-defined dispersion despite the incoherent nature of the EDCs.



Figure 19. Data for insulating samples. (a) EDCs at $k_{\rm F}$ with θ increasing from 0° (top) to 45° (bottom). (b) MDCs along the cuts marked in c (same colour coding in a-d). The top two MDCs are at E = 18 and 22 meV respectively; the rest are at E = 0 meV. (c) ARPES intensity versus **k** at T = 16 K (averaged over a 0 to 10 meV window). The high-intensity points map out the underlying Fermi surface ($k_{\rm F}$) versus angle θ . d, Nodal dispersion for a different sample with the same doping value.

3.5 Determination of energy gap

The energy gap of the superconducting samples was determined from half the spacing between coherence peaks in symmetrized spectra at their corresponding $k_{\rm F}$ (Figure 20e). For the non-superconducting sample, we determine the low-energy gap as the energy position where slop change occurs (intersection of red straight lines in Figure 20b).



Figure 20. Spectral function versus doping. (a) Doping levels δ of four samples for which spectra are plotted in b-e. b-e, Symmetrized EDCs for an insulating film at T=16K (b), a T_c =33K film at T=16K (c), a T_c =69K crystal at T=20K (d) and T_c =80K film at T=40K (e); the spectra are plotted from the antinode (top) to the node (bottom). The intersection of the red lines in b defines the gap in the insulator.

Figure 21 shows the angular anisotropy of the spectral gap (Δ) for all of our thin-film and single-crystal samples. The superconducting samples were measured at temperatures between 16 and 40K, well below their T_c ; the non-superconducting samples was measured at 16K. Normalizing the gaps to their maximal value at $\theta = 0^\circ$, we find that they follow a simple $|\cos(2\theta)|$ behaviour for all samples, superconducting and non-superconducting.

3.6 ARPES data on $Bi_2Sr_2CaCu_2O_{8+\delta}$ Samples with Different Doping Values

In order to better understand the electronic excitations in the insulator, we plot in Figure 20b its EDCs at \mathbf{k}_F , symmetrized to remove the effects of the Fermi function [53], and compare them with superconducting state spectra (Figure 20c-e) at various dopings indicated in Figure 20a. In Figure 20b-e, the top curve corresponds to the antinode ($\theta = 0^\circ$), whereas the lowest curve corresponds to the node ($\theta = 45^\circ$), with the Fermi surface angle θ increasing from top to bottom.

From the symmetrized EDCs shown in Figure 20b-e, we can see some common features in these samples with four different doping values:

- (1) All the samples have anisotropic energy gap that decreases monotonically from a maximal value at $\theta = 0^{\circ}$, to zero at $\theta = 45^{\circ}$.
- (2) Irrespective of doping level, each sample has well defined low energy feature in the spectra
 sharp peaks in the superconducting state (Figure 20c-e), while a break-like feature in
 the insulating state (Figure 20b).

3.7 Conclusion

Our observations imply that:



Figure 21. The spectral gap as a function of doping and angle around the Fermi surface. (a) The spectral gap $\Delta(\theta)$, normalized by its value at the antinode, versus ther Fermi surface angle θ . $\Delta(\theta)$ at all doping levels is consistent with the *d*-wave form $|cos(2\theta)|$ (black curve). (b) Maximum gap as a function of hole-doping.

- (1) The 'd-wave' gap is universal in the superconducting state of HTSCs and this d-wave nature persists through the insulator-to-superconductor transition.
- (2) The maximal energy gap values, plotted in Figure 21b, monotonically increase with underdoping [56], although they might decrease near the superconductor-insulator bountary.
- (3) The sharp quasiparticles of the superconducting state exist down to the lowest doping levels while rapidly losing spectral coherence weight, but are no longer visible on the insulating side. Nonetheless, a low-energy *d*-wave-like gap survives the phase-disordering transition. Obviously, the node must disappear as the Mott insulator is approached[57]. The simplest picture consistent with our data is that the insulating sample exhibits nodal liquid behavior, with a phase-incoherent version of the *d*-wave superconductor[58, 59, 60]. Addition of charged carriers to this nodal liquid leads to high-T_c superconductivity by establishing phase coherence.

CHAPTER 4

ELECTRONIC PHASE DIAGRAM OF HIGH-TEMPERATURE COPPER OXIDE SUPERCONDUCTORS

In this chapter, we will characterize the phase diagram of $Bi_2Sr_2CaCu_2O_{8+\delta}$ HTSCs by concentrating on the evolution of antinodal ARPES spectra with carrier concentration (or doping) and temperature. The discussion will be mostly based on the work published in PNAS [?].

4.1 Introduction

General features of the phase diagram of the high temperature cuprate superconductors have been known for some time. The superconducting transition temperature T_c has a domelike shape in the doping-temperature plane with a maximum near a doping $\delta \sim 0.167$ holes per Cu atom. Above the dome, there are two additional temperature scales seperating normal from superconducting state — T* [2, 61] and $T_{\rm coh}$ citeKaminski2003 lines. Below T* lines, spin excitations become gapped, whereas below $T_{\rm coh}$ line, doped carriers become coherent. Depending how these two lines merge, or how does superconductivity evolve from the normal state, there are two possible phase diagrams, which are shown in Figure 22. Which of these two phase diagrams is the appropriate one has critical implications for our understanding of the HTSC cuprates. In this chapter, we will address the role of these energy scales so as to characterize the phase diagram.



Figure 22. Schematic phase diagrams for two models[5, 6, 7, 8, 9, 10]. (a) A quantum critical point occuring near optimal doping. (b) A doped Mott insulator.

4.2 $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples

The range of sample doping values together with their T^{*} and T_{coh} used in this work is shown in Table I. The crystals were grown in traveling solvent floating zone furnaces, and the thin films were grown using an RF sputtering process. For all the samples, both films and single crystals, $T_c^{max} = 91$ K. All samples were characterized by X-ray diffraction, and their T_c's were determined by the temperature where the resistance R(T) becomes zero within the uncertainty of the measurement. The carrier (hole) concentration of the samples were changed through annealing process by changing their oxygen content. The doping values were determined from the experiential formula [62] $T_c / T_c^{max} = 1 - 82.6 (\delta - 0.16)^2$. Samples are labeled as OP for optimally doped, OD for overdoped, and UD for underdoped.

TABLE I	
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 $T_{\rm c}\,,\, {\rm DOPING}~(\delta),\, {\rm T}^*\,,\, {\rm AND}~ {\rm T}_{\rm coh}\, {\rm FOR}$ THE SAMPLES USED IN THIS WORK.

Sample	$T_{c}\left(K\right)$	δ (holes/Cu)	$T^{*}\left(K\right)$	$T_{coh}\left(K\right)$
UD55K	55	0.091	230	55
UD70K	70	0.107	220	70
UD85K	85	0.132	185	85
UD89K	89	0.144	156	89
OP91K	91	0.160	135	115
OD87K	87	0.183	110	
OD83K	83	0.193		
OD80K	80	0.198	95	200
OD67K	67	0.216	67	231
OD65K	65	0.219	65	
OD60K	60	0.224	60	250
OD58K	58	0.226	58	270
OD55K	55	0.229	55	

4.3 Choice of k point



Figure 23. ARPES intensity at 28 meV binding energy as a function of k_x and k_y for OD87K sample at T = 40K, which exhibits bilayer splitting. The main bonding Fermi surfaces are indicated by red curves, the antibonding Fermi surfaces by yellow curves, and the replica superlattices by white curves. The dashed line indicates the position of the shadow Fermi surface, which is not observed in our experiments. The antinodal k_F of the bonding band where all the data in this work were obtained, is indicated by a white point labelled AN.

In this work, we focus on a single k - point, namely the antinode, where the spectra show the most dramatic temperature and doping dependences.

As illustrated in Figure 23, which is the ARPES intensity at 28 meV binding energy for OD87K sample at superconducting state, bands coming from different origins are intangled

together: Fermi surfaces of the main boding (red curves), Fermi surfaces of the antibonding (yellow curves), the replica superlattices (white curves), and shadow Fermi surface as well (black dashed curves). Our k-point is chosen at the antinode of the bonding band in the Y-quadrant, which is indicated by a white dot, and the reasons are as follows:

- (1) The gap is maximal there;
- (2) Coherence is easily defined there;
- (3) The main and shadow bands do not intersect one another;
- (4) There is no interference from the replica superlattice bands either.

4.4 Spectral signature of T^{*}

For T^* , we need to identify where the spectral gap disappears. Therefore, in this section, we will focus on the evolution of antinodal energy gap with temperature at different dopings.

In Figure 24, we illustrate the two ways to determine the value of T^* , for an optimally doped sample OPT91K: (1) By measuring the energy gap with the increase of temperature until gap closes, as shown in panel (a); (2) By fitting the loss function at different temperature with a straight line, and the extrapolation of the line to zero yields the value of T^* . It turns out that these two methods are consistent to each other in determining the value of T^* . In the same ways, we plot the T^* as a function of doping, shown in Figure 25. In the In the deeply overdoped side, T^* is equal to T_c [40, 63, 64, 65], and then it grows linearly with underdoping.



Figure 24. Determination of T^{*} for an optimally doped sample of $T_c = 91K$. (a) Evolution of the antinodal spectra with temperature. Energy gap closes at T = 138K, i.e., T^{*}=138K. (b) Loss (L) of zero-energy spectral weight $(1 - I(\omega = 0)/I(\omega = \Delta))$ as a function of temperature. The corresponding antinodal spectra are shown in panel (a). L(T = 135K) = 0, i.e., T^{*}=135K. Within error bars, these two ways determining T^{*} are consistent.



Figure 25. T^* as a function of doping. Red double-triangles are data points. In the deeply overdoped side, T^* is equal to T_c , and then it grows linearly toward underdoping.

4.5 Spectral signature of T_{coh}

For T_{coh} , we need to identify where the sharp peak disappears. Thus in this section, we will focus on the evolution of the spectral lineshape with temperatures at different dopings.

Figure 26 shows the evolution of antinodal spectra with temperature for one deeply overdoped sample OD60K (panel (a)) and one moderately underdoped sample UD85K (panel (b)). All spectra for both samples are normalized at binding energy 0.4 eV. In panel (a), at low temperature T = 40K, which is below T_c, we see a very sharp quasiparticle peak. With the increase of temperature, the peak becomes less pronounced, but the lineshape of the high binding energy part remains the same. Once temperature is higher than 250K, we found that the lineshape of the whole spectra become very broad and temperature independent — T_{coh} for this sample is about 250K, which is much higher than it T_c (60K). For the UD85K sample, in panel (b), we also see a well-defined quasiparticle peak at low temperature, even though the size of the peak is smaller compared to that of OD60K. However, once the temperature increases to above T_c , the quasiparticle peak disappears, and the lineshape of the whole antinodal spectra do not change with temperature. Therefore, for the UD85K sample, its $T_{coh} \simeq 85K$, similar to its T_c value.

As discussed in the last section, for moderately and deeply overdoped samples, their antinodal spectra are gapless at $T > T_c$, and therefore the hole-partile symmetrized the EDCs show a peak centered at E_F , as illustrated in Figure 27a of an overdoped sample with $T_c = 60$ K. At low temperature, the peak is very sharp, easily identifiable, while with the increase of temperature, it becomes very broad. We find that for each spectrum, we can fit the broad, incoherent part with a Lorentzian centered at E_F , and the sharp, coherent piece with a Gaussian [66]. The procedure is illustrated in Figure 27b for a similar sample with $T_c = 58$ K. In panel (c), we plot the height of the sharp component of the spectra above that of the constant Lorentzian. One clearly sees a linear decrease with temperature, from which we determine T_{coh} — the temperature where the height difference is zero. The T_{coh} determined in this way — 250K — is consitent to what we observed directly from experiments on OD60K sample (panel (a)). Following this procedure, we identify the T_{coh} for samples of various dopings, and plot the T_{coh} as a function



Figure 26. Evolution of the antinodal spectra with temperature for two samples: (a) OD60K with doping value $\delta = 0.224$ holes/Cu, and (b) UD85K with doping value $\delta = 0.132$ holes/Cu. All spectra are normalized at binding energy 0.4 eV.

of doping δ in Figure 28. In the underdoped side, T_{coh} overlaps with superconducting dome; while in the overdoped side, it grows linearly toward doping.

4.6 Bermuda triangle

In Figure 29a, we plot T^* and T_{coh} at different doping values. We find that these two energy scales have opposite doping dependence, and they cross each other obove the superconducting dome near optimal doping, forming a "Bermuda triangle", where the antinodal spectra are both gapped and coherent [67, 68]. To illustrate this triangle, we plot spectra at fixed doping as a function of temperature. Figure 29b shows spectra for two optimally doped samples. At T



Figure 27. Determination of T_{coh} . (a) Symmetrized EDCs at antinodal at different temperature for OD60K sample. (b) Fits (black curve) of the symmetrized antinodal spectrum (red curve) to a narrow gaussian (blue curve) and a broad Lorentzian (green curve) for OD58K sample, taken at T = 120K. (c) Linearly decreasing intensity of the sharp spectral peak relative to the broad Lorentzian with increasing temperature for samples of three dopings. T_{coh} is where this intensity reaches zero.


Figure 28. T_{coh} as a function of doping. Blue double-triangles are data points. In the deeply and moderately underdoped side, T_{coh} is equal to T_c , and then it grows linearly toward doping.

= 90K (light-blue curve), the sample is just emerging from the superconducting state. With the increase of temperature, within the triangle region, the sharp peaks are weaker, but still exist, and the gap magnitude remains constant. Finally, for $T \ge 115$ K (pink curve), the sharp peaks disapper, whereas the spectral gap remains. This indicates that the $T_{\rm coh}$ line has been crossed, but not the T^{*} line. For $T \ge 138$ K (red curve), the spectral gap has completely filled



Figure 29. Bermuda triangle formed by crossing of the T^{*} and T_{coh} lines. (a) T^{*} and T_{coh} as a function of doping. (b) Evolution of symmetrized antinodal spectra with temperature of two optimally doped sample ($\delta = 0.16$). (c) Antinodal spectra at T = 100K for several samples.

in, and the spectra become very broad and temperature-independent. To further illustrate the crossing, in Figure 29c we also plot the evolution of antinodal spectra at 100K for several sample. Spectra with pseudogap but no sharp peaks are seen in the sample of low dopings (red and purple curves) — above T_{coh} but below T^{*} lines; spectra with pseudogap and sharp peaks is seen in near optimal doping (brown, blue, and light-blue curves) — below both T_{coh} and T^* lines; spectra gapless and with sharp peak are seen in high dopings (green and black curvs) — below T_{coh} but above T^{*} lines.

4.7 Strange metal



Figure 30. Antinodal spectra at \simeq 300K as a function of doping. (a) Dots indicate the doping values of the spectra of the same color plotted in (b). (b) Partical-hole symmetrized antinodal spectra at T \sim 300K for several samples.

Next, we will focus on the region above both T^* and T_{coh} line — the strange metal. In Figure 30b, we show the antinodal spectra of three different samples in the strange metal region. The dopings are indicated by the dots in panel (a), with colors coded according to their spectra. These spectra show two remarkable features: They are extremely broad in energy, exceeding any expected thermal broadening, and their line shapes, well described by a Lorentzian, are independent of doping. The large spectral widths indicate electronic excitations that cannot be characterized by a well-defined energy, implying that the electrons are strongly interacting.

4.8 Electronic phase diagram

Finally, we summarize our results by plotting the phase diagram shown in Figure 31. The solid dots are data point based on ARPES spectra at the antinode and are color coded corresponding to the four different regions in the normal state of the phase diagram. They correspond to the antinodal spectra that are:

- (1) incoherent and gapped (brown dots), in the underdoped region,
- (2) incoherent and gapless (red dots), in the high-temperature strang metal,
- (3) coherent and gapless (green dots), in the overdoped metal,
- (4) coherent and gapped (blue dots), in the Bermuda triangular region above optimal doping formed as a result of the crossing of T^{*} and T_{coh} lines.

In addition, we also plot T^* and T_{coh} as definded above by double triangles. Our experimental finding that the two temperature scales intersect is not consistent with a single quantum critical point near optimal doping, although more complicated quantum critical scenarios cannot be



Figure 31. Electronic phase diagram of $Bi_2Sr_2CaCu_2O_{8+\delta}$ versus hole doping, δ . Brown dots indicate incoherent gapped spectra, blue points coherent gapped spectra, green dots coherent gapless spectra, and red dots incoherent gapless spectra. The brown double triangles denote T^* , and the green double triangles T_{coh} . T_c denotes the transition temperature into the superconducting state (shaded gray and labeled d-wave SC.)

ruled out. For instance, quantum critical points exist at the ends of the dome[69, 70]. We emphasize that, below T_c , we find coherent and gapped antinodal spectra for all doping values, even for very underdoped samples [40]. However, the present experiments do not measure an order parameter, we therefore limit ourselves to calling T^* and T_{coh} "temperature scales".

CHAPTER 5

ONE GAP, TWO GAPS, UNIVERSALITY IN HIGH TEMPERATURE SUPERCONDUCTORS

In this chapter, we will present our detailed doping and temperature dependent ARPES results on Dy-doped Bi2212 samples: $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+\delta}$, and compare them with those on Ca-doped, and stiochiometric Bi2212 (pure Bi2212) samples. Through extensive comparison between different families of Bi2212 samples, we will investigate the universal as well as sample-specific features of low energy electronic states [71]. This chapter is predominantly based on our recently submitted manuscript.

5.1 Sample details

Four families of Bi2212 single crystals have been used in this work. All of them were grown via floating zone technique. T_c's have been altered further through annealing. Stoichiometric material, labeled Bi2212, have an optimal T_c of 91K. These crystals were underdoped to T_c=55K by varying the oxygen content. Ca-rich crytals (grown from material with a starting composition Bi_{2.1}Sr_{1.4}Ca_{1.5}Cu₂O_{8+ δ}) with an optimal T_c of 82K are labeled Ca. Two Dy-doped families were grown with starting compositions Bi_{2.1}Sr_{1.9}Ca_{1-x}Dy_xCu₂O_{8+ δ} with x = 0.1 and 0.3 are labeled Dy1 and Dy2, respectively. A full list of the samples used, T_c values, the maximum T_c values of their families, energy gaps at the antinode Δ_{AN} , and T_c/T^{max}_c values are shown in Table II. The T_c values are determined from the magnetization measurements (shown in Figure 32), and their antinodal energy gap Δ_{AN} are based on ARPES data. Samples' names are defined as the combination of their (1) family names (Bi2212, Ca, Dy1, and Dy2), (2) doping regions (OP denotes optimally doped, UD underdoped, and OD overdoped), and (3) T_c values. For example, Bi2212 OP91K is one optimally doped stoichiometric Bi2212 sample, T_c = 91K.

5.2 Determination of the energy gap

To determine energy gap, we first symmetrize ARPES spectra at Fermi energy to take account of Fermi function. If the symmetrized ARPES spectrum has discernible peak(s), we take the energy position of the peak as the gap value, as shown in Figure 33a; while for the one that does not have peaks, gap value is defined as the energy position where a slop change occurs, as indicated by a vertical black bar in Figure 33b.

TABLE 1	[]
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 $\rm T_c\,,\,T_c^{max}\,,\,\Delta_{AN},\,AND\,\,T_c\,/T_c^{max}\,FOR$ SAMPLES USED IN THIS WORK

Sample	$T_{c}\left(K\right)$	T_c^{max} (K)	$\Delta_{\rm AN}({\rm meV})$	T_c / T_c^{max}
Bi2212 OP91K	91	91	33	1
Bi2212 UD80K	80	91	48	0.879
Bi2212 UD67K	67	91	51	0.736
Bi2212 UD55K	55	91	61	0.604
Ca $OD79K$	79	82	38	0.963
Ca UD $54K$	54	82	54	0.659
Ca UD47K	47	82	62	0.573
Dy1 OD74K	74	86	28	0.861
Dy1 OP86K	86	86	42	1
Dy1 UD80K	80	86	50	0.930
Dy1 UD63K	63	86	61	0.733
Dy1 UD52K	52	86	69	0.605
Dy1 UD38K	38	86	83	0.442
Dy2 OP81K	81	81	55	1
Dy2 UD80K	80	81	59	0.988
Dy2 UD78K	78	81	60	0.963
Dy2 UD73K	73	81	64	0.901
Dy2 UD66K	66	81	65	0.815
Dy2 UD59K	59	81	64	0.728
Dy2 UD37K	37	81	78	0.457
Dy2 UD27K	27	81	82	0.333



Figure 32. Magnetization versus temperature curves for Ca-doped and Dy-doped samples. T_c is defined as the midpoint of the superconducting transition, indicated by the color circles.



Figure 33. Extraction of the energy gap from the symmetrized ARPES spectrum at $k_{\rm F}$. (a) Spectrum has clear peak and the peak position is the gap value. (b) Spectrum does not have clear peak, however, one can see a signature of slope change (as indicated by the vertical black bar). In this case, energy position of the slope change is taken as energy gap.



Figure 34. Demonstration of spectral coherent weight for Dy1 OP86K (upper panels) and Dy1 UD38K (lower panels). In panels (a) and (c), red curves are raw ARPES data, and the blue ones are backgrounds. The backgrounds are smoothed spectra far from $k_{\rm F}$ in the unoccupied side. All of the spectra were normalized at -0.4 eV. In panels (b) and (d), red curves are symmetrized spectra after background subtraction. The double peak for Dy1 OP86K (antinode) and the single peak for Dy1 UD38K (node) can be fit by Gaussians, which are shown as purple dashed curves.

5.3 Coherent spectral weight estimation

In Figure 34, we demonstrate how we extracted the coherent spectral weight by looking at the antinodal spectrum of Dy1 OPT86K (upper panels) and the nodal spectrum of Dy1 UD38K (lower panels). We took spectra far from Fermi momentum (k_F) as a background, and smoothed them to minimize the noise level when subtracting the background from the raw spectra. All raw spectra and backgrounds were normalized at -0.4 eV (panels (a) and (c)). After subtracting the background, we particle-hole symmetrized the spectra and fit the peaks with Gaussians, which are shown as solid red and dashed purple curves in panels (b) and (d), respectively. The coherent spectral weight is calculated as the ratio of the area under the Gaussian to that of the symmetrized background-subtracted spectra from -0.4 eV to +0.4 eV.

5.4 ARPES spectra and superconducting gap on Dy1 samples

The introduction of Dy leads to a small suppression of the optimal T_c and different spectroscopic behaviors compared to pure Bi2212. Here, we will begin our comparison by showing the ARPES data of two Dy1 samples (Bi₂Sr₂Ca_{1-x}Dy_xCu₂O_{8+ δ}, x=0.1): one optimally doped with $T_c = 86K$ (Dy1 OP86K), and one deeply underdoped with $T_c = 38K$ (Dy1 UD38K).

5.4.1 ARPES data on Dy1 OP86K sample

Figure 35 are symmetrized EDCs at $k_{\rm F}$ of Dy1 OP86K sample at 22K. The spectra are plotted from the node (bottom) to the antinode (top). All of these spectra show well-defined quasiparticle peak(s) over the entire Fermi surface.

Considering the 4-fold symmetry of Cu-O plane in HTSCs, in Figure 36a, we plot one quarter of the ARPES intensity map at BE = 40 meV in the first Brillouin zone in π/a , together with



Figure 35. Symmetrized ARPES spectra of Dy1 OP86K sample around the Fermi surface. The bottom spectrum is the symmetrized EDC at node, and the top one is at antinode.

the contour of the Fermi surface (grey cruves). Red means high intensity and blue means low intensity. Figure 36b is a plot of superconducting gap as a function of Fermi surface angle, which follows $|\cos 2\phi|$ d-wave form—blue curve. The gap energy was extracted from the peak positions of the spectra shown in Figure 35.



Figure 36. Intensity map and gap anisotropy of Dy1 OP86K sample. (a)Intensity map at binding energy 40 meV, i.e., $I(\vec{k}, \omega=40 \text{meV})$, in one quarter of the first Brillouin zone. ϕ is Fermi surface angle. (b) Plot of superconducting gap magnitude as a function of Fermi surface angle ϕ (0° is the antinode and 45° is the node).

5.4.2 ARPES data on Dy1 UD38 sample

Similarly, in Figure 37, we show the symmetrized EDCs at $k_{\rm F}$ from the node (bottom) to the antinode (top), for one deeply underdoped sample Dy1 UD38K. For this sample, the quasiparticle peak is easily indentifiable in the vicinity of the nodal region (red curves), but it becomes weaker and then disappears on moving towards the antinode (blue curves) (This is consistent with earlier work on Dy-doped Bi2212 and also Bi2201 [72, 73, 74, 75, 76]). This



Figure 37. Symmetrized ARPES spectra of Dy1 UD38K sample around Fermi surface at 22K, from the node (bottom) to the antinode (top). The spectra which do not have discernible peaks are highlighted with blue color, and the vertical black bars indicate the change of slope.

is very different from what we have seen in the Dy1 OP86K sample (Figure 35), or pure $Bi_2Sr_2CaCu_2O_{8+\delta}$ sample, even with the similar T_c 's ([40]).

The spectroscopic difference between Dy1 OP86K and Dy1 UD38K samples can also be seen from their intensity maps. Figure 38a shows the ARPES intensity of Dy1 UD38K sample at 82



Figure 38. Intensity map and gap anisotropy of Dy1 UD38K sample. (a)Intensity map at binding energy 82 meV, in one quarter of the first Brillouin zone, with the unit of $\pi/a.(b)$ Plot of superconducting gap magnitude as a function of Fermi surface angle Φ . The points where the gap function deviates from d-wave form are highlighted with blue color.

meV (~ Δ_{max}). Red color means high intensity and blue means low intensity. In this image, there is almost no intensity in the region close to Brillouin zone boundary. In other words, the low energy spectral weight gets completely wiped out in the antinodal region. In addition, the gap anisotropy of Dy1 UD38K sample behaves differently from that of the optimally doped sample, as shown in Figure 38b, the near-nodal gaps (red triangles) follows a d-wave form, while the gaps in the near-antinodal region does not (blue squares). In the near-nodal region, the ARPES spectra have easily indenfiable quasiparticle peaks (red curves in Figure 37), and the gaps were obtained from the peak postions; in the near-antinodal region, where the ARPES spectra do not have peaks (blue curves in Figure 37), the gap values were identified as the energy scales where slop change occurs (black bars on blue curves).

Despite the larger error bar associated with gap scale extraction in the absence of quasiparticles, it is nevertheless clear that the Dy1 UD38K sample has an energy gap that deviates markedly from the simple d-wave form. This observation is called "two-gap" in the UD regime, in contrast with a "single gap" near optimality (Figure 39b).

5.5 ARPES spectra and superconducting gap on Dy2 samples

In the same way, next, we show the ARPES data on two Dy2 samples: one optimally doped sample of $T_c = 81K$ (Dy2 OP86K) and one moderately underdoped sample of $T_c = 59K$ (Dy2 UD59K). These samples have more Dy content compared to Dy1. All of the data shown here were taken in the superconducting state. Figure 39 shows symmetrized EDCs at k_F , as well as gap anisotropies on these two Dy2 samples: Dy2 OP81K (panels (a) and (b)) and Dy2 UD59K (panels (c) and (d)). The Dy2 OP81K sample shows well-defined quasiparticle peaks over the entire Fermi surface (panel (a)) with a simple d-wave gap (blue curve in panel (b)); while for Dy2 UD59K sample, it shows well-defined quasiparticles only near the node (red spectra), but not near the antinode (blue spectra) (panel (c)), and its gap anisotropy follows the "two-gap" behavior: the near-nodal gaps (red triangles in panel (d)) follow a d-wave form, and their gap energy are obtained from the position of the quasiparticle peaks (red curves in panel (c)), but in the antinodal region, where the ARPES spectra do not show quasiparticle peaks (blue curve in panel (c)), the gaps deviate from the d-wave form (blue squares in panel (d)), and the gap



Figure 39. Superconducting state spectra and energy gap for optimally doped and highly underdoped Dy2 samples. (a) Symmetrized spectra at $k_{\rm F}$, from the antinode (top) to the node (bottom) for Dy2 OP81K sample. (b) The energy gap as a function of Fermi surface angle. The blue curve is a d-wave fit to the data. (c) The same as panel (a) for an UD59K sample. Curves with no discernible quasiparticle peaks are shown in blue. (d) Gap along the Fermi surface from data of panel (c). The points deviating from d-wave are denoted with blue squares.

values were indentified as the energy scales where slope changes (black straight crosses in panel (c)).

5.6 Comparion among Dy-doped, Ca-doped and pure Bi2212 samples

In this section, we will compare the ARPES data on various Dy-doped, Ca-doped and pure Bi2212 samples. Our comparison will be concentrated on the following aspects:

(1) Superconducting state antinodal spectra as a function of underdoping;

- (2) Gap anisotropies in the momentum space;
- (3) Evolution of coherent spectral weight with doping.

5.6.1 Doping evolution of antinodal spectra for each family

In Figure 40, we show the evolution of antinodal spectra for four different Bi2212 families: Dy1, Dy2, Ca and Bi2212. At the antinode, the energy gap is maximum, and as we shall see, the differences between various samples are the most striking at this place. From panels (a) and (b), which are spectra of Dy1 and Dy2, we see a sudden loss of quasiparticle weight for T_c 's blow 60K. These observations are in striking contrast to the pure Bi2212 and Ca-doped data (panel (c)), where we do see a systematic reduction of the quasiparticle peak with underdoping, but not a complete wipe out of the low-energy spectral weight. To the extent that the superconducting state peak-dip-hump lineshape [77, 78] originates from one broad normal-state spectral peak, the changes in spectra of Dy materials are not simply due to a loss of coherence, but more likely a loss of the entire spectral weight near the chemical potential.



Figure 40. Doping evolution of the antinodal spectra for four Bi2212 families: (a) Dy1; (b) Dy2; (c) Ca and pure Bi2212.



Figure 41. Antinodal ARPES spectra at superconducting state. (a) Spectra for OP samples of three families—Bi2212 (blue), Dy1 (green) and Dy2 (red). (b) Spectra for UD samples with similar $T_c (\sim 66K)$ for Bi2212 (blue) and Dy2 (red). (c) Same as in (b), but for four UD samples with T_c near 55K for Bi2212 (blue), Ca (gray), Dy1 (green) and Dy2 (red).

5.6.2 Comparison of antinodal spectra at similar doping/ T_c

Having shown the doping evolution of antinodal spectra in each of the four Bi2212 families, here we will maintain carrier concentration or T_c , comparing the antinodal spectra of samples from different families. In Figure 41a, we show antinodal ARPES spectra of optimally doped samples from three families: Bi2212, Dy1 and Dy2. All of the these spectra have well-defined quasiparticle peaks, but with the increase of the cotent of Dy, the antinodal gap Δ_{max} becomes larger and the quasiparticle peak becomes weaker. This trend continues down to moderately underdoped samples, as seen in Figure 41b, where we show underdoped Bi2212 and Dy2 samples with very similar $T_c \simeq 66$ K. For more severely UD samples, with $T_c \lesssim 60$ K, spectral changes in the Dy-substituted samples are far more dramatic. In Figure 41c, we see that quasiparticle peaks in the Dy samples are no longer visible, even well below T_c . In contrast, Bi2212 and Ca-doped samples with comparable T_c continue to exhibit quasiparticle peaks.

5.6.3 Comparison of gap anisotropy of samples from Dy2 and Ca families

We next show the gap anisotropies of samples from Dy2 and Ca families, which have different cation-substitutions, but almost the same T_c^{max} . In Figure 42, we compare Ca-doped samples (panels (a, b) and Dy2 samples (panels (c, d)) with essentially identical T_c . The near optimal samples, Ca OD79K (panel (a)) and Dy2 OP81K (panel (c)) both have a simple d-wave anisotropy (although different maximum gap values at the antinode). However, upon being underdoped to some extent, the two have markedly different spectral behaviors. The Dy2 UD59K sample (panel (d)) shows two-gap behavior, and an absence of quasiparticles near the antinode (Figure 39c); while the Ca UD54K sample (panel (b)) continues to exhibit sharp



Figure 42. Energy gap anisotropy of various samples. (a) Ca OD 79K (where $T_c^{max} = 82K$); (b) Ca UD54K; (c) Dy2 OP81K; (d) Dy2 UD59K.

quasiparticle peaks and a "single gap", despite a very similar T_c and not-so-different gap values as Dy2 UD59K.

5.6.4 Antinodal gap as a function of doping

Having established the qualitative differences in the gap anistropies for various samples as a function of underdoping, we next summarize the doping evolution of the antinodal gap energy. Instead of estimating the carrier concentration in our samples using an empirical formula [62] (that may or may not be valid for various cation substituions), we prefer to use the measured T_c/T_c^{max} to label the doping. From Figure 43, we see the antinodal energy gap grows monotonically with underdoping. This is consistent with the known increase in the gap with underdoping.

5.6.5 Quasiparticle weight at antinode and node

As seen previously in this chapter, once become moderately or deeply underdoped, Dydoped samples lose low energy weight at the antinodal spectra, and their gap anisotropies show "two-gap" behavior, so the "one-gap" versus "two-gap" behavior has a direct correlation with the coherent spectral weight Z. In Figure 44, we plot the doping evolution of coherent spectral weight at both the antinode (panel (a)) and the node (panel (b)) for the four families. The measured T_c/T_c^{max} is used to label the doping. The procedure used to estimate the weight is demonstrated in Figure 34. At the antinode, Dy1 and Dy2 samples both show a sudden and complete loss of Z with underdoping (a similar behavior has been seen in YBa₂Cu₃O_{6+x} [79]), which coincides with the appearance of two-gap behavior. In marked contrast to the Dy samples, the Bi2212 and Ca samples that exhibit a single d-wave gap show a gradual drop in



Figure 43. The antinodal energy gap as a function of doping for various samples. The doping is characterized by the measured quantity $t = T_c/T_c^{max}$, with UD samples shown to the left of t = 1 and OD samples to the right.



Figure 44. (a) The coherent spectral weight for antinodal quasiparticles as a function of doping. The Dy-doped samples exhibit a rapid suppression of this weight to zero for UD $T_c/T_c^{max} < 0.7 - 0.8$, while the Ca-doped samples show robust antinodal peaks wven for $T_c/T_c^{max} \simeq 0.5$. (b) The coherent spectral weight for nodal quasiparticles as a function of

doping, which is seen to be much more robust than the antinodal one. The doping is characterized by the measured quantity $t = T_c/T_c^{max}$. All results are at temperature well below T_c .

the antinodal Z. On the other hand, we find that the nodal excitations are much less sensitive to how the sample is underdoped compared to the antinodal ones. The nodal quasiparticle weight Z in panel (b) decreases smoothly with underdoping for all families of samples, as expected for a doped Mott insulator [80].

5.7 Discussion

By comparing ARPES data on BSCCO samples of four families: Dy1, Dy2, Ca, and Bi2212, we have examined the universality of the one-gap versus two-gap behavior. At low temperature, Bi2212 and Ca samples exhibit a single d-wave gap, and show a greadual drop in the antinodal coherent weight, while for moderately and deeply underdoped Dy-doped samples, they have twogap structure and completely lose quasiparticle weight near the antinode[81, 82, 83, 84, 85, 86]. Two possiblilies, not mutually exclusive, could be the causes of this behavior in Dy-doped samples: disorder and competing order. However, it is not a priori clear why certain cation substitutions (Dy) should lead to more electronic disorder than others (Ca). One possibility is that Dy has a local moment, but there is no direct experimental evidence for this. The two-gap behavior in UD samples, with a large antinodal gap that persists above T_{c} , is suggestive of an order parameter, distinct from d-wave superconductivity, that sets in at the pseudogap temperature T^* , but our ARPES measurements do not directely probe order parameters. However, if we assume that the two-gap behavior is an indication of a competing order, we can conclude the following. The presence or absence of a competing order depends sensitively on cation substitutioon, and is not a universal feature of HTSC materials. The defining characteristics of HTSC — like the superconducting dome (T_c versus doping), sharp nodal quasiparticles, an antinodal gap that decreases monotonically with doping, and the normal state pseudogap are independent of whether the material exhibits one-gap or two-gap behavior. Thus, insofar as the two-gap structure implies a competing order, the latter is not a necessary ingredient for the phenomenon of high temperature superconductivity.

CHAPTER 6

CRYSTAL GROWTH AND CHARACTERIZATIONS ON LA-DOPED BI2212 SINGLE CRYSTALS

In this chapter, we will present the details of the synthesis and single-crystal growth of $Bi_2Sr_{2-x}La_xCaCu_2O_{8+\delta}$. We will also discuss several characterization measurements performed on these crystals.

6.1 Synthesis of polycrystalline samples

We have prepared $Bi_2Sr_{2-x}La_xCaCu_2O_{8+\delta}$ samples of two different La concentrations: La/Sr=0.1/1.8 and La/Sr=0.2/1.7, which are called BiLa1 and BiLa2, respectively. Solid state reaction was used to make the polycrystalline feed rods[87, 88, 89, 90, 91].

Powders of Bi₂O₃, SrCO₃, CaCO₃,CuO and La₂O₃ were dried and mixed in the desired cation ratio Bi: Sr: La: Ca: Cu = 2.1: (1.9-x): x: 1:2 (x=0.1 for BiLa1 and x=0.2 for BiLa2), and then calcinated at 800°C first and then repeatly at 825°C with intermediate grinding to eliminate traces of carbonate (refer to the phase diagram shown in Figure 45 [11]). The calcined powders were finally compressed into rods of about 100 mm in length and 8 mm in diameter under a hydrostatic pressure of 27 Kpsi. These rods were then sintered at 825°C for 10h with 20% O_2/Ar gas flow.



Figure 45. High temperature phase diagram of $Bi_x Sr_2 CaCu_2 O_{8+\delta}$ [11].

6.2 Crystal Growth with Floating Zone Method

6.2.1 Congruent and Incongruent Melting

According to the melting behavior, chemical compounds can be divided into two main categories: congruently and incongruently melting materials. Fot a congruently melting compound, the composition of the liquid is the same as that of its initial solid, and it can directly be grown via slow cooling from the melt; while an incongruently melting solid decomposes into another substance as it melts, and therefore cannot directly be grown from the melt. Most of the high- T_c superconductor materials are incongruently melting ones.

The principles of congruent and incongruent melting can be understood by looking at Figure 46, which shows a schematic partial phase diagram of a congruently as well as an incongruently melting compound AB (here a binary compound with stoichiometry AB is used to represent the phase diagram).



Figure 46. Two types of phase diagram for a binary compound AB: congruent melting (a) and incongruent melting (b) [12].

In Figure 46a, between the composition ranges A and AB or AB and B, it is a simple eutectic system, "x" and "z" are the two eutectic points, and T_1 and T_2 are the two eutectic temperatures. No changes will be observed at T_1 and T_2 on heating pure AB, only when another component A or B is added. In Figure 46b, the compound AB melts incongruently at temperature T₂ to give a mixture of solid A and liquid of composition "x". On further heating, solid A gradually dissolves and the liquid moves along the liquid curve in the direction "xl". At temperature T₃ the liquid composition has reached "l" and the last solid A disappears. The point "x" is an invariant point where three phases coexist: solids A, AB and liquid. It is peritectic point because the composition of the liquid cannot be represented by positive quantities of the two coexisting solids, i.e., "x" does not lie between A and AB, which is the case for an eutectic point (Figure 46a). A characteristic feature of a peritectic is that it is not a minimum point in the liquid line, as eutectic is. Note that between "x" and "m", the system would behave in an identical fashion to the case of congruent melting. During crystal growth via floating zone technique, at temperature between T_1 and T_2 , where the composition of the solvent would have choice between "x" and "m", the compound AB is separated from the system as newly grown crystal on top of the seed rod.

6.2.2 Crystal Growth

Maintaining a stable condition during crystal growth is extremely important because this is crucial to keeping the composition of the crystal unchanged. For high- T_c superconductor materials, whose growth rates are generally very low (a few milimeters per day, because of incongruent melting as discussed in the previous section), the porosity of the polycrystalline feed rod could cause a solvent soaking problem. It means that the solvent would penetrate into the feed rod by capillary action during the crystal growth, diminish the amount of the solvent, change the solvent composition and eventually the feed rod would become "unbrella" shaped and the stable growth condition get destroyed. In order to avoid porosity, we usually do a "fast-scan" to densify the polycrystalline rods before using them as feed rods for crystal growth, in which the polycrystalline feed rod was passed through the molten zone at a much higher speed, about $30\sim40$ mm/h for Bi₂Sr₂CaCu₂O_{8+ δ} materials.



Figure 47. Crystal growth via Floating Zone technique. (a) The bottom of the feed rod & the top of the seed rod have started to melt, but the two rods are still separated. (b) Molten zone has just formed, and is held by the surface tension between the two rods. (c) Molten zone becomes stable, with sharp and flat liquid/solid interfaces at +3mm and -3mm. A densifed rod (La/Sr=0.2/1.7) obtained after a "fast-scan" is shown in (d). A as-grown BiLa2 crystal is shown in (e). The crystal is short because of the incomplete crystal growth due to the collapse of the molten zone.

All of the crystal growth experiments were carried out in a NEC image furnace with double ellipsoidal reflectors (Type SC-M15HD, Nichiden Machinery Ltd., Japan). 750W halogen lamps was used as the radiation source. A 100 mm long feed rod of stoichiometric $Bi_2Sr_{1.9-x}La_xCaCu_2O_{8+\delta}$ with (x=0.1 or 0.2) was suspended from the upper shaft by a platinum wire. A 40 mm long rod (acting as a seed rod) with the same chemical stoichiometry was mounted to the lower shaft. During crystal growth, the upper and lower shafts were counter rotated to achieve a uniform melt composition and homogeneous radial temperature distribution. 20% O₂/Ar was flowed over the rod at a speed of 200 ccm.

To establish the molten zone, the bottom of the upper feed rod and the top of the lower seed rod were heated until they began to melt, and then the lower seed rod was raised into contact with the upper rod. By fine adjustment of the lamp power, a stable molten zone with a constent size would be established. In Figure 47, panels a, b and c show three important phases during crystal growth. The upper feed rod and the lower seed rod were moving downward in a synchronized mode,

- (a) The bottom of the feed rod & the top of the seed rod have started to melt with no molten zone formed yet;
- (b) A molten zone is formed between the feed & seed rods;
- (c) Molten zone becomes stable with sharp and flat solid-liquid interface.

The floating molten zone is held in place by the surface tension of the liquid. The crystal grows at the top of the seed rod, driven by the vertical temperature gradient. However, for the case of La-doped Bi2212, the molten zone was never stablized, and the situation was even worse when more La was added. During the crystal growth, it was very hard to obtain a reasonably flat and sharp lower solid/liquid interface, because the crystals did not grow evenly along the radial direction, which caused a big bulge in the molten zone. With more new liquid feeded in, the surface tension would not be strong enough to hold so much liquid, and eventually, part of the solvent would spill along the seed rod, or even the whole molten zone would be lost. In Figure 47d and e, we show the densified La-doped Bi2212 (La/Sr=0.2/1.7) rod, and one BiLa2 as-grown crystal. This crystal is short because of the incomplete crystal growth due to the collapse of the molten zone. As we will see later, because of the instable growth condition, La was not eventually distributed along the crystal, and many grain boundaries were created on the surface of cleaved crystals as well.

6.3 **Results and Discussion**

The composition and phase purities of all samples were verified via X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDS) measurements. A scanning electron microscope (SEM) was used to check the surface quality of cleaved crystals. Annealings under different temperature and partial pressure of oxygen were performed to get samples of different T_c 's. The magnetic properties were investigated using a SQUID magnetometer.

6.3.1 XRD results

Powder XRD measurements were performed (PANalytical X'Pert Pro, $K\alpha$ radiation) on Bi₂Sr_{2-x}La_xCaCu₂O_{8+ δ} crystals. Crystals were ground to avoid preferred orientation. In Figure 48, we show the spectra of a typical BiLa1 crystal, with the standard Bi2212 pattern


Figure 48. XRD spectra of $Bi_2Sr_{2-x}La_xCaCu_2O_{8+\delta}$ crystal. Crystals for XRD measurements were ground to avoid preferred orientation. The green bars indicate the standard pattern for Bi2212 phase.

indicated by the green bars. By analyzing the XRD peaks, we conclude that our La-doped crystals have no traces of Bi2201 or Bi2223 phases, or carbonate.

6.3.2 SEM and EDS results

Chemical compositions of the La-doped crystals were tested by using a Oxford Link Isis EDS system on a Hitachi S-2700 scanning electron microscope, and 20 KeV was used as the



Figure 49. Photograph of the grown BiLa1 crystal boule(top) and secondary electron SEM micrographs of the BiLa1 samples cleaved from different sections of the crystal boule. On the photograph, section C15 is the starting point of the crystal growth, and C2 is the final quenched zone. Samples for SEM mesurements were cleaved from the sections between C6 and C14.

accelerating voltage. In Figure 49, the upper panel shows the photograph of the grown BiLa1 crystal boule. In order to check the compositional homogeneity along the growth direction, we sliced the crystal boule into 18 sections, with section C15 the starting point during the crystal growth, and C2 the final quenched zone. Samples for the SEM measurments were cleaved from the sections between C6 and C14, as shown in the lower panels, at $200 \times$ magnification. Brighter regions have more electrons, or higher mass density. The "cracks" reveal the grain boundaries, which were created during the crystal growth.

The results of EDS measurements on both BiLa1 and BiLa2 crystals (upper: BiLa1, lower: BiLa2) are shown in Figure 50. For each of the crystals, the right panel shows raw EDS spectra of samples cleaved from different sections of the crystals, and the left table lists the analyzed results. Spectra were only focused on the L α peaks of La. The analysis was done by fitting the EDS spectra with Gaussians, but only considering the number of electrons coming from the K-shell for elements Ca and Cu, L-shell for Sr and La, and M-shell for Bi (we did not consider oxygen because Oxygen is very light, and thus its peaks only appear in the low energy part). According to this result, the La is not evenly distributed along the crystal within error bar (\pm 0.03 or 0.04 for both crystals). Unfortunately, the EDS equipment we have does not have a calibration for this compound, these results do not have quantitatve meaning, but only give us a rough idea about the distribution of La.

6.3.3 SQUID results

The magnetic properties of La-doped Bi2212 samples were tested via SQUID measurements, and the results are shown in Figure 51. For both crystals BiLa1 (panel a) and BiLa2 (panel

Crystal BiLa1

Sample Bila1_C6 Bila1_c7 Bila1_c8 Bila1_c10 Bila1_c10 Bila1_c10 Bila1_c10 Bila1_c10 Bila1_c10 Bila1_c10 Bila1_c10 Bila1_c11 Bila1_c12 Bila1_c13 Bila1_c14	Co-K 15.94 15.67 16.02 14.52 15.11 14.85 15.26 15.25 14.25	Cu-K 7.44 7.43 7.41 7.53 7.44 7.53 7.44 7.70 7.24 7.60	5L 18.18 18.24 18.18 19.03 18.73 18.73 18.19 17.73 18.51 19.37	Lo-L 0.87 1.15 0.71 1.77 0.85 1.23 0.94 0.55 1.08	C16 C17 C18, seec BI-M 57.57 57.51 57.68 57.37 57.77 58.29 58.37 58.37 58.46 57.70	Intensity (a.u.)	BiLa1 C6 C7 C7 C9 C10 C11 C12 C13 C14 4.5 5.0 5.5 6.0 Energy (eV)
Crys Remainin sample BiLa2_C2 BiLa2_C3 BiLa2_C4 BiLa2_C5	tal E feed Cok 15.52 15.43 15.77	C9 C9 C0-K 7,45 7,51 7,51 7,52	2 57 ^{C6} C5 54-L 17.55 17.59 17.21 17.22	a-l 1.49 1.87 2.06 2.32	22 C1 BI-M 57.99 57.73 57.93 57.95	Intensity (a.u.)	BiLa2 C2 C3 C3 C4 C5 C6 C7 C7 C8 C9
BiLa2_C6 BiLa2_C7 BiLa2_C8 BiLa2_C9	15.45 15.81 15.09 15.51	7.43 7.50 7.50 7.67	17.16 16.96 17.13 17.43	1.91 2.39 3.36 2.28	58.05 57.35 56.92 57.11		4.5 5.0 5.5 6.0 Energy (eV)

Figure 50. EDS results of BiLa1 (upper) and BiLa2 (lower) crystals. For both cases, the right panel shows the raw EDS spectra of samples cleaved from different sections of the crystal. Sections C6 to C14 for BiLa1, and sections C2 to C9 for BiLa2. Spectra are normalized to the intensity of Bi. The vertical black lines indicate the positions of La L α peaks. The left tables list the analyzed results: possible cations as well as their atomic ratios(atom%), by only considering the number of electrons from the K-shell for Ca and Cu, L-shell for Sr and La, and M-shell for Bi. The spectra were fitted by Gaussians. The result for La is highlighted.



Figure 51. Magnetization versus temperature curves. (a) and (b) are curves for samples cleaved from different sections of crystals BiLa1 and BiLa2, respectively. Samples were annealed at 450°C with 20% O₂/Ar gas flow. The variation of T_c values for each crystal is probaby caused by the inhomogeneity of La content. The overall T_c of BiLa2 crystal is lower than BiLa1. (c), curves for one sample after being annealing at the 450°C but with different oxygen partial pressure. This sample was cleaved from section C13 from crystal BiLa1.

b), samples were cleaved from their different sections and annealed at 450°C with 20% O_2/Ar gas flow. In the spectra, the sudden change of the magnetization shows that they are all superconductors. Since all of the samples were annealed under the same condition, we suppose the variation of T_c 's along the same crystal is caused by the inhomogeneity of La. Interestingly, the spectra of C9 and C14 for crystal BiLa1 are almost identical, which is consistent to what we see from the photograph — C14 is above the starting point C15, and C9 is the section after new molten zone was built due to the loss of solvent. The lost liquid formed a "bump" in section C11. Through further annealing at different oxygen partial pressure, we found that the introduction of La actually make Bi2212 samples more underdoped (as shown in panel c). The more content of La added, the more underdoped the samples are, which can be seen from the overall T_c shift between BiLa1 and BiLa2 crystals.

6.4 Conclusion

Two La-doped Bi2212 crystals with different La contents have been grown via floating zone technique. Even though our crystals are of the pure Bi2212 phase, La is not evenly distributed along the growth direction, which is caused by the instable molten zone during the crystal growth. The situation is even wore when more La is added. One of the possible reasons could be that, there are two sites for La to substitute, Sr and Ca, and our starting materials did not have the right stiochiometric ratios for obtaining stable crystallization processes. In addition, after introducing La, the as-grown Bi2212 crystals become underdoped, which is different from the pure Bi2212 crystals (with no cation-substitution).

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- Emergence of High-Tc Superconductivity from a strange metal phase via two crossovers Aladdin Award presentation, Physical Science Laboratory, Madison, WI (Sep 2011)
- One-gap versus Two-gap in Bi2212 High Temperature Superconductors Physics Festival, Physics Department, UIC (Feb 2011)
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Publications

J. Zhao, U. Chatterjee, D. Ai, D.G. Hinks, H. Zheng, J.-P. Castellan, S. Rosenkranz, H. Claus, M.R. Norman, M. Randeria, J.C. Campuzano, One gap, two gaps, and universality in high temperature superconductors. *submitted*.

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