EVOLUTION OF THE EXCITATION SPECTRUM OF CUPRATE SUPERCONDUCTORS WITH DOPING AND TEMPERATURE

BY

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DISSERTATION

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Abstract

Understanding the mechanism by which $d$-wave superconductivity in the cuprates emerges and is optimized by doping a Mott insulator is one of the major outstanding problems in physics. A key unresolved question in this field is how the strength of electron pairing evolves as a function of doping and temperature and whether pairing strength and the $T_c$ of the sample are related, as they are in simple BCS superconductors. To address these questions, we have developed several new experimental techniques with the scanning tunneling microscope to measure the excitation spectra in the cuprates on the atomic scale as a function of doping and temperature. In this thesis, we will describe these techniques as well as a series of new experiments that reveal a surprisingly simple picture of how superconductivity in the cuprates is optimized. We will first show that over a wide range of doping (optimal to overdoped), the pairing gaps in these systems nucleate in nanoscale regions at temperatures above $T_c$ unlike in the conventional superconductors where the superconducting order parameter sets in at the bulk $T_c$. These regions proliferate as the temperature is lowered, resulting in a spatial distribution of gap sizes in the superconducting state. Analysis of our data shows no correlation between the inhomogeneous pairing gaps and either the energy scale of the boson modes or the strength of the local electron-boson coupling as measured by the local excitation spectra. This spatially inhomogeneous pairing strength is in fact determined by the unusual electronic excitations of the normal state, suggesting
that strong electron-electron interactions rather than low-energy (<0.1 eV) electron-boson interactions are responsible for superconductivity in the cuprates. In contrast, the excitation spectra in the underdoped samples show multiple features that can’t be fit to a simple $d$-wave order parameter. However, these spectra show a universal low energy excitation spectrum, indicating that the pairing strength near the nodes is independent of doping. The transition temperature $T_c$ in this doping regime correlates with the fraction of the Fermi surface over which the samples exhibit the universal $d$-wave spectrum. Optimal $T_c$ is achieved when all parts of the Fermi surface follow this universal behavior. Increasing temperature above $T_c$ turns the universal spectrum into an arc of gapless excitations, while overdoping breaks down the universal nodal behavior.
This thesis is dedicated to my parents.
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Chapter 1

Introduction to Superconductivity

1.1 Conventional superconductivity

Superconductivity is the phenomenon where a material loses its electrical resistance when cooled below a characteristic transition temperature $T_c$ (figure 1-01). It is a remarkable example of quantum effects on a macroscopic scale, where a finite fraction of electrons is condensed into a superfluid state that extends throughout the volume of a superconductor and moves as a whole. After its discovery [Onnes 1911] by H. Kammerlingh Onnes in 1911, it took 45 years for a complete and satisfactory theoretical picture of the classical superconductors to emerge [Bardeen et al. 1957].

![Figure 1-01 - Discovery of Superconductivity](image)

Electrical resistance goes to zero in Mercury at 4.2 K shown by Kammerlingh Onnes for the first time [Onnes 1911].
This theory explained that the conduction electrons in these materials are bound together into pairs known as Cooper pairs by phonons of the lattice vibrations below the transition temperature \( T_c \). These bosonic Cooper pairs condense to give a macroscopic wave function, which is oblivious to any scattering and hence the material shows zero electrical resistance. As the electrons are paired, there is an energy cost associated with breaking these pairs, which is called the superconducting (SC) gap. The SC gap is used as an order parameter to describe the phase transformation and it can be directly measured by conventional tunneling experiments [Giaever et al. 1962]. This pairing potential ‘\( \Delta \)’ can be seen in the single particle density of states (DOS) probed in a quantum tunneling experiment (figure 1-02).

![Image of tunneling gap](image_url)

**Figure 1-02 - The Tunneling Gap in Conventional Superconductors** - The gap is an order parameter that opens up symmetrically about the Fermi energy in the tunneling density of states spectrum at the bulk \( T_c \) of a conventional superconductor. Sharp coherence peaks are seen at low temperatures. [Pan et al. 1998]
The superconducting DOS, $N_s(E)$ is related to the normal state DOS, $N(0)$ by the simple relation [Tinkham 1996]:

$$\frac{N_s(E)}{N(0)} = \begin{cases} \frac{E}{\sqrt{E^2 - \Delta^2}} & (E > \Delta) \\ 0 & (E < \Delta) \end{cases}$$

(1.1)

This equation implies that there is no DOS up to the energy $E < \Delta$ as can be seen in the spectrum at the lowest temperature in figure 1-02. In order to conserve the total DOS, sharp peaks known as coherence peaks are observed at $E = \Delta$. This is a highly simplified case for classical superconductors with an isotropic gap. The equations are modified for more complicated situations as discussed later. Most classical superconductors are metals or metal alloys and have $T_c$s in the range of 1-20 K.

1.2 High Temperature Superconductivity (HTSC)

In 1986, Bednorz and Muller [Bednorz et al. 1986] at IBM Zurich discovered superconductivity in a new class of materials. The first such superconductor to be discovered is the Lanthanum-Barium-Copper-Oxide (LBCO) system (figure 1-03). Many other systems with different chemical compositions are now known. Unlike conventional superconductors, which are either metals or metal alloys, these materials are layered crystals and are bad conductors at room temperature. They surprisingly have much higher $T_c$s than those of the conventional ones – hence, they are known as High Temperature Superconductors (HTSCs).
The most common class of HTSCs is the cuprate superconductor, which has 
\( \text{CuO}_2 \) plane as one or more of the layers in its unit cell. It is believed that the charge 
carriers responsible for superconductivity flow in the \( \text{CuO}_2 \) plane, and the nearby 
planes act as charge reservoirs by adding or taking away electrons from the \( \text{CuO}_2 \) 
plane [Timusk et al. 1999]. This is because the Cu-O bands are the lowest-energy 
electronic states and therefore directly determine the macroscopic electronic 
properties. Although superconductivity in HTSC and conventional materials seem to 
have similar phenomenology, they have different origins at the microscopic level. In 
conventional superconductors, the SC order parameter is isotropic, i.e., it has an s- 
wave symmetry (see figure 1-04) in momentum space, while in HTSCs, interference 
and DC SQUID experiments [Van Harlingen 1995] have shown that the order 
parameter is anisotropic and has \( d \)-wave symmetry, which means that the gap is 
gle angle dependent and has four lobes and as many nodes (figure 1-04) reminiscent of 
the \( d_{x^2-y^2} \) orbital.

Figure 1-03 – Crystal Structure of \( \text{La}_2\text{Ba}_x\text{CuO}_4 \) – the first High-\( T_c \) superconductor 
was discovered in 1986 by Swiss scientists Bednorz and Muller at IBM Zurich. [Bednorz 
et al. 1986]
**Figure 1-04 – Order Parameter** – The superconducting gap is isotropic in conventional superconductors (left) whereas it has $d$-wave four-fold symmetry and shows nodes in cuprates (right).

A direct measurement of the superconducting gap having $d$-wave symmetry has been obtained by AngleResolved Photo-Emission Spectroscopy (ARPES) [Damascelli et al. 2003] that has the capability of probing the DOS in the momentum space. Figure 1-05 (extracted from [Ronning et al. 1998]) shows the band structure with a truncated Fermi surface and the gap structure. The top part of the figure 1-05a shows the location of the $d$-wave gap in the first brillouin zone. The inset in figure 1-05b (extracted from [Ding et al. 1996a]) shows quarter of the first brillouin zone of the superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ in momentum space. The gap measured from ARPES monotonically decreases from the anti-node (angle with the largest gap) to the node at 45 degrees, where the gap is zero.
1.3 Mott Physics

Another remarkable property of the HTSC materials is that they are obtained from what is known as a Mott insulator. Without doping, the CuO₂ lattice is half-filled, with one electron per Cu site. As the bands are half filled, band theory predicts it to be a metal but any transport of current requires the electron to “hop” to its neighboring site, which has a high-energy barrier due to the Coulomb electrostatic repulsion (see figure 1-06). This makes the material an insulator.
Figure 1-06- Half-filled CuO$_2$ Plane- Orange disks represent Cu atoms along with their $d_{x^2-y^2}$ orbitals while blue disks are O atoms with $p$ orbitals, which form a square lattice in the xy plane. White arrows show the spin of electrons. At half-filling, anti-ferromagnetic insulating phase arises because of Coulomb repulsion between neighboring electrons and Pauli principle. See text for more details.

In this insulating state, we can calculate the correction to the ground state energy generated by a virtual hopping of an electron to its neighbor sites and back. For such a process to be allowed, Pauli’s exclusion principle requires the spins of neighboring electrons to be anti-ferromagnetically aligned. Hence, the phase diagram shows an anti-ferromagnetic phase at low doping. This can be mathematically understood in the one-band Hubbard model proposed by Anderson [Anderson 1997], which contains a single kinetic-energy term proportional to the nearest-neighbor hopping amplitude $t$, in addition to the Hubbard $U$ term that favors electron localization and results in “frustration” of the kinetic energy:

$$H = -t \sum_{\langle ij \rangle \sigma} (c_{i\sigma}^* c_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$  \hspace{1cm} (1.2)
Here, $c_{i\alpha}^*$ ($c_{i\alpha}$) creates (annihilates) an electron or hole on site $i$ with spin $\alpha$, \langle ij \rangle identifies nearest-neighbor pairs, and \( n_{i\alpha} = c_{i\alpha}^* c_{i\alpha} \) is the number operator. As can be seen, in the strong coupling limit (\( U >> t \)) at half filling (one electron per Cu site), the anti-ferromagnetic state [Anderson 1950] results from the fact that, when nearest-neighbor spins are anti-parallel, the electrons gain kinetic energy by undergoing virtual hopping to neighboring sites as hopping for parallel spins is prohibited because of Pauli principle. This can be further simplified to the $t$-$J$ Hamiltonian [Dagotto et al. 1994], which is more commonly used in studying the low-lying excitations of the half filled anti-ferromagnetic insulator:

$$H = -t \sum_{\langle ij \rangle \sigma} (\tilde{c}_{i\sigma}^{\dagger} \tilde{c}_{j\sigma} + h.c.) + J \sum_{\langle ij \rangle} \left( S_i \cdot S_j - \frac{n_in_j}{4} \right)$$ (1.3)

Where the operator $\tilde{c}_{i\sigma} = c_{i\sigma} (1 - n_{i-\sigma})$ excludes double occupancy, \( J = 4t^2/U \) is the anti-ferromagnetic exchange coupling constant, and $S_i$ is the spin operator. At half filling, as charge excitations are gapped, the low energy spin excitations are governed by the anti-ferromagnetic Heisenberg Hamiltonian $H = J \sum S_i \cdot S_j$. The $t$-$J$ model, away from half-filling, describes a system of interacting spins and mobile holes known as the doped anti-ferromagnet. Reader is encouraged to look at the reference [Anderson 1997].

In simpler language, hole-doping the CuO$_2$ plane creates sites with no electrons and allows the electrons to hop through these “vacant” sites without having to cross any electrostatic energy barrier for conduction, thereby weakening
the anti-ferromagnetic insulating state. Further doping destroys the Mott insulator phase completely and gives way to superconductivity. At the time of writing, the mechanism of superconductivity is not well understood. The transition temperature, $T_c$, depends on the hole doping. It forms a dome as shown in the phase diagram (figure 1-07). The composition with the highest $T_c$ is called optimally (OP) doped, while less or more than this doping is called under-doped (UD) or over-doped (OV) respectively.

**Figure 1-07 - The Cuprate Phase Diagram** – Different phases of cuprates as a function of temperature and doping. Increasing hole doping kills the Mott Insulator phase and gives rise to $d$-wave superconductivity. The superconducting transition temperature, $T_c$, has a doping dependence as shown by the dome and it peaks at optimal doping (OP). Further doping (over-doped OV) reduces the superconducting phase and gives metallic state. Under-doped (UD) phase shows a Pseudogap above the $T_c$, characterized by parts of the Fermi surface being gapped. The Pseudogap persists to a temperature defined by $T^* > T_c$. 
1.4 Pseudogap

With further doping, the material can be driven into a normal metallic phase where Fermi liquid theory can describe its properties. In under-doped to moderately over-doped materials the superconducting phase in HTSC gives way to the Pseudogap (PG) phase as the temperature is raised, unlike conventional superconductors where there is a clear SC-normal metal transition (see figure 1-02). The Pseudogap persists up to a temperature defined by $T^*$. In fact, earlier work [Renner et al. 1998] on underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) using a Scanning Tunneling Microscope (STM) shows a gap at the Fermi energy above the bulk $T_c$ of the sample as shown in figure 1-08.

![Figure 1-08 – Pseudogap from STM – Junction between a metal tip and UD Bi-2212 with $T_c$=83 K. A gap can be observed up to near room temperature. [Renner et al. 1998]]
This gap increases in size as doping is decreased and persists to even higher temperatures as shown in figure 1-09. The pseudogap has been the most intensively studied part of the cuprate phase diagram as indicated by the large number of groups simultaneously working in the field.

Figure 1-09 – Doping Dependence of Pseudogap – (a) Doping dependence of STM spectra from [Renner et al. 1998]. (b) Compilation of the gap in Bi-2212 measured by various techniques as a function of doping. The dashed line is a linear fit of the average gap at a given doping. Extracted from [Fischer et al. 2007].

ARPES shows that for underdoped samples, the gaps near the nodes actually disappear on raising the temperature giving way to the so-called Fermi arcs while the anti-nodal gaps persist to higher temperatures as shown in figure 1-10 (extracted from [Norman et al. 1998a]). The first pioneering paper [Ding et al.
1996b] showed the doping as well as temperature dependence of the spectral function at the antinode. This paper showed which part of the Fermi surface was contributing to the pseudogap.

![Figure 1-10 - Fermi Arcs in UD Bi-2212](image)

(a)-(c) Spectra taken at the three points in the Brillouin zone as shown in (d) on an UD sample with $T_c = 85$ K at various temperatures (solid lines). The dotted curves are for a Pt sample in electrical contact with the sample to match their chemical potential. (e) The spectral gap denoted my the mid point has a different size in different points of the zone and is closing at different temperatures. Extracted from [Norman et al. 1998a].

More recently, a paper by the Stanford ARPES group [Lee et al. 2007] showed the detailed dependence of doping and temperature on the Fermi arcs, a schematic of which is shown in figure 1-11. Their data also show an abrupt onset of another gap at the bulk $T_c$. As can be seen in the schematic, the most underdoped sample shows the largest anti-nodal gap and the smallest arc length above the bulk $T_c$ of the samples. According to Lee and coworkers [Lee et al. 2007], $T_c$ marks an abrupt opening of a gap that they associate with pairing in these Fermi arc regions.
Other than tunneling and ARPES measurements, evidence of the Pseudogap can be seen in many different experimental techniques such as Nuclear Magnetic Resonance (NMR), Raman scattering, optical conductivity, magnetic neutron scattering, electronic specific heat, muon spin resonance, etc. Timusk and Statt [Timusk et al. 1999] provide a comprehensive treatise of most of these techniques. The PG phase is by far the most controversial and most debated part of the phase
diagram. At the moment there are many competing ideas describing the origin of PG. There are two major interpretations:

1. **Pseudogap is a manifestation of preformed pairs:** In this scenario, electrons form pairs at a temperature $T^*$ that can be much larger than the critical temperature $T_c$ where superconductivity appears. $T^*$s on the order of 300 K have been measured in underdoped cuprates where $T_c$ is about 80 K. Superconductivity does not appear at $T^*$ because large phase fluctuations of the pairing field cannot order at this temperature. Hence, in this interpretation, the pseudogap is produced by incoherent phase fluctuations of the pairing field. In other words, the pseudogap is a normal state precursor of the superconducting gap due to local, dynamic pairing correlations. This point of view is supported by a quantitative approach of the attractive pairing model [Emery et al. 1995] and also by the Nernst effect [Wang et al. 2006] and magnetic susceptibility measurements [Wang et al. 2005].

2. **Pseudogap is unrelated to and perhaps competes with superconductivity:** In this class of scenarios, many different origins of the pseudogap have been put forward, such as the formation of electronic stripes, anti-ferromagnetic ordering, exotic order parameters competing with superconductivity, etc. Many experiments including ARPES [Lee et al. 2007] and STM [Boyer et al. 2007], show the presence of two energy scales in the problem- the lower energy scale often being associated with pairing
while the higher energy scale is associated with pseudogap physics. Some interpretations claim that the pseudogap and the superconducting gap are unrelated to each other and in some cases even compete with superconductivity.

Here we discuss the Nernst measurements [Wang et al. 2006] on hole doped cuprates in some detail as it will become relevant in the remainder of this thesis. In the case of high-$T_c$ superconductors, Nernst effect measures the motion of superconducting vortices in the vortex liquid phase, which is a signature of fluctuating superconductivity. This signal persists above the bulk $T_c$ of the sample up to an onset temperature depicted as $T_{onset}$ in figure 1-12.

![Figure 1-12 - Nernst Effect in Cuprates](image)

**Figure 1-12 – Nernst Effect in Cuprates** – The phase diagram of La$_{2-x}$Sr$_x$CuO$_4$ (left; numbers on the contour curves indicate the value of the Nernst coefficient $v$ in nV/KT) and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (right) showing the Nernst region between $T_c$ and $T_{onset}$. The $T_{onset}$ curve peaks at a different doping as compared to $T_c$. (Extracted from [Wang et al. 2006]).
Torque magnetometry measurements on BSCCO samples [Wang et al. 2005] show diamagnetic response up to the same $T_{\text{onset}}$ and thus corroborate the fluctuating superconductivity picture. It may be noted here that the $T_{\text{onset}}$ line lies somewhere between the PG onset ($T^*$) line and the bulk $T_c$ in all high-$T_c$ superconductors. Our STM measurements can qualitatively explain the modified phase diagram as discussed in the subsequent chapters.

We can alternatively electron dope a Mott insulator to make it superconducting. In this thesis we would concern ourselves only with hole-doped superconductors. Even in hole-doped cuprate superconductors, a number of families of high-temperature superconductors have been discovered, all of which have shown evidence of a pseudogap [Timusk et al. 1999]. Within each family the properties vary with the doping level through the control of carrier density. Properties can also be changed through substitution of impurities into the copper-oxygen planes. The system that has received the largest amount of attention is YBa$_2$Cu$_3$O$_{6+\delta}$ (YBCO-123) with less work done on the closely related systems YBa$_2$Cu$_4$O$_8$ (YBCO-124) and Pb$_2$Sr$_2$(Y/Ca)Cu$_3$O$_8$ (PSYCCO). These systems are characterized by a CuO$_2$ bi-layer as well as a third layer containing copper: chains in the case of YBCO 123, double chains for YBCO 124 and isolated twofold coordinated coppers for PSYCCO. A second important bi-layer system is Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi 2212) and the more recently discovered thallium and mercury versions (Tl-2212 and Hg-2212). Single-layer materials include Bi$_2$Sr$_{2-y}$La$_y$CuO$_6$ (Bi-2201), the widely studied La$_{2-x}$Sr$_x$CuO$_4$ (LaSr-214) with a low $T_c < 40$ K as well as the 90 K materials Tl$_2$Sr$_2$CuO$_{6+\delta}$ (Tl-2201). There are technical reasons why all the experimental probes
have not been used with success on all the families of high-temperature superconductors. For example, magnetic neutron scattering requires very large single crystals and has almost exclusively been done on YBCO-123 and LaSr-214. On the other hand, tunneling spectroscopy and Angle-Resolved Photo Emission Spectroscopy (ARPES) are surface-sensitive probes where the focus has been on Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$, which cleaves easily in vacuum along the BiO planes normal to the c-direction yielding a high-quality virgin surface. Techniques like dc conductivity, ab-plane transport and nuclear magnetic resonance (NMR)- being more tolerant with the quality of the crystals- have been applied with success to a larger number of high-temperature superconducting (HTSC) systems.

As this thesis concerns with STM experiments on cuprates, it will primarily concentrate on the Bi-Sr-Ca-Cu-O (BSCCO) system – both the bi-layer Bi-2212 as well as monolayer Bi-2201. Before we do that, let’s discuss the technique employed to study these superconductors, namely scanning tunneling microscopy in the next chapter.
Chapter 2

Scanning Tunneling Microscopy

2.1 Why perform Scanning Tunneling Microscopy on Cuprate Superconductors?

As mentioned in the previous chapter, the conduction electrons form cooper pairs that are responsible for carrying the current without any dissipation in a superconductor. As the electrons are paired, there is an energy cost associated with breaking these pairs, which is called the superconducting (SC) gap. The SC gap is used as an order parameter to describe the phase transition and it can be directly measured by conventional tunneling experiments. In HTSCs, the SC gap changes on the atomic scale, unlike in conventional superconductors where the gap is homogeneous. Such variation in the local density of states (LDOS) requires the use of a technique that can probe these changes on the atomic scale. A high resolution Scanning Tunneling Microscope (STM) is a tool aptly suited for such experiments. In order to study a system with such a rich phase diagram we need to perform a systematic measurement of the excitation spectrum at different temperatures and different doping levels. Specifically, if we want to study the evolution of the LDOS with temperature on these systems, a Variable Temperature Scanning Tunneling Microscope (VTSTM) is a very powerful tool. Finally, tracking the same sample area as the temperature is changed is important to understand the behavior of the
inhomogeneity as a function of temperature. The following section describes the various properties of our home-built VTSTM that we use for this study and then explains lattice tracking spectroscopy.

2.2 Variable Temperature Scanning Tunneling Microscopy

Gerd Binnig and Heinrich Rohrer at IBM Zürich invented [Binnig et al. 1982] the STM in 1981, for which they were awarded the Nobel Prize in Physics in 1986. STM probes the density of states of a material using tunneling current. For STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution. With this resolution, the individual atoms within materials can be imaged and manipulated. The STM can be used not only in ultra high vacuum but also in air and various other liquid or gas ambiances, and at temperatures ranging from near zero Kelvin to a few hundred degrees Celsius. The basic concept is explained below.

2.3 Tunneling Basics

We have two home-built VTSTMs with the capability to do ultra high vacuum (UHV) tunneling experiments from 6 K up to room temperature. Scanning Tunneling Microscopy relies on tunneling between a sharp metallic tip and in our case, a superconductor in ultra high vacuum. The cartoon in figure 2-01 explains the principle behind vacuum tunneling.
When two conducting materials are brought close to one another, so that
tunneling of electrons is possible, the chemical potentials of the two materials have
to match in equilibrium, as any difference will allow an electron current without an
electrostatic potential difference. Alternately, applying a bias would make a
preferential tunneling current to flow from one material to another. The vacuum
tunneling current can be derived by a simple Fermi Golden Rule analysis, which
gives the following result [Chen 1993]:

\[ I = \frac{4\pi e}{h} \int_{-\infty}^{\infty} [f(E_F - eV + \epsilon) - f(E_F + \epsilon)] \times \rho_\delta(E_F - eV + \epsilon) \rho_F(E_F + \epsilon) d\epsilon \]

(2.1)

**Figure 2-01 – Elastic Tunneling** - (Left) Schematic description of a tunnel junction
between a metal and a superconductor. The energy is plotted along the vertical axis while
the density of states (DOS) is along horizontal axis- a metal has a flat DOS whereas there
is a superconducting gap symmetric about the Fermi energy for a superconductor.
(Right) An STM tunnel junction- where a tip moves across the sample with a constant
tunnel current. The trajectory of the tip closely follows the contours of the surface.
Here, $I$ is the tunneling current, $f(E)=\left[1+\exp\left(\frac{(E-E_F)}{k_BT}\right)\right]^{-1}$ is the Fermi function, $E$ is the energy, $E_F$ is the chemical potential, $V$ is the applied bias, $M$ is the tunneling matrix element between states of the respective electrodes, and $\rho_S(E)$ and $\rho_T(E)$ are the density of states (DOS) of the two electrodes. A tunneling current is the product of DOS of electrons on one side and density of unoccupied states on the other. The above equation represents the difference of the current flowing from one sample to another and vice versa. If there is no potential, the net current is zero. Applying a bias creates a preferred direction of electron flow. For low temperatures, the Fermi function can be approximated by a step function, which simplifies the expression for the current to:

$$I = \frac{4\pi e}{\hbar} \int_0^e \rho_S(E_F - eV + \varepsilon) \rho_T(E_F + \varepsilon) |M|^2 \, d\varepsilon$$

(2.2)

Bardeen [Bardeen 1961] showed that under certain assumptions the magnitude of the matrix element $|M|$ can be assumed to be energy-independent for small energies close to the Fermi energy and hence can be taken out of the integral. The matrix element, however, has exponential dependence on the tip sample separation, $d$, given by:

$$|M|^2 = \exp\left(-d\sqrt{\frac{8m\phi}{\hbar^2}}\right)$$

(2.3)

Where $m$ is the electron mass, $\phi$ is the mean of the work functions of the tip and the sample [Chen 1993], which are typically 3 - 5 eV. Also, since a metal (tip)
has featureless DOS [Ashcroft et al. 1976] near the Fermi energy we can modify the

equation (2.2) to:

$$I = \frac{4\pi e}{\hbar} \rho_T \left| M \right|^2 \int_0^{eV} \rho_s(E_F - eV + \varepsilon)d\varepsilon$$

(2.4)

Differentiating the equation (2.4) with respect to the bias implies that the
differential conductance is proportional to the DOS of the sample.

$$\frac{dI}{dV} \propto \rho_s(E_F - eV)$$

(2.5)

In other words, if we were to measure the differential conductance at
different locations of a sample we can find out the spatial variation of the DOS of the
material.

For completeness, the differential conductance at higher temperatures also
has a derivative of the Fermi function inside the integral (see equation 2.1) given by:

$$\frac{dI}{dV} \propto \int d\varepsilon \frac{df}{d\varepsilon}(\varepsilon + eV,T) \rho_s$$

(2.6)

As we will be working at elevated temperatures with our VTSTM, it becomes
essential to account for thermal broadening in our analysis. The following section
describes how this simple idea is used to probe the DOS of a specific sample using an
STM.

2.4 System Design

An STM relies on the same basic principle of tunneling discussed above.
Depicted in figure 2-02 are a design and a picture of the microscope. We use a sharp
metallic tip (we use Pt/Ir or W tips) mounted on a piezoelectric (a piezoelectric material changes its shape on application of voltage) scanner while the sample sits on a sample holder facing down on the piezo-legs. Typical deformation of these piezoelectric tubes is about an angstrom per volt, which is also weakly temperature dependent. The sample holder has three ramps for each of the piezoelectric legs on the microscope stage. The sample initially a few mm apart from the tip is brought within tunneling range (typically 5-10 Å) by a stick-slip mechanism by rotating the sample holder relative to the piezo-legs without the tip ever touching the sample surface (crashing). The reader is encouraged to look at the appendix for a detailed explanation of the sample approach and other experimental procedures.

Figure 2-02 - The Microscope Head - Drawing (left) and Picture (right) of the Microscope. The microscope is a Besocke design [Besocke 1987]. It is suspended from springs to dampen vibrations. The STM head is kept small (~1 inch in height) to minimize thermal drift. Reader is encouraged to look at the appendix for more details.
2.5 Topography

Once in tunneling range, the scanner-piezo is moved over the surface maintaining a constant current with a negative feedback loop. The voltage applied to the piezo-scanner in order to maintain the constant current when it is moved over the surface is what is recorded and displayed. This is called constant current topography (figure 2-03). We can easily visualize atomic corrugation using this technique.

![Figure 2-03 - Constant Current Topography](image) - Atomic terraces on the surface of Cu 111 single crystal showing impurities (left) as well as surface waves (right).

2.6 Spectroscopy

Using a lock-in amplifier and a small AC modulation (\(dV\)) the differential conductance (see appendix) and hence the DOS can also be measured at every location on the sample simultaneously with topography. This capability of mapping the DOS with atomic precision, known as spectroscopy, is what makes STM a key
experimental technique. The energy resolution of these spectroscopic measurements is limited by the temperature $k_B T$. The small lock-in AC modulation $edV$ is typically chosen to be 20-40% of the temperature resolution $k_B T$. Figure 2-04 shows the topography and the conductance measurements done simultaneously.

![Figure 2-04 – Spectroscopy](image)

The entire setup is in ultra high vacuum (UHV) with pressures < $10^{-10}$ Torr to be able to do vacuum tunneling (see appendix). Before each experiment, the tip is prepared and characterized on a clean metal surface (usually Cu or Au) as it is important to make sure that the tip is sharp, stable and metallic – the prerequisites
to tunneling with atomic resolution and spectroscopy. Clean metal surfaces such as Cu or Au are obtained by sputtering with Argon and subsequent annealing. The samples under study (typically HTSCs in our case) are cleaved in UHV to obtain a pristine clean surface for tunneling.

In a VTSTM, the temperature of the setup at which tunneling measurements are made can be varied. In our machines, a constant Helium flow is maintained through the tube line shown in the drawing in figure 2-02 along with a heater, which is run with a negative feedback loop to maintain a constant set point temperature. The temperature is maintained within 0.01 K accuracy of the set point. This technique is particularly useful if one wants to study phase transition in a material.

Previous STM measurements at low temperatures have reported that the superconducting gap in cuprate superconductors shows significant variation on a scale of 15-20 Å [Cren et al. 2000; Howald et al. 2001; Pan et al. 2001]. Thus average measurements alone are not sufficient to determine what the system is doing at the microscopic level. In this regard, our VTSTM also gives us the ability to map the same area while changing the temperature by 100-150 K. As one changes the temperature, due to the mismatch in the thermal expansion/contraction of the different parts of the setup, there is drift, which dies down exponentially with time. Typically the drift is about 1000 Å/hr immediately after the temperature is changed while there is almost no drift when thermal equilibrium is achieved. We can stay in the same region by accounting for this drift and applying appropriate voltages to the piezo-legs while scanning. This entire process takes about 24 hours. The net thermal drift is about 100 Å/K, which can be accounted for by applying appropriate voltages
to the legs of the microscope. In short, we now have the capability to stay at one particular location on a crystal and see how its DOS evolves as we change the temperature.

Our system design of a very compact STM head helps in keeping the drift to a minimum as a function of temperature. Using these machines we have been able to probe the phase diagram of the cuprates both as a function of doping and temperature. In the following chapters, we will describe the material system, the experimental results and explain how our interpretation relates to other spatially averaged techniques.
Chapter 3

The high-$T_c$ Superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

3.1 Introduction

In this chapter we will introduce the material Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (BSCCO or Bi-2212) that we have primarily studied with our STM. Single crystal BSCCO is grown by the traveling solvent floating zone technique. The as grown sample is usually optimally doped. Over doping can be accomplished by annealing these as grown crystals under high oxygen pressures while annealing to high temperatures in oxygen-deficient conditions gives under doped crystals. It is perhaps the best material to do surface measurements owing to its ability to give clean atomically flat surfaces on cleaving as shown in figure 3-01.

![Image](image.png)

Figure 3-01 - Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ - Optical image of the shiny surface of BSCCO upon cleaving
Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (BSCCO) is a layered compound with two CuO$_2$ planes per half unit cell as shown in figure 3-02. It has weaker bonds between the two adjacent BiO planes, which make it very easy to cleave in order to get a clean surface. BSCCO at optimal doping has a $T_c$ of 94 K. We have studied this material system with various doping-levels, ranging from underdoped ($T_c = 35$ K; henceforth named UD35) to optimal ($T_c = 91$ K; OP91) to overdoped ($T_c = 65$ K; OV65) samples at different temperatures in the phase diagram. Oxygen atoms present in the interstitial sites in the crystal control the doping. Heavily underdoped samples are obtained by adding Dy in place of Ca as Dy contributes an extra electron per Ca site. The severely underdoped samples (UD35 and UD58) in our study have the chemical composition: Bi$_2$Sr$_2$Dy$_{0.2}$Ca$_{0.8}$Cu$_2$O$_{8+x}$. We don't find any spectroscopic signature of Dy in the energy range of our study.

Figure 3-02 shows an atomically resolved topograph of the BiO plane of BSCCO. The “zigzag” pattern is characteristic of BSCCO, which has a b-axis supermodulation running though out the crystal with a periodicity of 28.3 Å [Gao et al. 1988]. This supermodulation is due to mismatch between the BiO bond-lengths and the CuO bond-lengths in adjacent layers. The incommensurate superstructure along the [110] direction modulates the atomic positions in every layer of BSCCO. The inset in the figure shows a typical differential conductance spectrum in the superconducting state. BiO plane is insulating. Cu atoms sit exactly below the Bi atoms as can be seen in the crystal structure. The tunneling of electrons presumably happens between the tip surface and the closest CuO plane through the BiO plane.
**Figure 3-02 - Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ on the Atomic Scale** (Left) Crystal structure showing the weak BiO bonds, where it tends to cleave. (Right) Atomically resolved 180 Å STM topograph of the BiO plane with the b-axis supermodulation [Gao et al. 1988]. Inset shows a representative DOS ($dI/dV$) spectrum at 40 K for an OP91 sample.

A representative DOS spectrum (inset figure 3-02) shows an asymmetric background. The reason for this asymmetry is not entirely settled but, has been attributed to the band structure, van hove singularity or because of the proximity to an anti-ferromagnetic insulator [Anderson et al. 2006]. This background can be taken out by performing lattice-tracking spectroscopy as discussed in the next chapter. On top of this asymmetric background, the spectrum shows a decrease in the DOS at the Fermi energy due to electron pairing. The v-shape of the spectrum is due to the fact that the gap parameter has $d$-wave symmetry in momentum space, given by $\Delta_0|\cos k_xa - \cos k_ya|/2$, where $k_x$ and $k_y$ are the momentum vectors and $a$ is the lattice constant. Hence, in specific directions (anti-nodes) in the momentum...
space, the gap value has a maximum, $\Delta_0$, while in some directions (nodes) the gap value goes to zero. As an STM measurement averages over all momentum directions, the V-shaped DOS spectrum in BSCCO reflects the fact that there are low energy states available to tunnel into even below the maximum gap energy $\Delta_0$. At low temperatures, $\Delta_0$ coincides with the coherence peaks as shown in the inset.

![Graphs showing s-wave and d-wave gaps](image)

**Figure 3-03 – d-wave Fit** – Zero temperature DOS spectrum with an s-wave gap (left) and a d-wave gap (right) of 25 meV. A 0.01 meV inverse lifetime broadening is added to ensure there are no singularities at the coherence peaks.

Modeling the DOS spectra (equation 1.1) with an s-wave and a d-wave gap makes the point clearer as shown in figure 3-03. Clearly, the DOS spectrum (figure 3-02 inset) resembles the V-shaped tunneling spectrum implying the existence of a d-wave gap.

### 3.2 Inhomogeneity

So far we showed the spectra at one location on the sample and that it resembles a d-wave gap with an asymmetric background. As STM offers the
capability to look at the excitation spectrum as a function of position on the sample, we show in figure 3-04 with a false color scale, the spectra taken along a line on the sample.

![Image of Figure 3-04](image)

**Figure 3-04 - Inhomogeneity** – $dl/dV$ spectra measured along a line (white-dashed line, left image) on OP91 sample at 40 K shows variation on atomic scale (right). The superconducting gap as well as the asymmetric background changes on atomic scale.

As can be seen, there is inherent inhomogeneity in the sample at all energies. In particular, we observe that the gap is varying on atomic scale on the sample. This inhomogeneous distribution of gaps (reported earlier by [Cren et al. 2000; Howald et al. 2001; Pan et al. 2001]) is shown with atomic registry in a ‘gap map’ in figure
3-05 along with the probability distribution, which signifies what fraction of the sample has a specific gap size.

![Gap Map](image)

**Figure 3-05 – Gap Map** – (Left) False scale color plot of the gap size at every location on the sample in two dimensions. (Right) Histogram shows the probability distribution of gaps in the sample.

A typical gap map in a given region requires measuring about 30,000 spectra, which takes two days on average. The correlation length of the gap distribution is about 15-20 Å and hence a gap map of 400 Å is a good representative of the sample. The inhomogeneity in these samples is intrinsic as the system is a doped material. In the subsequent chapters, we will talk about what happens to these inhomogeneous pairing gaps as a function of temperature and doping.
Chapter 4

Lattice Tracking Spectroscopy

4.1 Introduction

As we saw in the previous chapter, the inhomogeneity is intrinsic to BSCCO. The DOS spectrum is very different for even neighboring atoms. Hence, any measurement of the spectral evolution of the DOS with temperature requires the atomic registry to be maintained. This is a rather challenging task to achieve experimentally because of the associated lateral drift in changing the temperature as different components of the STM head have different expansion coefficients. In order to reduce this thermal mismatch, extreme care has been taken in designing the system head to keep it as compact as possible in order to have overall small lateral drift. Nothing in the real world is ideal. Even after taking such precautions our STM images drift about 100 Å per Kelvin.

In order to facilitate tracking the same area, a large areal scan (~ 700 Å) is taken at the first equilibrium temperature. As can be seen in figure 4-01, the topograph shows various features that are unique to the specific area. On changing the temperature, the area in the box can be tracked by matching the highlighted features. It’s analogous to ascertaining one’s orientation by looking at the constellations among the stars.
Figure 4-01 – Lattice Tracking – 700 Å topograph of BSCCO. Black square box represents the target area to perform atomic scale measurements. The yellow circle and arrows point out unique structures on the topograph that can be used to track the target area while changing the temperature.

After all the measurements at a certain equilibrium temperature have been performed, the temperature is changed slowly to the new temperature. This induces lateral drift in the scan area on the order of about 100 Å per Kelvin, which can be corrected for by adjusting the voltages on the leg-piezos of the STM head. Once centered near the desired area at the desired temperature, the system is left to equilibrate. Depending on the temperature, the equilibration time can vary from 8
hours to 24 hours to be able to perform the next set of careful measurements. Extra precaution is taken that there be no tip changes during the entire run of the experiment as any change in the tip will invariably affect the matrix element in the DOS (see equation 2.1).

We have been able to maintain a stable STM junction with the same tip in the same area for over 125 days while changing the temperature through the $T_c$ of the sample and thus have been able to visualize the gap formation on atomic scale. Figure 4-02 shows the spectral evolution of a superconducting gap with temperature at a fixed atomic site on an overdoped $T_c = 65$ K sample.

![Graph](image)

**Figure 4-02 – DOS Evolution with Temperature** – Notice that a remnant gap exists above the bulk $T_c = 65$ K. The gap vanishes at a higher temperature $T_p = 76$ K.
As can be clearly seen, the superconducting gap at low temperature evolves into an asymmetric background at higher temperatures. It is important to note that, no normalization of the spectra at different temperatures has been employed. The raw data under the same setup conditions at various temperatures has been plotted. All the ‘action’ in the spectra is happening in the energy window of 100 meV around the Fermi energy (zero bias) while the rest of the conductance value stays the same over the entire temperature range. On closer look (figure 4-03), the first thing that is evident is that the spectrum smoothly evolves through the bulk $T_c$ of the sample. There is a clear depression in the density of the states near the Fermi energy at 68 K, which is higher than the bulk $T_c$ (65 K) of the sample. At 76 K, a featureless background with no suppression in the DOS is observed.

![Figure 4-03 - Taking Out the Background](image)

Figure 4-03 – Taking Out the Background – Dividing the highest temperature (76 K) asymmetric background in (a) out from the lower temperature spectra shows spectra symmetric about the Fermi energy in an 0V65 BSCCO sample.

Dividing each of the low temperature DOS spectra with the highest temperature featureless background gives us the ratio:
\[ R(r,V,T) = \frac{[dI/dV(r,V,T)]_S}{[dI/dV(r,V,T)]_N} = \frac{N_s(r,V,T)}{N_N(r,V)} \]  

(4.1)

Here, \( N_s(r,V,T) \) and \( N_N(r,V) \) are the respective superconducting and normal density of states at atomic site \( r \) as a function of energy (eV). This ratio, which is independent of the tunneling matrix element, will be used to extract the temperature dependence of the energy gap. Within the temperature window of the current study (up to 110 K), as shown in figure 4-03, a temperature independent conductance is only observed in overdoped samples of Bi$_2$Sr$_2$CaCu$_2$O$_{y_b}$ at temperatures well above \( T_c \). We extend our experimental technique to study samples at other doping in the subsequent chapters. We will explain the challenges and how we circumvent them in the next chapter. This chapter focuses on the quantitative analysis of the local temperature dependence of electronic states on overdoped samples. Our results can be found in this reference [Pasupathy et al. 2008].

As there is an inhomogeneous distribution of gaps in the sample, gaps of different sizes have different temperature evolution as shown in figure 4-04. In fact, we can divide out the normal background from each of these spectra and look at the evolution of the superconducting gap as a function of temperature as discussed in the next section. For this analysis, we have tracked a total of 13 different locations showing different gap sizes on the same sample. Tracking of these locations is good to 0.1 Å. About 40 minutes were required to obtain data at a given location at a given temperature. This measurement, unfortunately, cannot be automated with our current setup and hence is extremely labor intensive. The time and labor required
per measurement are the main reasons behind the number of locations being not statistically significant, but the data overall are indeed representative of the entire overdoped BSCCO sample.

Figure 4-04 - Inhomogeneous Gap versus Temperature Evolution - (a)-(d) show increasing gap sizes at different locations on the same sample. Every gap has its own temperature $T_g$ where it vanishes and is replaced by an asymmetric background.
4.2 Temperature Dependence of the Local Pairing Gap & Quasi-Particle Lifetime

Figure 4-05 shows the temperature evolution of the conductance ratio, \( R(r,V,T) \), in overdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta} \) samples at two representative locations of the sample with different low-temperature energy gaps. Motivated by the fact that the low temperature ratio resembles the line-shape expected from a single energy gap in the spectrum, we compare these ratios with the line-shape obtained from the thermally broadened density of states of a \( d \)-wave superconductor:

\[
\frac{N_5(r,V,T)}{N_5(r,V)} = \frac{1}{\pi} \int dE \frac{df(E + V,T)}{dE} \int_0^\pi d\theta \text{Re} \left( \frac{E - i\Gamma(r,T)}{\sqrt{(E - i\Gamma(r,T))^2 - \Delta(r,T)^2 \cos^2 2\theta}} \right)
\]

(4.2)

Here, \( i \) is the square root of -1, \( \Delta(r,T) \) is the local gap (considered energy independent for low energies), \( \Gamma(r,T) \) corresponds to the local inverse lifetime of the quasi-particle excitations [Dynes et al. 1978], and \( f(E,T) \) is the Fermi function. It must be noted that this analysis neglects the complication due to the \( k \)-dependence of the band structure as well as higher order angular terms in the superconducting gap. In general, we find that the model in equation (4.2) provides an excellent fit to the experimental data at low energies (where the slope of \( R \) versus \( V \) is inversely proportional to the gap \( \Delta \)), for all points on the overdoped samples.
Figure 4-05 – Fitting to a d-wave – The conductance ratio \( R = \frac{[dI/dV(V,T)]}{[dI/dV(V,T>>T_c)]} \) (circles) obtained by dividing by the asymmetric gap-less spectrum. Fits to the ratio with the use of a thermally broadened d-wave BCS model are depicted as lines. In general, the fits work well at low \( V \) where the slope of the ratio is inversely proportional to the gap.

Using this model, we can extract the local values of \( \Delta(r,T) \) and \( \Gamma(r,T) \) for the 13 different locations, which show that at each point the gaps decrease monotonically with increasing temperature and close at a local temperature \( T_p(r) > T_c \) (figure 4-06A). We find that \( \Gamma(r,T) \)'s needed for the fit are much smaller than the gaps at all locations at low temperatures (figure 4-06B).
Figure 4-06 – BCS Fit with Lifetime Broadening - (A) Extracted values of the pairing gap for several different locations plotted as a function of temperature. The gray line indicates the resistive $T_c$. (B) Extracted inverse lifetime broadening at different temperatures plotted as a function of the corresponding low-temperature gap. (Inset) The average inverse lifetime broadening as a function of temperature.

With increasing temperature, the smaller gaps close first, with the largest gaps surviving to temperatures well above $T_c$. Regions of the sample with smaller gaps also show $R(r,V,T)$ which exceeds that predicted from the local $d$-wave model in equation (4.2) for $eV \sim \Delta(r,T)$. This behavior is likely due to localization effects experienced by the quasiparticles in small gap regions that cannot penetrate the larger gap region [Fang et al. 2006]. The extracted values of $\Gamma(r,T)$ also agree with this scenario – the regions with the smallest gaps show no inverse lifetime broadening whereas the larger gap regions have a small inverse lifetime broadening even at low temperatures (figure 4-06B). The variation in $\Gamma(r,T)$ is a consequence of the fact that the excitations in the large gap regions can decay into nearby regions with smaller energy gap, but not vice-versa.
As the smaller gaps begin to close with increasing temperature, the $\Gamma(r,T)$s in the large gap regions begin to increase rapidly. This correlation between $\Delta(r,T)$ and $\Gamma(r,T)$ is shown in figure 4-06B for different temperatures. Overall, the analysis of the experimental data for all regions on the sample demonstrates that the spatially averaged $\Gamma(T)$ shows a dramatic increase at a temperature $T\sim T_c$, when the sample loses long-range phase coherence (inset, figure 4-06B). This observation is in accordance with previous macroscopically averaged measurements [Norman et al. 1998b] on samples in the overdoped regime; however, previous measurements did not correlate inhomogeneous behavior of the gaps and quasi-particle lifetimes.

We can also use this procedure to extract the features associated with strong coupling of electrons to bosonic modes, which is discussed in the next chapter.
Chapter 5

Electron Boson Coupling

5.1 In Classical Superconductors

It is known that superconductivity in metals and metal alloys is mediated via electron phonon interaction [Schrieffer 1964; McMillan et al. 1965; Carbotte 1990; Tinkham 1996]. In the 1960s, Ivar Giaever pioneered electron-tunneling experiments with superconductor tunnel junctions [Giaever et al. 1961; Giaever et al. 1962], which are by far the most convincing evidence for phonon-mediated superconductivity, for which he was awarded the Nobel Prize in 1973. Figure 5-01 is taken from [Giaever et al. 1962] that shows the presence of bumps in the ratio of the conductance in the superconducting divided by the normal state, \( R = \frac{\frac{dI}{dV}}{\frac{dI}{dV}}_N \) at specific energies outside the superconducting gap, which is attributed to the phonon modes of the material.
Figure 5-01 – Normalized Conductance in Lead – The tunneling ratio was obtained in the superconducting state and in the normal state in a superconductor – insulator – metal junction (Pb-MgO-Mg). The junction was driven into the normal state by applying a magnetic field. Signature of “bumps” can clearly be seen beyond the superconducting gap. These have been attributed to the phonons in the system. [Giaever et al. 1962]

It may be noted that the normal state background in these classical superconductors can be obtained by applying a magnetic field above the critical field, which is typically in the range of 1-2 T. Figure 5-02 (extracted from [McMillan et al. 1969]) shows the superconducting and normal state of Al-I-Sn tunnel junction, which can be divided to obtain the ratio $R$. 
Figure 5-02 - Superconducting and Normal Spectra - Solid line represents the superconducting spectra, whereas the dashed line is the normal state spectrum for the Al-Insulator-Sn junction. Notice that there are multiple features in the superconducting spectrum near the Fermi energy whereas at high energies the normal state spectrum coincides with the superconducting one. Extracted from [McMillan et al. 1969].

In high-$T_c$ superconductors, however, the critical fields are of the order of 150 T, which cannot be achieved in a laboratory. The highest accessible fields in practice are only about 50 T. However, we can warm up the sample while tracking a chosen area to obtain the normal state spectrum at any given lattice site, as shown in the previous chapter. It is this idea that will be exploited to look for signatures of electron-boson interaction in high-$T_c$ superconductors.

For classical superconductors, Eliashberg’s equations [Carbotte 1990] in 1960 followed by a more detailed analysis of the phonon spectrum by McMillan and Rowell [McMillan et al. 1965] in 1965 give a quantitative explanation for the presence of phonon signatures in the tunneling spectra. In the Eliashberg theory of superconductivity, the pairing gap $\Delta$ is given by:
\[ \Delta = \hbar \omega_c \exp\left(\frac{\lambda - \mu^*}{1 + \lambda}\right) \]  

(5.1)

Here \( \hbar \omega_c \) is a cutoff frequency related to the boson density of states, \( \lambda \) is the effective coupling constant and \( \mu^* \) is the Coulomb pseudopotential. In order to increase the size of the gap and \( T_c \), previous experiments on metallic alloys have focused on either increasing the energy range over which the bosons are coupled to the electrons (\( \hbar \omega_c \)) or alternatively, increasing the coupling to the bosons \( \lambda \).

Strong coupling (\( \lambda \sim 1 \)) to a bosonic mode at \( \omega \) results in structure in the tunneling density of states at an energy \( \Delta + \omega \). A change in the energy of the boson shifts the energy scale at which the strong coupling features are observed relative to the gap. On the other hand, increasing the coupling constant does not change the energy at which the features are observed but instead magnifies the size of the strong coupling features seen in the tunneling conductance. In the Lead-Thallium-Bismuth alloys, for example, tuning the percentage of thallium and bismuth in lead does not lead to a significant change in the phonon energies [Dynes et al. 1975]. However, the coupling constant increases monotonically on changing the alloy composition from \( \text{Pb}_{0.6}\text{Tl}_{0.4} \) through \( \text{Pb} \) to \( \text{Pb}_{0.65}\text{Bi}_{0.35} \). Such changes in the coupling constant result in a corresponding increase in the magnitude of the strong-coupling features seen in the tunneling conductance (figure 5-03A, from [Dynes et al. 1975]). It is seen that (figure 5-03B) the RMS value of the deviations from the BCS density of states (over the energy range 0-10 mV) scales with the size of the gap.
Figure 5-03 – Evidence for Phonons Driving Superconductivity – (A) Strong-coupling deviations from the BCS theory for a series of Pb-based alloy superconductors (extracted from [Carbotte 1990]). While the phonon energy does not change significantly across the different materials, the coupling to the phonon increases. This increase causes a corresponding increase in the size of the deviations. (B) RMS value of the deviations in the energy range 0-10 meV for different samples in (A) scale linearly with the superconducting gap size.

5.2 In High-\(T_c\) Superconductors

We are going to exploit the same idea in the case of high-\(T_c\) superconductors. Having established that our measurements can be examined within the context of a local \(d\)-wave gap model in equation (4.2) in the previous chapter, we examine the deviation of the conductance ratio from this model for \(E > \Delta\). Although other effects such as inelastic tunneling [McMillan et al. 1969; Pilgram et al. 2006] can cause such deviations, only strong coupling of electrons to bosonic modes is known to cause the superconducting state tunneling conductance to dip strongly below the normal state [Scalapino et al. 1966; McMillan et al. 1969]. As illustrated in figure 5-04, all points on the samples show a voltage range (around 50-80 meV) in which
the conductance ratio $R(r;V,T)$ is reduced below one and show systematic deviations from the local $d$-wave model.

![Graph](image)

**Figure 5-04 – Parasitic Bosons** – (A) The low-temperature ($T = 30$ K) conductance ratio plotted for several gaps. The conductance ratios deviate systematically from the $d$-wave model (equation 4.2, thin lines) and go below unity over a range of voltages ($50$-$80$ meV), indicating strong coupling to bosonic modes. (B) The positive-bias conductance ratios are referenced to the local gap for all the locations studied, showing that the magnitude of the tip hump feature is similar at all locations. The line is the average of all the locations. (Inset) Gap-referenced conductance ratios for negative bias. (C) The RMSD of the conductance ratios from the $d$-wave model for positive (blue circles) and negative (red circles) bias over the energy range 20-120 meV. No correlation is seen between the magnitude of the deviations and the gap size. Compare this to figure 5-03.

Analogous to previous work on conventional superconductors [Carbotte 1990], these deviations provide a quantitative method to determine the strength of electron-boson coupling. The analysis of the spectra based on the features of $R(r;V,T)$ instead of the bare $dI/dV(r;V,T)$ or $d^2I/dV^2(r;V,T)$ avoids complications due to the spatial variation of normal state features and tunneling matrix element variations [Scalapino 2006]. Although many previous studies, including those
using an STM [Lee et al. 2006a; Niestemska et al. 2007], have examined electron-boson features in the 20-120 meV range, a quantitative comparison of the electron-boson coupling at different locations of the sample with different pairing gaps has not been accomplished. The comparison of $R(r,V,T)$ at different locations allows us to quantitatively evaluate the role of bosonic features in the development of the pairing gaps and their inhomogeneity. We discuss this matter in more detail after discussing our results [Pasupathy et al. 2008].

To study the relative strength of electron-boson coupling at different locations on the sample, we consider that the strong coupling to a bosonic mode at energy $\Omega$ in a superconductor results in features in the conductance ratio at $eV = \Delta + \Omega$ [McMillan et al. 1969; Eschrig et al. 2003; Lee et al. 2006a]. Since the pairing gap is locally varying, we plot the $R(r,V,T)$ as a function of $eV - \Delta(r)$ for different atomic sites on the sample with low temperature $\Delta(r)$ ranging between 15 and 32 meV, as shown in figure 5-04B (and inset for negative bias). This figure demonstrates that different locations on the sample show remarkably similar $R(r,V,T)$ curves in magnitude and shape, once we take into account their varying pairing gaps. The only significant difference between the spectra occurs at low energies, where lifetime broadening effects, discussed in the previous chapter, play a role. A quantitative measure of the strength of the local coupling constant is the RMS deviation of $R(r,V,T)$ from the weak-coupling $d$-wave model (equation 4.2) in the energy range 20-120 meV beyond the gap. These deviations show no correlation (for both positive and negative biases, figure 5-04C) with the size of the local gap within our experimental error.
5.3 Conclusion

For boson-mediated pairing, variation of the pairing gap can be caused by changes in either the local boson energy or the local coupling between the boson and electrons [Carbotte 1990]. Such changes are reflected directly in the size and energy range of the strong-coupling features in the conductance ratio. As showed earlier in this chapter, in metallic alloy systems [Dynes et al. 1975; Kihlstrom et al. 1981] where pairing is controlled by strong electron-phonon coupling, the magnitude of strong coupling features in the conductance ratio scales with the gap size. Since both the energy scale of the boson modes and the local electron-boson coupling do not correlate strongly with the magnitude of the local pairing gap in our samples, we conclude [Pasupathy et al. 2008] that the coupling to bosons in the range of 20-120 meV cannot be responsible for these inhomogeneous pairing gaps. The absence of such scaling for the low-energy boson modes in \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \) indicates that the coupling constant is not increasing in proportion to the gap size.

Our results [Pasupathy et al. 2008], however, are contradictory to STM results from another group at Cornell University. In their paper, Davis and co-workers [Lee et al. 2006a] concentrate on the dip feature seen in the DOS spectrum in the deeply superconducting state and take its derivative \( (d^2I/dV^2) \) to extract the associated boson energy feature. They perform extensive measurements of the boson energy feature on samples with different doping and report that the boson energy feature shows a distribution, which anti-correlates with the superconducting gap (see figure 5-05). This result is contradictory to a BCS type mechanism where
the superconducting gap is proportional to the boson strength (see equation 5.1). Also, varying the doping doesn't alter the boson energy distribution, which they claim is a signature that the dip in the spectrum is not associated with a magnetic mode as the magnetic mode is known to show strong doping dependence in this material [Sidis et al. 2004]. In fact, they conclude this doping independence of the boson energy distribution comes from the phonon contribution to the spectrum because the doping, in principle, shouldn't alter the lattice vibrations. To further support their case that this is a phonon contribution, they report an unusual isotope effect also seen in another study [Gweon et al. 2004]. They perform STM studies on special samples replacing the $^{16}$O atoms with heavier isotopes $^{18}$O. The authors show that the change does not affect the gap size or the transition temperature of the sample but it does affect the bosonic feature in the spectra (figure 5-05c), which strengthens their argument to identify the bosonic mode as a phonon. In further investigation, the authors specify the phonon as a vibration mode consistent with the B1g buckling mode [Cuk et al. 2004; Slezak et al. 2008].

We cannot comment on the origin of the electron boson interaction coming from phonons, as we don't have data from samples of different doping. We, however, do take notice of a few aspects of their analysis, which are different from ours and perhaps can clarify the contradiction seen in the two results. Firstly, the measurement of the positive peak in $d^2I/dV^2$, even though backed by a theoretical model [Balatsky et al. 2006], is quite different from the measurements in classical superconductors, where a negative peak in the second derivative is identified with the position of the phonon modes.
Figure 5-05 - Electron Boson Interaction and Isotope Effect – (a) Histograms of energy gaps Δ for BSCCO samples with different doping, black being strongly overdoped and blue strongly underdoped. (b) Histograms of measured boson energies Ω, from $d^2I/dV^2$-imaging measurements performed simultaneously with (a). (c) Two dimensional - histograms for different isotopes ($^{16}$O ($T_c = 76$ K) in blue while $^{18}$O ($T_c = 88$ K) in red) of BSCCO. Both the plots show weak correlation of Ω with Δ. The vertical shift is accidental and is attributed to hole density. The horizontal shift of Ω for the same Δ is attributed to isotope effect. Adapted from [Lee et al. 2006a].

Secondly, they do not perform measurements of the normal state at elevated temperatures and hence cannot normalize their data to perform the second derivative analysis correctly. We believe that the asymmetric normal state background in cuprates might be responsible for the change in the location of the second derivative peaks and hence their conclusion might be a systematic artifact of their analysis. Lastly, the presence of the pseudogap in the lower doping or the
smaller lifetime in regions with larger gaps can also affect the background spectrum, which can affect where the actual boson energy scale lies. This could be the reason for the disagreement between the phonon energies reported by them (52 meV) and the boson energy (38 meV) reported in our analysis. The only way to correctly extract the boson energy is by taking out contribution from the normal state spectrum.

In conclusion, we believe that the energy variations in the bosonic mode reported by the Cornell STM group are originating from a systematic error in the method instead of physical causes. Our data does show that there is a depression in the $R(r, V, T)$ at around $38 \pm 3$ meV, which is a signature of electron-boson coupling in BSCCO but, it seems to be parasitic and does not explain the variation in the pairing gaps and hence cannot be the underlying mechanism for superconductivity. In the next chapter, we focus on spectroscopic measurements of the electronic excitations in the normal state as a potential candidate to explain the inhomogeneity in the superconducting gaps.
Chapter 6

The Normal State of a High-$T_c$ Superconductor

In the previous chapter we provided evidence against electron boson coupling as the mechanism for high-$T_c$ superconductivity. In search of a better candidate to describe the origin of the inhomogeneity in the pairing interaction in the cuprates, we focus on spectroscopic measurements of the electronic excitations in the normal state and their correlation with the inhomogeneity in the superconducting gaps (reported in [Pasupathy et al. 2008]).

Figure 6-01 – Gap Map in the Superconducting and Normal State – Tracking the same area, which shows a variety of gap distribution (left) in the superconducting state ($50 \, K < T_c = 62 \, K$) to (right) high temperature normal state where almost all part of the sample (99%) has no gap represented by white. Adapted from [Pasupathy et al. 2008].
To reach the normal state, the temperature has to be high enough such that almost all the local pairing gaps have collapsed. For overdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ samples (hole doping $x = 0.24$, $T_c = 62$ K), less than 1% of the sample shows a gap at 93 K as shown in figure 6-01. Above 90 K, the tunneling spectra, examples of which are shown in figure 6-02, are gapless at all locations on the sample but show asymmetric behavior for electron and hole tunneling.

**Figure 6-02 – Gapless Normal State** – Spectra obtained at evenly spaced locations along a 250 Å line in the normal state ($T = 93$ K) of an overdoped BSCCO sample with $T_c = 62$ K
6.1 Correlation with the Superconducting State

Careful examination of these spectra, over a wide range of energies, shows that electronic excitations in the sample are still spatially inhomogeneous at temperatures well above when pairs first form in the sample.

Figure 6-03 – Correlation – (A) Superconducting gap map and (B) normal state conductance map in the same area are anti-correlated as shown by the red curve (angle averaged) in (C). The length scale of the anti-correlation is similar to the auto-correlation of the individual gap maps and conductance maps. Adapted from [Pasupathy et al. 2008].
The spatial inhomogeneity of the normal state’s electronic excitations can be measured using conductance ($dI/dV$) maps (discussed in section 2.6) at various voltages, which show variations on the order of 20 Å, as shown in figure 6-03. The magnitude of the variations is strongest for the conductance map obtained at the Fermi level, but such variations persist up to a few hundred meV (figure 6-04).

**Figure 6-04 – Conductance Maps near Fermi Energy** – (A) – (F) Normalized conductance maps in the normal state at energies as labeled all anti-correlate with the gap map in the superconducting state in the same area. (G) The anti-correlation is highest at the Fermi energy (-0.75). Adapted from [Pasupathy et al. 2008].
The spatial variations of the normal state conductance can be compared with the low temperature variations of the gap by using our lattice tracking technique (discussed in chapter 4). Shown in figure 6-03A is a gap map measured at 50 K over the exact same area of the sample as figure 6-03B. We can see a remarkable similarity between this gap map and the conductance map at the Fermi energy — regions with a lower normal state conductance at the Fermi level nucleate superconducting gaps at higher temperatures resulting in larger low temperature gaps. Quantifying these correlations in figure 6-03C, we show that the normal state conductance map and the low temperature gap map are strongly anti-correlated (-0.75). Further, both these maps have very similar auto-correlation lengths indicating that the spatial variation of the normal state is intimately linked to that of the low temperature gap. There is correlation between the superconducting gap and normal state conductance maps even at other energies near the Fermi energy (figure 6-04). These measurements show that the variation of the superconducting state in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ samples, which for typical superconductors is characterized by a temperature-dependent superconducting coherence length, appears to be for the most part determined by the spatial variation of the normal state at high temperatures.

Since our measurements show that the spatial variation of the normal state conductance and the low temperature pairing gap maps are intimately connected, we can associate an average normal state spectrum with a low temperature gap value. We thus average together normal state spectra of regions of the sample that show identical low temperature gaps, and plot these average spectra in figure 6-05.
Figure 6-05 – Normal State Background Foreshadows Gap Size Variation – (A) Average normal-state \( T = 93 \) K spectra measured in different regions that show distinct low-temperature superconducting gaps \( \Delta(0) \). Systematic changes can be seen in the shape and position of the hump feature seen for the hole like excitations. (Inset) Differential conductance of the normal state at the Fermi energy as a function of \( \Delta(0) \). (B) The energy corresponding to the hump feature in the spectra as a function of \( \Delta \). Adapted from [Pasupathy et al. 2008].

As this figure shows, systematic differences in the normal state spectra foreshadow the eventual variation of the gap in the superconducting state. In particular, the systematic shift of a hump in the normal state tunneling spectra at negative bias, in the range of -150 to -300 meV, (figure 6-05A) as well as the value of tunneling conductance at the Fermi energy (figure 6-05A inset) track the size of the superconducting gap observed at low temperatures. While the tunneling matrix element as well as the density of states of the tip both influence the shape of the tunneling conductance in the normal state, the features of the normal state and the correlation reported in figure 6-05 have been observed in measurements using several different micro-tips.
It is important to compare our measurements of the normal state with those obtained from other spectroscopic techniques. In both angle-resolved photoemission (ARPES) and optical spectroscopy, strong renormalization of the single-particle excitations has been observed over an energy range of ~200-400 meV below the Fermi energy in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ samples \cite{Campuzano2003, Cuk2005, Graf2007, Hwang2007, Meevasana2007}. Such effects have been previously interpreted as either due to the coupling of electrons with a spectrum of bosonic excitations (such as spin fluctuations) or as a consequence of the energy band structure (such as the bilayer splitting) of this compound \cite{Damaschke2003}. It is difficult to associate the normal state features that we measure with coupling to bosonic excitations due to their strong electron-hole asymmetry. Although we strictly cannot rule out bosonic excitations as the origin of these features, candidate bosons would have to couple very asymmetrically to the tunneling of electrons and holes. Assigning these features to effects calculated from a simple non-interacting band structure can also be questioned given both the strong spatial variation at the atomic scale of the normal state spectra we observe, and the strong renormalization of single-particle states at similar energies in other spectroscopic studies of the normal state. Instead, these features might be the excitations of a doped Mott insulator where the electron and hole excitations are naturally asymmetric as a consequence of the strong Coulomb interaction \cite{Paramekanti2001, Anderson2006, Haule2007}. Some recent calculations indeed produce a hump in hole-like excitations that correlate with the strength of pairing \cite{Paramekanti2001, Haule2007}. 
Although there is no clear consensus on a model for these excitations, our experiments [Pasupathy et al. 2008] show that the spectroscopic features of this state are indeed the origin of the nanoscale variation of the pairing strength in the superconducting state. Further experiments in samples at different hole doping levels at higher temperatures will be required to provide the detailed evolution of these atomic scale spectroscopic features of the normal state across the phase diagram.

From a broader perspective, we have used the spatial variation of the pairing gaps, which gives rise to a range of pairing temperatures in nanoscale regions of our samples above \( T_c \), as a diagnostic tool to find clues to the underlying mechanism of superconductivity. Temperature-dependent lattice tracking spectroscopy has allowed us to demonstrate that electron-boson coupling in the 20-120 meV range does not cause the variation of pairing gaps and onset temperatures in our samples as discussed in the previous chapter. In contrast, we find that the high-energy (up to \( \sim 400 \) mV) hole-like excitations of the normal state are a direct predictor of strength of pairing and its spatial variation. The anti-correlation between the normal state conductance at the Fermi level and local strength of pairing also runs contrary to a BCS-like pairing mechanism where the coupling to bosons is proportional to the density of states at the Fermi energy [Carbotte 1990].
Figure 6-06 – Origin of Inhomogeneity – (A) Gap map \(T = 50 \text{ K}; T_c = 62 \text{ K}\) (B) Normal state \(T = 93 \text{ K}\) conductance map \(dl/dV_0\) at \(E_F\) (C) Topograph (D) Conductance map at -800 meV showing resonances scattered in space. (A)-(D) are in the same area. (E) The variation in the gap map, normal state, conductance map, and topography after averaging along the a-axis. (F) Correlation between the -900 meV resonances and the gap map (green) and between the -900 meV resonances and \(dl/dV_0\) (red). Also shown for comparison (blue) is the correlation between \(dl/dV_0\) and the gap map. [Pasupathy et al. 2008]
6.2 Summary

To conclude this chapter, we address the question of the underlying cause of variations of the normal state excitations in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ samples. Our analysis finds that both structural and electronic features of the samples contribute to such variations. We find that there are small correlations (about 10%) of the normal state conductance maps with the structural supermodulation along the b-axis in these samples as shown in figure 6-06, which has been reported by the Cornell STM group [Slezak et al. 2008]. Similarly, we find that maps of electronic resonances around -900 meV previously probed in similar samples with STM [McElroy et al. 2005a] are correlated with the normal state conductance maps (about 30%). Our measurements show that structural and chemical inhomogeneity affects both the excitations of the normal state and the superconducting gap. Shown in figure 6-06A is a gap map of an overdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ sample ($T_c = 62$ K) taken at 50 K. Shown in figure 6-06B is the conductance at the Fermi level measured in the normal state ($T = 93$ K). Figure 6-06C shows the topograph taken at high positive bias (800 mV) in the same area of the sample showing the b-axis supermodulation. To show the correlation between these quantities, we average these maps along the a-axis. The resultant variation in the gap, normal state conductance as well as the topographic height is shown in figure 6-06E, clearly showing that both the gap as well as the normal state conductance are affected by the b-axis supermodulation.

Shown in figure 6-06D is a map of the conductance at -900 meV taken in the
normal state showing a number of resonances. These resonances affect both the gap map as well as the normal state conductance as shown in the correlation functions plotted in figure 6-06F. While the resonances have a ~ 30% effect on gap and the normal state, the normal state anticorrelates much more strongly with the gap map as shown earlier in the chapter. Our conclusion from such studies is that while a variety of factors can influence the low temperature gap, changes in the gap are foreshadowed by similar changes in the normal state excitation spectrum of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$.

As is common to several correlated systems, many structural and electronic features can influence the onset and strength of collective phenomena [Dagotto 2005]. Our ability to correlate nanoscale excitation spectra between two distinct electronic states at the same atomic site provides a new experimental method to study correlated phenomena in compounds with heterogeneous chemical and structural properties.
Chapter 7

Visualizing Pair Formation on the Atomic Scale

7.1 Introduction

In the previous chapters, we discussed pair formation at a given lattice site on an over-doped sample and its connection with the normal state. In this chapter, we will take a more general and statistical approach to visualize pair formation (reported in [Gomes et al. 2007]) in nanometer-sized areas of samples with different doping. We know that pairing of electrons in conventional superconductors occurs at the superconducting transition temperature, \( T_c \), creating an energy gap \( \Delta \) in the electronic density of states (DOS) [Tinkham 1996]. But, in the previous chapters, we saw that there is a remnant gap above the bulk \( T_c \) of an over-doped sample. It’s been known from various other experimental measurements that, in the high-\( T_c \) superconductors, a partial gap in the DOS exists below a temperature \( T^* > T_c \) [Timusk et al. 1999]. A key question is whether the gap in the DOS above \( T_c \) is associated with pairing, and what determines the temperature at which incoherent pairs form. In this chapter, we discuss spatially resolved measurements of gap formation on Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) samples with different \( T_c \)s (hole concentration \( x = 0.12 \) to 0.22). In what will follow, we will show that over a wide range of doping (0.16 \( \leq x \leq 0.22 \)) we find that pairing gaps nucleate in nanoscale regions above \( T_c \). These regions proliferate as the temperature is lowered,
resulting in a spatial distribution of gap sizes $\Delta$ in the superconducting state [Howald et al. 2001; Pan et al. 2001; McElroy et al. 2005a]. Despite the inhomogeneity, we find that every pairing gap $\Delta$ develops locally at a temperature $T_p$, following the relation $2\Delta/k_B T_p = 7.9 \pm 0.5$. At very low doping ($x \leq 0.14$), systematic changes in the DOS indicate the presence of another phenomenon [Tallon et al. 2001; Kivelson et al. 2003; Norman et al. 2005; Lee et al. 2006b], which is unrelated and perhaps competes with electron pairing, which we will take up in chapter 9. We will also discuss how our observation of nanometer-sized pairing regions provides the missing microscopic basis for understanding recent reports [Corson et al. 1999; Xu et al. 2000; Wang et al. 2005; Wang et al. 2006] of fluctuating superconducting response above $T_c$ in hole-doped high-$T_c$ cuprate superconductors.

7.2 Revisiting Atomic Scale Measurements

As our instrument allows us to track specific areas of the sample on the atomic scale as a function of temperature, we can use it to develop a systematic approach for the analysis of the data at different doping and temperatures. We first consider the measurements on the most overdoped sample, with $x = 0.22$. At this doping, pseudogap effects have been reported to be either weak or absent [Timusk et al. 1999; Tallon et al. 2001], allowing us to interpret gaps in the DOS as those associated with superconductivity.
Lets remind ourselves what we saw in chapter 4. Figure 7-01 (similar to figure 4-02) shows spectroscopy measurements for an overdoped sample with \( T_c = 65 \) K (OV65) performed at a specific atomic site over a range of temperatures close to \( T_c \). From such spectra, we determine two important quantities. First, we measure the maximum value of the local gap \( \Delta \sim 24 \) meV.

![Graph](image)

**Figure 7-01 – Spectroscopy at an Atomic Site** – (a) Spectra taken at the different temperatures at the same atomic location (within 0.1 Å) as indicated. (b) Topography showing the atomic location on the sample where the spectra were taken. (c) Low \( T \) (20 K) and high \( T \) (100 K) spectrum showing gap going away at higher temperatures. [Gomes et al. 2007]
Second, we estimate the temperature $T_p \sim 72$-80 K at which $\Delta$ is no longer measurable, using the criterion that at this temperature $dl/dV(V = 0) \geq dl/dV$ (for all $V > 0$). Above $T_p$ the spectra shows a bias-asymmetric background in the DOS which changes little with increasing temperature—indicating that the pairing gap is either absent or no longer relevant at this atomic site. Based on this procedure, we find that the data in figure 7-01 can be described by the relation $2\Delta/k_BT_p \sim 7.7$. While this measurement at a single atomic site is not statistically significant, it establishes the procedure that we extend to large sets of similar measurements in the next section.

7.3 Statistical Measurements: The Rule of 8

The evolution of the pairing gap with temperature can be examined statistically using spectroscopic mapping measurements over large areas ($\sim 300$ Å) of the sample as a function of temperature. Such experiments allow direct visualization on the atomic scale of the development of gaps. In the superconducting state ($T < T_c$), the overdoped OV65 sample shows (figure 7-02a) a distribution of $\Delta$ [Howald et al. 2001; Pan et al. 2001]. With increasing temperature, gap maps and related histograms on the OV65 sample display a rapid increase of ungapped regions (figure 7-02a-d). Although the temperatures over which the gaps collapse locally are relatively close to $T_c$ for this sample, these measurements clearly demonstrate that gaps persist locally on the nanoscale over a range of temperatures $T_p$. These results are reminiscent of recent calculations of the evolution of pairing
gaps with temperature in a \( d \)-wave superconductor with spatially varying pairing correlations [Andersen et al. 2006].

**Figure 7-02 – Gap Evolution for OV65 Samples with \( T \)** – (a)-(d) Gap maps taken on the same 300 Å area as shown in the inset of (d). At each temperature and atomic site, the value of the gap can be extracted from local spectroscopic measurements by using the experimental criterion that the local \( dl/dV \) has a maximum at \( V=+\Delta \), as demonstrated by data in figure 7-01a.
A great deal of information about the nucleation of pairing on the atomic scale can be extracted from data in figure 7-02. Here, we focus on extracting the relation between a given local $\Delta$ measured at $T < T_c$ and the temperature $T_p$ at which it collapses. From the gap maps in figure 7-02, we can extract the percentage of the sample that is ungapped at a given temperature (points in figure 7-03b).

![Figure 7-03 - Gap versus $T_p$ Scaling](image)

**Figure 7-03 - Gap versus $T_p$ Scaling** – (a) The histograms represent the probability distribution of the pairing gaps at different temperatures. (b) The smooth line shows the probability $P(< \Delta)$ that the gaps are less than a given $\Delta$ (lower x-axis). This is obtained for a given energy by summing the lowest temperature histogram of $\Delta$ to that voltage. The percentage of ungapped area of the sample (points) is plotted as a function of temperature (upper x-axis). The scaling between the two x-axes is $2\Delta/k_B T_p = 7.8$. The vertical bars represent the standard deviation arising from the finite statistics and the energy and conductance resolution of the spectra measured.

To compare, we use the histogram of $\Delta$s measured at the lowest temperature to compute the probability $P(< \Delta)$ that the gaps are less than a given $\Delta$ (solid line). A linear relationship between local $\Delta$ and $T_p$ would require that the x-axis of these two measurements be related by a simple ratio. The best-fit ratio extracted in figure 7-03b is $2\Delta/k_B T_p = 7.8 \pm 0.3$. This relation shows that despite the strong variation of
the superconducting gaps on the nanoscale in the overdoped sample, they all collapse following the same local criterion.

Having established the relation between local $\Delta$ and $T_p$ for the pairing gaps in the OV65 sample, we can study the temperature evolution of gaps in the DOS measured on samples with different dopings. In figure 7-04, we show such measurements on an over-doped sample OV83 with the bulk $T_c = 83$ K.

![Gap Evolution for OV83 Samples with T](image)

**Figure 7-04 - Gap Evolution for OV83 Samples with T** - (Top row) Gap maps at different temperatures in different 300 Å areas of the OV83 sample. The gap maps taken above $T_c$ show a similar evolution as in the case of OV65 samples and the same formation of nanoscale islands where pairing can be found. (Bottom row) The histogram statistics and the percentage of ungapped regions for different temperatures show the same scaling criterion, $2\Delta/k_BT_p = 7.8$. 

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Here, the gaps are larger than that in OV65 samples as can be seen in the low temperature gap map and the histogram in figure 7-04. Accordingly, higher temperatures need to be accessed to kill these gaps. Even at 105 K, 35% of the sample fraction of OV83 has a gap, whereas in case of OV65 samples, only 20% sample fraction has a gap at 74 K and by 93 K almost the entire sample (99%) is gapless as was shown in figure 6-01. Even though the gap sizes are different, a similar analysis of the linear relationship between $\Delta$ and their corresponding $T_p$s as was done for OV65 sample yields the relation: $2\Delta/k_B T_p = 7.8 \pm 0.2$.

We now extend our analysis to optimally doped samples. In contrast to the overdoped samples, which develop ungapped regions rapidly while crossing $T_c$, the optimal doped sample is still entirely gapped 10 K above its $T_c$ as shown in figure 7-05b. The loss of phase coherence at $T_c$ only affects the sharpness of the peaks in the spectra at $V = \pm \Delta$, while the gap in the superconducting state smoothly evolves into that measured above $T_c$ (see figure 7-05a) [Renner et al. 1998].
Figure 7-05 - Gap Evolution for OP93 Samples with $T$ – (a) Representative spectra taken at different temperatures (offset for clarity) on an OP93 sample. The coherence peaks diminish in intensity on raising the temperature through $T_c$, but a peak in the spectrum persists at positive bias. (b)–(d) Gap maps taken over 300 Å areas at different temperatures on the OP93 sample.

High-resolution gap maps measured at different temperatures (figure 7-05b-d) show that the distributions of gaps just above and below $T_c$ are essentially the same except for some broadening. Figure 7-06 shows the evolution of gap histogram
with temperature. As can be seen in figure 7-06, the 100 K gap histogram (orange) appears shifted further in gap size as compared to the one at 80 K (purple).

![Figure 7-06 - Gap Distribution with T](image_url)

**Figure 7-06 – Gap Distribution with T** – Gap distributions for OP93 samples taken at 40 K, 80 K (superconducting), 100 K and 120 K (non-superconducting). The gaps evolve continuously through $T_c$ and all gaps survive at 100 K.

The difference seen in the two histograms implies that the spectral peak position might have shifted on raising the temperature. We believe that such a shift can be accounted for by thermal broadening via two mechanisms. Firstly, the Fermi distribution becomes broader with increasing temperature due to which the conductance peak moves to higher voltage [Giaever et al. 1961]. Secondly, the quasiparticle lifetime broadening is known to increase as $T$ goes through $T_c$ [Norman et al. 1998b]. Both these effects can be modeled using the $d$-wave DOS in equation 4.2. We find that a 40 mV gap (typical of optimally doped samples) at $T=0$
has a peak position that increases with temperature. The shift due to the Fermi distribution is \(\sim 3\text{mV}\) between 80 K and 100 K. This, together with the addition of a modest lifetime broadening (5-10 meV) can explain the shift in the peak position between 80 K and 100 K.

Further increase in the temperature results in an inhomogeneous collapse of gaps. The spatial collapse of the gaps is comparable to that observed in the overdoped samples (figure 7-02), except that the temperature range for \(T_p\)s over which gaps collapse is much larger for the OP93 sample (105-160 K) as compared to the OV83 (80-120 K) sample, which in turn is larger than the OV65 sample (64-80 K). Figure 7-07 shows the representative spectra evolution with temperature for OV65 samples while figure 7-08 shows the same for OP93 samples.

![Figure 7-07](image)

**Figure 7-07 – Representative Spectra in OV65 Samples** – (a) 40 K and (b) 70 K spectra along a line on the sample. Low temperature (40 K) spectra show deep superconducting gaps everywhere with sharp coherence peaks whereas at higher temperature (70 K), just 5 K above the \(T_c = 65\) K, the spectra show a mix of gapped as well as ungapped regions.
Figure 7-08 – Representative Spectra in OP93 Samples – (a) 40 K spectra along a line across the sample show deep superconducting gaps everywhere. (b) 100 K spectra along a line on the sample show shallow gaps everywhere with no sharp coherence peaks. Only when the temperature is raised to 135 K (c), the spectra show a mix of gapped as well as ungapped regions.

As can be seen on comparison of the two figures for representative spectra of OV65 and OP93 samples with temperature, the range of temperatures for gap collapse is very different. Despite this difference we can use the comparison between $P(<\Delta)$ measured at the lowest temperature with the percentage of the ungapped regions measured as a function of temperature to test our local pairing hypothesis for samples at various doping. The measurements of these two quantities are displayed in figure 7-09, where a single temperature-gap scaling relation $2\Delta/k_B T_p = 8.0$ has been used to plot data on all samples in this study. There are a total of about a million spectra all following this local criterion.
Figure 7-09 – The Rule of 8 – The solid lines show the integral of the gap distributions versus gap size (lower x-axis) for the three different doping levels discussed in this section. The points show the percentage of ungapped regions as a function of $T$ (upper x axis). The scaling between the two axes is $2\Delta/k_B T_p = 8.0$.

From figure 7-09 it is clear that overdoped and optimally doped samples have identical gap-temperature scaling ratios, which together with consistency of their low temperature spectra with a $d$-wave superconducting gap, implies that we can interpret these gaps as those due to pairing. These results clearly show that pairing gaps and the temperature at which they collapse (which can be equal to or larger than $T_c$) follow a universal local criterion over a wide range of doping. The extracted ratio also shows that the local pairing gap is far more fragile to increases in temperature as compared to the conventional BCS superconductors, for which the ratio is in the range of 3.5-5 [Tinkham 1996]. Surprisingly, the ratio is insensitive
to the size of the gap, for gaps ranging from \(~15\) mV to \(50\) mV, indicating that even the smallest gaps are very far from the BCS limit.

### 7.4 The Underdoped Case: Violation of the Rule of 8

![Image: Gap map and graph showing violation of the Rule of 8]

**Figure 7-10 – Violation of the Rule of 8** – (left) Gap map at an elevated temperature (180 K) for an UD73 sample. There are very few ungapped regions. (b) The solid lines show the integral of the gap distributions versus gap size (lower x-axis) for the two different UD samples - UD83 and UD73. The points show the percentage of ungapped regions as a function of \(T\) (upper x-axis) for the same samples. The scaling between the two axes is \(2\Delta/k_B T_p = 8.0\). Clearly, this rule doesn’t apply to the UD samples.

Our local pairing hypothesis however appears to fail in the underdoped regime (figure 7-10). As can be seen, these gaps are larger in size and persist to higher temperatures than \(T_p\) obtained from the relationship of \(2\Delta/k_B T_p = 8.0\). While such a pairing hypothesis has its shortcomings, such as ignoring the possibility of a proximity effect, we show that the deviation from this picture in underdoped samples is most likely due to complication of two energy scales in this doping
regime. Figure 7-11 shows representative spectra measured at temperatures both in
the superconducting state and above $T_c$ for an underdoped sample with bulk $T_c = 73$
K (UD73). Above $T_c$, the spectra still show large gaps but the coherence peaks are
not seen [Renner et al. 1998].

![Representative Spectra in UD73 Samples](image)

**Figure 7-11 – Representative Spectra in UD73 Samples** – (a) 20 K spectra along a line
across the sample show gaps everywhere. Coherence peaks are observed only in some parts
while about 30% of the regions show presence of a lower energy feature indicated with an
arrow. (b) 80 K spectra along a line on the sample show V-shaped spectra with gaps
everywhere. No lower energy feature is observed.

This is very different from the overdoped and optimally doped samples, which
show electron-hole asymmetric spectra without a gap at high temperatures. In
contrast, the underdoped UD73 samples show very different V-shaped spectra with
an ill-defined gap according to our procedure of defining the gap as the energy
corresponding to maximum conductance on the positive bias. Figure 7-12 compares
the representative spectra at elevated temperatures for samples with different
doping.
Clearly, such V-shaped spectra are related to the strong pseudogap behavior in underdoped cuprates [Hanaguri et al. 2004; McElroy et al. 2005b]; however, these spectra and their pseudogap behaviour are qualitatively different from the pseudogaps observed on optimal and overdoped samples above $T_c$. Such a difference is also seen in ARPES measurements where the gap closes in overdoped samples but fills-in for underdoped samples [Norman et al. 1998a]. A key question is whether all gaps in the underdoped regime as measured by STM can be ascribed to pairing. We find that for $T << T_c$, greater than 30% of the spectra on the underdoped sample show “kinks” in the spectra at low bias indicating the importance of a lower energy scale, as shown in figure 7-11 and figure 7-13 [Howald et al. 2001; Hanaguri et al. 2004; McElroy et al. 2005b; Valla et al. 2006; Boyer et al. 2007].
The probability of observing such spectra in optimal or overdoped samples is negligible. Spectroscopic mapping with STM can be utilized to determine the spatial variation and distribution of each energy scale (figure 7-13). The presence of this additional energy scale indicates that the large gaps seen in underdoped samples cannot be simply associated with pairing. Evidence for two energy scales, one related to pairing and one related to strong pseudogap behaviour in underdoped cuprates has been accumulating from photoemission [Tanaka et al. 2006; Lee et al. 2007], STM ([Boyer et al. 2007; Pushp et al. 2009]) and Raman measurements [Le Tacon et al. 2006]. The underdoped spectra cannot be fit to a simple $d$-wave because of the presence of multiple features. In contrast, at doping levels beyond optimal doping, results from these experiments can be captured with a single energy scale as has been shown by us [Pushp et al. 2009]. We will talk more about our results on the underdoped samples in the subsequent chapters.
7.5 Summary

To summarize we show a table of all the different samples measured in this study to bring out the relationship between a given gap and its $T_p$. The sample $T_c$ is found by susceptibility measurements performed with a SQUID. The average gap ($\Delta_{avg}$) is extracted from the gap maps at the lowest temperatures studied. The ratio $2\Delta/k_B T_p$ is extracted from the best fit between the low temperature gap histograms and the gap maps at various temperatures.

Table 1: Samples and Gap Statistics

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$T_c$ (K)</th>
<th>Doping</th>
<th>$\Delta_{avg}$ (mV)</th>
<th>$2\Delta/k_B T_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OV65</td>
<td>65</td>
<td>0.22</td>
<td>26</td>
<td>7.8 ± 0.3</td>
</tr>
<tr>
<td>OV83</td>
<td>88</td>
<td>0.19</td>
<td>38</td>
<td>7.8 ± 0.2</td>
</tr>
<tr>
<td>OP93</td>
<td>93</td>
<td>0.16</td>
<td>52</td>
<td>8.1 ± 0.2</td>
</tr>
<tr>
<td>UD83</td>
<td>83</td>
<td>0.14</td>
<td>61</td>
<td>7.9 ± 0.6</td>
</tr>
<tr>
<td>UD73</td>
<td>73</td>
<td>0.12</td>
<td>66</td>
<td>*</td>
</tr>
</tbody>
</table>

* Cannot extract from data.

The low temperature histogram of all the gap maps for the five samples measured in this study is shown in figure 7-14. As can be clearly seen, the mean of the gaps is increasing as the samples are underdoped. The scaling curves for the OP-OV samples as well as UD samples are also plotted to show their difference.
Figure 7-14 – What does it all mean? – (a) Low temperature histograms of all the samples measured in this study. The distributions are recorded at 40 K for OV64, OV83 and OP93 samples, at 50 K for UD83 and at 20 K for UD73 samples. (b) The doping can be classified into two – OP and OV samples follow the rule of 8 while the UD samples do not.
Our ability to visualize the development of gaps and the local pairing hypothesis, which we have established quantitatively on optimal and overdoped samples provides a microscopic picture to understand several key aspects of the cuprate phase diagram. In figure 7-15, we summarize our observations of the spatially inhomogeneous development of the gaps with a color plot showing the percentage of areas that are gapped as a function of temperature at specific doping.

Figure 7-15 – Schematic Phase Diagram of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ - Points indicate temperatures and doping levels where large area gap maps were obtained. The colors are the percentage of the sample that is gapped at a given temperature and doping as measured in the gap maps. The $T_{p,\text{max}}$ line is the temperature at which $<10\%$ of the samples is gapped. The lower solid line denotes the bulk $T_c$. 

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The rising percentage of the gapped regions in various samples with lowering temperature probed in our experiments on the atomic scale, remarkably matches the onset of the suppression of low energy excitations probed by other techniques [Damaschke et al. 2003]. As we discussed above, for the optimal and overdoped samples a single energy gap can describe all of our findings, strongly suggesting that the onset of the gap is indeed due to pairing, which occurs locally at $T_p$. The apparent $T^*$ line is controlled by the largest pairing gaps ($T_p(\text{max})$) for these samples.

In contrast, for underdoped samples our data supports the notion of two energy scales. The $T^*$ line is controlled by the larger of the two scales which appears to be unrelated to pairing. Our data suggests that the $T_p(\text{max})$ line could be well below $T^*$ for low doping. This possibility is also supported by measurements of fluctuating superconductivity, which have shown that the onset temperatures for these fluctuations are well below $T^*$ for underdoped samples [Corson et al. 1999; Xu et al. 2000; Wang et al. 2005; Wang et al. 2006]. A comparison of our data to those from Nernst and magnetization measurements on similar Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ samples [Wang et al. 2006] shows that the macroscopic signature of the fluctuating superconducting state appears when $\sim$50% of the sample develops a pairing gap. Given that an adequate amount of pairing has to develop in the samples for the vortex response to be well defined, our measurements provide the missing microscopic basis for the onset of the vortex response. Our observation of local
pairing over a range of temperatures, as well as the Nernst and magnetization measurements, all show that $T_c$ in Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ system marks the onset of phase coherence and not the formation of pairs as in BCS superconductors.

Finally, the local paring criterion extracted from a large number of measurements on Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ at various dopings and temperatures has important implications for the mechanism of pairing in cuprates. In conventional superconductors, the strength of the coupling of electrons to phonons determines both $\Delta$ and $T_c$, with stronger coupling resulting in an increase of both these quantities. However, in the strong-coupling limit, the ratio $2\Delta/k_B T_c$ is dependent on $\Delta$ and increases from the universal BCS ratio of 3.5 [Tinkham 1996]. The extension of BCS theory based on the Eliashberg equations captures this behavior for conventional superconductors [Carbotte 1990]. Our observation of the insensitivity of the large ratio $2\Delta/k_B T_p = 7.9 \pm 0.5$ to the size of local $\Delta$s (from 15-50 mV), the local disorder, as well as doping is hence fundamentally different from the expectations [Balatsky et al. 2006] from an electron-boson pairing mechanism based on an Eliashberg-type theory. A successful theory of cuprates would have to explain not only how pairing correlations can nucleate in isolated nanoscale regions at high temperatures but also the robustness of the local pairing criterion discussed here [Gomes et al. 2007].

This chapter gives a lot of evidence that the gaps in the OP-OV samples of the bi-layer Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ are indeed pairing gaps. This result is also true for the monolayer Bi$_2$Sr$_{2-y}$La$_y$CuO$_{6+x}$ as discussed in the next chapter.
Chapter 8

Pair Formation in the Single-Layer Cuprate

$\text{Bi}_2\text{Sr}_{2-y}\text{La}_y\text{CuO}_{6+\delta}$

8.1 Introduction

In the previous chapter, we established that the pairing gaps in the bi-layer cuprate superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) nucleate in nanoscale regions and proliferate as the temperature is lowered [Gomes et al. 2007]. We showed that every pairing gap, $\Delta$, develops locally at a temperature $T_p$, following the relation $2\Delta/k_B T_p = 7.8 \pm 0.5$. This relationship holds true for a surprisingly large doping range (optimal to over-doped) despite the inhomogeneities that are characteristic of these samples. In order to draw more general conclusions about the robustness of this ratio it is crucial to investigate other high-$T_c$ superconductors. In this chapter, we show a similar relationship exhibited by the monolayer cuprate superconductor $\text{Bi}_2\text{Sr}_{2-y}\text{La}_y\text{CuO}_{6+\delta}$ (Bi-2201). In the optimal to over-doped regime in Bi-2201, we have determined a relation: $2\Delta/k_B T_p = 7.6 \pm 0.4$, where delta is the gap at a specific lattice site and $T_p$ is the temperature where the gap vanishes. This relationship is true for all gaps smaller than 50 meV but breaks down for larger gaps.
8.2 Comparison of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ with Bi$_2$Sr$_{2-y}$La$_y$CuO$_{6+\delta}$

Just as the Bi-2212 samples, the single layer Bi$_2$Sr$_{2-y}$La$_y$CuO$_{6+\delta}$ samples are also grown by the floating zone technique [Ono et al. 2003]. In contrast to the bi-layer Bi-2212, where doping can be varied by changing the oxygen concentration in the crystal, doping in Bi-2201 is varied by replacing the constituent atoms by atoms of similar sizes but different valence (for example, Bi with Pb or in our case Sr with La, etc.) as shown in figure 8-01.

![Crystal Structure](image)

**Figure 8-01 – Crystal Structure** – (left) Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (right) Bi$_2$Sr$_{2-y}$La$_y$CuO$_{6+\delta}$ crystal structure showing different layers and weak BiO bonds where they tend to cleave. Doping is controlled by oxygen in Bi-2212 while by substituting Lanthanum for Strontium in Bi-2201.

Both these materials have weak bonds located between the BiO layers as shown in figure 8-01 and hence frequently give nice atomically flat BiO surfaces on cleaving. The topographies look very similar showing the well-understood [Gao et al. 1988] $b$-axis super modulation as shown in figure 8-02.
Such substitution induces additional disorder resulting in an even more inhomogeneous distribution of gaps in the monolayer samples as compared to that of Bi-2212 samples (figure 8-03).

Figure 8-02 – Topography – Atomic resolution topographies of (left) Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (right) Bi$_2$Sr$_{2-y}$La$_y$CuO$_{6+δ}$ showing BiO layers and b-axis supermodulation.

Figure 8-03 – Gap Distribution – Optimally doped Bi-2201 with bulk $T_c = 33$ K (red) shows a more inhomogeneous distribution of gaps as compared to optimally doped Bi-2212 with $T_c = 93$ K (blue).
In what will follow, we will show that despite this lattice induced disorder the relationship between the pairing gap at low temperature and the temperature where it collapses is robust.

Figure 8-04 – Spectroscopy at an Atomic Site – (a) Topography showing the atomic location on the sample where the spectra were taken. (b) Spectra taken at the different temperatures at the same atomic location (within 0.1 Å) for an overdoped samples with $T_c = 25$ K (OV25). Even at lowest temperatures the spectrum doesn’t show sharp coherence peaks, which is attributed to disorder.

Figure 8-04 shows the evolution of the DOS with temperature at a given lattice site on an overdoped Bi-2201 sample with $T_c = 25$ K (we label this sample as OV25) as indicated in the topography. From the spectrum at the lowest temperature, we obtain the maximum value of the local pairing gap. It has been reported before [Kugler et al. 2001; Sugimoto et al. 2006] that the gaps in Bi-2201 do not show as prominent coherence peaks as are typically seen in Bi-2212 samples. This is attributed to the presence of more disorder [Eisaki et al. 2004] in the Bi-2201 samples and hence larger lifetime broadening. We define the value of a
gap to be the maximum on the positive side in the $dl/dV$ (dG) spectrum shown by the arrow in figure 8-04b. Next, we estimate the temperature at which the gap goes away leaving an asymmetric normal state background. We define $T_p$ when the corresponding spectrum satisfies $dl/dV(V=0) > dl/dV$ (for all $V>0$). Using this exercise for the point shown in figure 8-04, we obtain a value of $\Delta = 21$ meV while $T_p \sim 70$ K which gives us the ratio for $2\Delta/k_B T_p = 7.4$. We extend this procedure to analyze large areas ($\sim 300 \, \text{Å}$) of the samples of different doping-levels as a function of temperature.

Figure 8-05a shows gap maps of an over-doped Bi-2201 sample with a $T_c$ of 19 K (we label this sample as OV19) measured at 12 K in the superconducting state. The OV19 sample shows a distribution of gaps with gaps ranging from 0 to 70 meV. Interestingly, there are a few regions in this sample with no gap even in the superconducting state (12 K). With increasing temperature while tracking the target area, the fraction of gapless regions increases as shown in figures 8-05a-d. The smaller gaps vanish first followed by the larger ones as is also shown in the histogram of the gap distribution in figure 8-05e. In order to extract a relationship between a given local delta measured at $T < T_c$ and the temperature $T_p$ where it collapses, we first measure the fraction of gapless regions at various temperatures. As was done in the previous chapter, we then sum over the lowest temperature histogram in energy so as to obtain the solid line shown in figure 8-05f, which represents the fraction $P(<\Delta)$ of the gaps that are less than a given gap-value, $\Delta$, in the superconducting state. A linear relationship between local gap and $T_p$ would require that the x-axes of these two plots should have a simple scaling factor.
Figure 8-05 – Gap Evolution for OV19 Samples with $T$ - (a)-(d) Gap maps taken on the same 300 Å area. At each temperature and atomic site, the value of the gap can be extracted from local spectroscopic measurements by using the experimental criterion that the local $dl/dV$ has a maximum at $V'$=$+\Delta$. (e) Histogram of the gap size distribution with $T$. (f) The smooth line shows the probability $P(<\Delta)$ that the gaps are less than a given $\Delta$ (lower x-axis). This is obtained for a given energy by summing the lowest temperature histogram of $\Delta$ to that voltage. The percentage of ungapped area of the sample (points) is plotted as a function of temperature (upper x-axis). The scaling between the two x-axes is $2\Delta/k_B T_p = 7.6$. 
The best-fit ratio extracted for the OV19 sample is \(2\Delta/k_B T_p = 7.6\). This relation shows that despite a wide distribution of the pairing gaps on the nanoscale in the OV19 sample, these gaps collapse following the same local criterion. It may be noted here that majority of the OV19 sample is still gapped at 30 K (above \(T_c = 19\) K), implying that the pseudogap region is fairly large even in the over-doped side of the phase diagram for Bi-2201 as has been previously reported [Kugler et al. 2001]. This is different from over-doped Bi-2212 where at such high doping, pseudogap is almost non-existent [Gomes et al. 2007].

We now extend our analysis to the optimally doped Bi-2201 sample with a \(T_c\) of 33 K (label OP33). In figure 8-06a-d, we show the gap map evolution of different representative areas (~300 Å) of the OP33 sample at temperatures well above \(T_c = 33\) K. Tracking the same area of the sample through such high temperatures is not feasible with our current setup but, we argue that 300 Å is a large enough area (about 20 times the coherence as well as the correlation length) and hence is representative of the whole sample. In contrast to the over-doped OV19 sample, where gapless regions exist even below \(T_c\), the OP33 sample shows almost entirely gapped regions at 50 K (figure 8-06a), which is more than 15 K above its bulk \(T_c\) of 33 K. On raising the temperature further, not only the fraction of gapless regions increases, the fraction of larger gaps also registers an increase.
Figure – 8-06 – Gap Evolution for OP33 Samples – (a)-(d) Gap maps at different temperatures in different 300 Å areas of the OP33 sample. (e) Smaller gaps disappear on warming up. The smooth line shows the probability $P(<\Delta)$ that the gaps are less than a given $\Delta$ (lower x-axis). This is obtained for a given energy by summing the lowest temperature histogram of $\Delta$ to that voltage. The percentage of ungapped area of the sample (squares) is plotted as a function of temperature (upper x-axis). The scaling between the two x-axes is $2\Delta/k_B T_{\text{ph}} = 7.6$. (f) Conductance peak of large gaps move to higher energy on warming up because of thermal broadening.
All pairing gaps should decrease in size as the temperature is raised and should collapse at their corresponding $T_p$s [Gomes et al. 2007]. Then why is it that some gaps are vanishing while others are growing in size in these samples? These seemingly contradicting results can be explained by taking into account the thermal broadening at high temperatures. The small gaps on reaching their respective $T_p$s do collapse as the temperature is raised whereas the big gaps because of the way we define the gap (i.e. the maximum on the positive side in the LDOS spectrum) register an even higher value due to thermal broadening at such high temperatures. Figure 8-06f shows an example of a large gap (65 meV), i.e., the maximum of the spectrum on the positive side, increasing in size as the temperature is raised while tracking the same lattice site. This is true for the larger gaps ($\Delta > 50$ meV).

Recording the fraction of gapless regions with temperature and the summed low temperature gap distribution ($P(<\Delta)$ at 20 K as shown in figure 8-06e), we find that for the OP33 sample, a linear scale exists between the local gap $\Delta$ and the temperature $T_p$ where it collapses given by $2\Delta/k_B T_p = 7.6$. This analysis seems robust for gaps smaller than 50 meV for both OV19 and OP33 samples. In general, gaps smaller than 50 meV on collapse leave an electron-hole asymmetric spectrum whereas gaps larger than 50 meV show a V-shaped normal state with an ill-defined gap [Gomes et al. 2007]. These larger gaps in the optimally doped Bi-2201 samples are reminiscent of the gaps observed in the under-doped Bi-2212. In fact, the low temperature spectra in the OP Bi-2201 sample show low energy kink features (figure 8-07) similar to that of the UD Bi-2212 samples as shown in figure 7-11a in chapter 7.
8.3 Two Energy Scales

Figure 8-07 – Multiple Features in the Spectrum - 20 K spectra taken along a line across the sample show gaps everywhere. Coherence peaks are observed only in some parts while some regions show presence of a lower energy feature indicated with an arrow.

A recent ARPES study reported that a gap opens in the nodal direction in these materials (Bi-2212) at their bulk $T_c$ [Lee et al. 2007]. A recent STM study [Boyer et al. 2007] associates these kinks with the opening of this new gap at bulk $T_c$ of the sample where they show that these features abruptly appear at $T_c$ as shown in figure 8-08.
Figure 8-08 - Multiple Features in the Spectrum - (a) A set of spectra with different gap sizes ranging from 7 meV to 50 meV at 6 K (b) Gap map showing inhomogeneous distribution of gaps in a 180 Å area. (c) Normalized spectra obtained by dividing the spectra in (a) by their respective high T (16 K) spectra obtained at the same atomic locations. (d) Gap map of the normalized spectra obtained by the same method as in (c) for the entire area in (b) shows increased homogeneity. (Adapted from [Boyer et al. 2007]).

Low temperature (6 K) excitation spectra at eight different locations representative of the inhomogeneity (figure 8-08b) in the sample show small energy kinks, which can be brought out by dividing these spectra with their respective excitation spectrum at a temperature 1 K above the bulk $T_c$ (15 K) of the sample.
(figure 8-08c). On division all these spectra show very similar spectrum with a more homogeneous energy scale as shown in figure 8-08d in the same sample area.

While we agree on a broad scale that the nodal excitations are more homogeneous in these samples (we will talk about these universal nodal excitations in the next chapter), we don’t agree with the MIT group in their interpretation that the low energy kink turns on right at the bulk $T_c$ of the sample. We argue that by normalizing the low temperature spectra with spectra obtained so close to the bulk $T_c$, Boyer et al. in their analysis [Boyer et al. 2007], presume that a gap opens up near the bulk $T_c$. Hence, their interpretation is an artifact of the normalization procedure.

In fact, we have observed that these kinks do not necessarily vanish at the bulk $T_c$ and a few of them persist at temperatures above the bulk $T_c$ of the samples as shown in figure 8-09, where one can see a hint of a kink feature certainly up to 30 K and maybe even up to 37 K, i.e., up to 12 K above the bulk $T_c (= 25$ K) of the sample.

![Figure 8-09 – Kinks above $T_c$](image)

Figure 8-09 – Kinks above $T_c$ – Kinks are visible above the bulk $T_c = 25$ K for an OV25 sample as seen in the red curve (30 K). Cyan curve (37 K) also shows a hint of a kink.
Figure 8-10 – Inhomogeneity – (left) Normalized conductance $dG (T=19 \text{ K})/dG (T=50 \text{ K})$ at six different locations for OP33 sample (offset for clarity). (Right) Same spectra as on the left but plotted on top of one another show lack of homogeneity near the node (zero bias).

Another counter example of their claim is shown in figure 8-10 that shows spectra taken at 19 K normalized by that taken at 50 K at six different locations on an OP33 sample. If the kinks were to vanish at $T_c$, normalization of the low temperature spectra with the respective spectra obtained at much higher temperatures (50 K, in this case) should, in principle, show homogeneous spectra near the kink energy. This is clearly not the case for the six spectra laid on top of one another.

8.4 Summary

To conclude this chapter, we have established that just as in the bi-layer Bi-2212, a very similar relationship between the local gap and its $T_p$ exists for Bi-2201 samples in the optimally doped to over-doped region of the phase diagram for gaps less than 50 meV despite the gap distribution being even more inhomogeneous than
that of Bi-2212. Quantitatively, the ratio of $2\Delta/k_B T_p = 7.6$ for Bi-2201 is very close to 7.8 reported for Bi-2212 samples [Gomes et al. 2007], implying the universality of local pairing in high-$T_c$ cuprates. At low temperatures, Bi-2201 samples for all doping studied and UD Bi-2212 (chapter 7) samples show low energy kink features, which are more homogeneous than the higher energy gap. These kinks become difficult to detect in the vicinity of the bulk $T_c$ (but not right at $T_c$) of these samples and seem related to superconductivity. In the next chapter, we delve further into the low energy kink features in UD Bi-2212 samples and show that they are intricately related to pairing in these samples.
Chapter 9

Universal Nodal Excitations in Underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

9.1 Introduction

In this chapter, we concentrate on the underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ samples and discuss how the density of states spectrum in this regime ties with that of the rest of the phase diagram in cuprates. Understanding the mechanism by which $d$-wave superconductivity in the cuprates emerges and is optimized by doping the Mott insulator is one of the major outstanding problems in condensed matter physics. In this chapter, we will show that our high-resolution scanning tunneling microscopy measurements of the high transition temperature ($T_c$) superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ reveal that samples with different $T_c$s in the low doping regime follow a remarkably universal $d$-wave low energy excitation spectrum. We demonstrate that $T_c$ instead correlates with the fraction of the Fermi surface over which the samples exhibit the universal spectrum. Optimal $T_c$ is achieved when all parts of the Fermi surface follow this universal behavior. Increasing temperature above $T_c$ turns the universal spectrum into an arc of gapless excitations, while overdoping breaks down the universal nodal behavior. All these results have been reported in this reference [Pushp et al. 2009].
Central to the current debate on the mechanism underlying high-temperature superconductivity is the question of whether pairing strength in the cuprates is diminished as these systems approach the Mott insulator limit with reduced hole density. The panoply of physical phenomena in lightly doped cuprates near the Mott state uncovered over the last two decades, from observation of the pseudogap behavior [Timusk et al. 1999; Lee et al. 2006b] to fluctuating superconductivity [Wang et al. 2005; Wang et al. 2006] above $T_c$ to the possibility of other competing orders [Emery et al. 1999; Norman et al. 2005; LeBoeuf et al. 2007] have made addressing this question challenging. In a simple $d$-wave superconductor, a single energy scale suffices to completely describe the excitation spectrum, the associated pairing energy gap (including its angular and temperature dependence) as well as the transition temperature, $T_c$, of the sample. As was shown in the previous chapters, excitation spectrum of optimally doped to overdoped Bi-2212 samples can be fit to a simple $d$-wave gap function once the asymmetric background was taken into account. In the underdoped cuprates, however, there is increasing evidence [Le Tacon et al. 2006; Boyer et al. 2007; Gomes et al. 2007; Lee et al. 2007; Kondo et al. 2009] showing that a single energy scale is insufficient to describe the anisotropy of the energy gap because different behavior is seen near the node (45 degrees to the Cu-O bond direction) and the anti-node (along the Cu-O bond direction). The temperature evolution of the spectroscopic measurements has also shown a dichotomy between nodal and anti-nodal gaps, showing different temperature dependence [Kanigel et al. 2006; Tanaka et al. 2006; Lee et al. 2007]. Theoretical proposals for addressing these phenomena
include those based on phase fluctuations [Norman et al. 2007; Anderson 2008; Chien et al. 2009], incipient order [Norman et al. 2005], breakup of the Fermi surface due to umklapp scattering [Honerkamp et al. 2001], and incoherence of anti-nodal quasiparticles [Anderson et al. 2009]. Although it is clear that the gap near the anti-node increases as one approaches the Mott insulator [Campuzano et al. 2003], the behavior of the gap near the node still remains debated, with different measurements showing both increasing [Campuzano et al. 2003; Damascelli et al. 2003; Sutherland et al. 2003] and decreasing [Tallon et al. 2001; Le Tacon et al. 2006; Tanaka et al. 2006] trends with underdoping. Whether pairing gaps associated with nodal excitations track the samples’ $T_c$, as expected for simple $d$-wave superconductors, is an unresolved question that deeply affects our understanding of superconductivity in the cuprates. The answer to this question can determine if the pairing is derived from the strong electronic correlations of the Mott state and identify the mechanism by which $d$-wave superconductivity is optimized in proximity to an insulating ground state.

To elucidate the nature of the nodal and anti-nodal gaps as a function of doping and temperature, we show data on Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (BSCCO) in the doping range $0.07 < x < 0.24$ and temperature range 5-120 K. As was shown in the previous chapters, using lattice-tracking spectroscopy, spectroscopic measurements in our homebuilt STM can be performed with sub-meV energy resolution on the same atomic location as a function of temperature [Gomes et al. 2007; Pasupathy et al. 2008]. Although STM spectroscopy does not have intrinsic angular resolution, information about the nodal gap can be obtained from the spectrum near the Fermi
energy whereas the anti-nodal excitations occur at higher energy. We can use this information to extract the behavior of the nodal gap.

9.2 Homogeneity in Inhomogeneity

The complexity of the excitation spectrum in underdoped BSCCO samples (figure 9-01a) is seen in lattice-tracking spectroscopy measurements, in which we track the temperature evolution of tunneling spectra at a given atomic location. This spectrum (typical for this sample) shows a higher energy gap, $\Delta_0$, (black arrow, figure 9-01a), a smaller “kink” within the higher energy gap (red arrow, figure 9-01a) as well as an overall background, all of which are position dependent. For comparison, lattice-tracking spectroscopy measurements for an overdoped sample are shown in figure 9-01b, which was discussed in chapter 4.

Figure 9-01 – Spectra Comparison with Doping – Spectra (offset for clarity) taken with T while tracking the same atomic location in (a) UD61 (Underdoped; $T_c = 61$ K) sample and (b) OV65 (Overdoped; $T_c = 65$ K) sample. UD61 spectra show multiple features.
As is typical for BSCCO of all doping values, $\Delta_0$, determined by the maximum conductance on the positive side, shows strong spatial inhomogeneity [Howald et al. 2001; McElroy et al. 2005b] on the sample (figure 9-02).

![Figure 9-02 - Sorting the Inhomogeneity](image)

**Figure 9-02 - Sorting the Inhomogeneity** - A special map at 13 K for a UD58 sample. The colored regions represent areas where $\Delta_0$ is nearest to the correspondingly colored spectrum in figure 9-01a. Adapted from [Pushp et al. 2009].

The spatial average of the higher energy gap compares well with angle resolved photoemission spectroscopy (ARPES) measurements of the anti-nodal gap [Campuzano et al. 2003; Damascelli et al. 2003] and therefore we identify it as such. $\Delta_0$ shows relatively small temperature dependence and evolves smoothly through $T_c$ into the anti-nodal pseudogap [Gomes et al. 2007], while the “kink” shows strong temperature dependence (figure 9-03). We show this contrast by...
averaging together spectra from locations of the sample with the same $\Delta_0$ and plot the resultant spectra (figure 9-03) as a function of temperature.

**Figure 9-03 – Homogeneity in inhomogeneity** - $\Delta_0$ sorted, averaged spectra at different $T$s for a UD58 sample. The spectra are normalized by the mean over the entire bias range (each offset by 0.5). Homogeneity in the low energy spectra is lost upon raising the temperature through $T_c$. Adapted from [Pushp et al. 2009].
We note that at low temperatures the low energy spectra (below the kink) are substantially more homogeneous than the $\Delta_0$ [Howald et al. 2001; McElroy et al. 2005b]. However, the low energy homogeneity is lost upon raising the temperature through $T_c$ [Boyer et al. 2007].

9.3 Gap versus Angle Extraction Procedure

Clearly, the shape of the tunneling spectra in underdoped samples (figure 9-01a & 9-03) cannot be fit to a simple $d$-wave $\cos(2\theta)$ form, as it can be for overdoped samples [Pasupathy et al. 2008] as we showed in the previous chapters. In order to quantitatively understand the shape of the energy gap in momentum space, we model the spectrum using an angle dependent BCS-like gap where we allow the gap function to deviate from the $\cos(2\theta)$ form while maintaining overall $d$-wave symmetry. With evidence [Campuzano et al. 2003; Kanigel et al. 2007] from ARPES measurements showing that the spectral function is BCS-like at the node as well as at the anti-node, we model our spectra using a sum of BCS-like gaps. If we assume that the gap varies monotonically from the node to the anti-node and that the lifetime broadening is small at low temperatures, then we can fit the spectra uniquely with high accuracy as shown in figure 9-04. The fitting procedure described below allows us to extract the energy gap as a function of angle from the measured spectra.
In order to fit the spectra shown in figure 9-04A, we assume that the differential conductance at a voltage bias $V$ and temperature $T$, is given by a sum of BCS gaps:

$$\frac{dl}{dV}(V) = \int dE \frac{df(E + V,T)}{dE} \sum_{j=1}^{N} \text{Re} \frac{(E - i\Gamma)}{\sqrt{(E - i\Gamma)^2 - \Delta_j^2}} \times W_j$$

(9.1)

Here $E$ is the energy, $f$ is the Fermi function, $N$ is the desired number of bins, $i$ is the square root of -1, $\Delta_j$ are gaps each with a weight $W_j$ and $\Gamma$ is the inverse of quasiparticle lifetime (a small non-zero value of $\Gamma \sim 3-5$ meV is required to match the experimentally observed conductance at the Fermi energy). Fitting the experimental spectrum then reduces to finding the weighting coefficients $W_j$, which can be done using a simple least squares fit. Figure 9-04B shows the weights obtained from these fits to the spectra shown in figure 9-04A.

**Figure 9-04 – Fitting the Spectra** – (A) Average $dl/dV$ spectra from $\Delta_0$ sorted spectra (offset by 35 pS) on UD58 sample and their fit (blue line). Procedure has been applied separately for the positive and negative bias. (B) The weights of the corresponding positive side fits in (A), expressed as a fraction of the total weight of each gap size (each offset by 0.15). Adapted from [Pushp et al. 2009].
The sum over different gap sizes in equation 9.1 is formally equivalent to a sum over momenta (or different angles) for a given energy. In particular, the choice \( \Delta_j = \Delta_0 \cos(j \pi / 2N) \) with \( W_j \) set to a constant results in the simple \( d \)-wave case. For sufficiently large \( N \), we can always choose \( \Delta_j \) to be uniformly spaced.

Let us assume that the density of states can be represented as an integral over angular contributions, where each angle follows the BCS form with a gap \( \Delta(\theta) \) and background density of states \( N(\theta) \). Also, denote the total number of states between the node \( (\theta = \pi / 4) \) and a particular angle as \( C(\theta) = \int_0^{\pi / 4} N(\theta') d\theta' \). Note that \( C(\theta) \) is linear with \( \theta \) for a perfectly cylindrical hole barrel, but it can be determined from angle resolved photoemission (ARPES) in the normal state. The tunneling conductance should be given by

\[
\frac{dI}{dV}(V) = \frac{4M}{\pi} \int dE \frac{df(E + V, T)}{dE} \int_0^{\pi / 4} \text{Re} \frac{(E - i\Gamma)}{\sqrt{(E - i\Gamma)^2 - \Delta^2(\theta)}} N(\theta) d\theta
\]

Here \( M \) is a tunneling matrix element. If we change integration variables from \( \theta \) to \( \Delta \), equation 9.2 becomes

\[
\frac{dI}{dV}(V) = \frac{M}{\Delta_0} \int dE \frac{df(E + V, T)}{dE} \int_0^{\Delta} \text{Re} \frac{(E - i\Gamma)}{\sqrt{(E - i\Gamma)^2 - \Delta^2}} N(\Delta) d\Delta
\]

The quantity \( W_j \) in our fit in equation 9.1 is, within a matrix element, a good approximation of \( N(\Delta)d\Delta \). Therefore the cumulative weight \( C_j = \sum_{j=1}^{j} W_j \) is an approximation of \( C(\Delta) = \int_0^{\Delta} N(\Delta') d\Delta' \). We plot \( \Delta \) versus the summed weight \( C_j \) (basically summing y-axis in figure 9-04B upto a given \( \Delta \)) in figure 9-05A. Knowing
$C(\Delta)$ and $C(\theta)$, and assuming that $\Delta(\theta)$ is a monotonic function of $\theta$, we can determine $\Delta(\theta)$, by finding the value of $\Delta$ for which $C(\Delta)=C(\theta)$. Once again, we note that in the case of a simple cylindrical Fermi surface, figure 9-05A is essentially a plot of $\Delta$ versus a parameter proportional to $\theta$.

![Graph](image)

**Figure 9-05 – Gap versus Angle Extraction** – (A) Cumulative weights (x-axis) obtained by summing the corresponding histogram for each gap size (y-axis) of figure 9-04B. (B) Gap as a function of angle as extracted from the fits, using the ARPES band structure from [Norman et al. 1995].

We can use a more realistic model of the background density of states based on modeling of the ARPES data [Norman et al. 1995], to arrive at $\Delta(\theta)$ as shown in figure 9-05B. To do this, we first identify the value of cumulative weight that corresponds to the anti-node. We accomplish this by identifying the maximum gap that is required to fit a given spectra from the gap distributions, which should correspond to the anti-nodal gap. The second step is to use the realistic model of the photoemission data to compute $C(\theta)$, which is simply an integral of the density of states. We have used the common parameterization of the Fermi surface by Norman et al. [Norman et al. 1995] to compute this quantity, and it is easy to sum the
density of states to get $C(\theta)$. The scaling between $C(\Delta)$ and $C(\theta)$ is adjusted by requiring that $C(\Delta_{anti-node})=C(\theta=0)$, which is essentially a scaling to ensure that the largest gap occurs at the anti-node. Finally, we choose the value of $\Delta$ for which $C(\Delta)=C(\theta)$ to obtain $\Delta(\theta)$. We note that slightly different assumptions about the shape of the Fermi surface results in a few degrees (5 or so) of difference in the final results of $\Delta(\theta)$ from our procedure. Most importantly, we emphasize that this procedure is an unbiased method to determine the shape of $\Delta(\theta)$ that provides the best fit to the spectra. Alternatively, one can choose an analytical form of the function $\Delta(\theta)$, which approximates the results of our procedure, and show that it can capture the shape of the spectra in each sample accurately.

Hence, this generalized approach in extracting the distribution of $W_f$ from the spectra by using the model in equation 9.1 allows us to determine the angular dependence of $\Delta(\theta)$ from the STM spectra and more precisely isolate the universal behavior of the low-energy excitation spectrum. Another way to view the results of the fitting procedure is that the functions $\Delta(\theta)$ plotted in figure 9-05B provide the most accurate fit to the spectra shown in figure 9-04A and can capture all the energy and spatial dependence of the data.

Slightly different results are obtained from fits to the unoccupied (positive) and occupied (negative) side of the spectrum. This is because the excitation spectrum from STM on Bi-2212 is significantly asymmetric. For underdoped samples, the spectrum is nearly flat on the positive bias (unoccupied) side beyond the highest gap energy scale, while on the negative (occupied) side, the differential conductance increases on moving away from the Fermi level even beyond the gap
(figure 9-04A). Therefore, we choose to perform the gap versus angle fits on the unoccupied side to reduce background effects. For completeness, we show a comparison of the gap versus angle from both sides in figure 9-06. As can be seen, slightly different results are obtained from fits to the unoccupied and occupied side of the spectrum, but the trend is consistent between both.

![Graph showing gap versus angle](image)

**Figure 9-06 – Fitting on the Occupied Side** – Gap versus angle determined from unoccupied (red) and occupied (blue) side give very similar results.

We emphasize that although the deviation from universal $d$-wave is less pronounced on the occupied side it is still clearly present and the angle at which it
occurs is not significantly different. We also point out that photoemission experiments measure only the occupied side, where the effect is subtle. The occupied side also leads to generally larger anti-nodal gaps, which is unsurprising considering that the sloping background looks similar to the nodal region of an extremely large gap. In the remaining of this chapter, we will describe results from our analysis of our data on the unoccupied side.

The uniformity and shape of the spectra at low energy are the results of a position independent \( \cos(2\theta) \) form of \( \Delta(\theta) \) near the node, while the “kink” in the spectra at higher energies signals the deviation of \( \Delta(\theta) \) from the \( \cos(2\theta) \) form at an angle away from the node. Previous attempts by the Cornell STM group to extract gap versus angle with the use of Quasi-Particle Interference (QPI) [Kohsaka et al. 2008] have not yielded results on the nature of nodal quasi-particles as can be seen in the figure 9-07. This is because in trying to fit the large gap values near the anti-nodes by adding higher quadrature terms to the fit, Davis and co-workers [Kohsaka et al. 2008] miss the information near the nodes.

![Figure 9-07 – QPI Model – Gap versus angle for samples with different doping (indicated by \( T_c \)) determined from QPI (offset for clarity). Adding extra quadrature \( \cos(6\theta) \) term in the parameterization of gap (\( \Delta \)) versus angle (\( \theta \)): \( \Delta(\theta) = \Delta_{QPI}[B\cos(2\theta) + (1 - B)\cos(6\theta)] \) can capture the anti-nodal gaps but misses the nodal structure completely. Extracted from [Kohsaka et al. 2008].](image-url)
Moreover, the deviation of $\Delta(\theta)$ for underdoped BSCCO that we observe from STM measurements is very similar to recently reported ARPES measurements in other underdoped samples [He et al. 2009; Kondo et al. 2009; Yoshida et al. 2009]. For instance, ARPES measurements by Yoshida et al. [Yoshida et al. 2009] on La$_{2-x}$Sr$_x$CuO$_4$ show gap versus angle plot deviating from a simple $d$-wave fit (figure 9-08), which is very similar to what we observe.

![Figure 9-08 - Gap versus Angle Deviation from ARPES - Momentum dependence of the energy gap at $T = 20$ K in La$_{2-x}$Sr$_x$CuO$_4$ with various doping levels shows deviation from a simple $d$-wave fit. Leading edge midpoints (LEM) $\Delta_{\text{LEM}}$ relative to that at the node. Inset shows LEM near the node for $x=0.07$ below and above $T_c = 14$ K. Extracted from [Yoshida et al. 2009].](image)

However, systematic study of the $\Delta(\theta)$ with doping and temperature uncovers its universal structure, its connection to samples’ $T_c$, and the Fermi arc behavior in underdoped samples as discussed in the next section.
9.4 Doping Dependence of the Nodal Excitations

To understand the behavior of the nodal gap with diminishing doping, we have measured [Pushp et al. 2009] the excitation spectra on a range of underdoped samples at $T << T_c$. Figure 9-09A shows spectra (spatially averaged by anti-nodal gap size) taken from three underdoped samples with $T_c = 74, 58$ and $35$ K. We can clearly see that each sample displays a low-energy region where the spectra are relatively homogeneous, and large inhomogeneity beyond the “kink” energy. For a $d$-wave superconductor, the slope of the spectrum near zero bias is inversely proportional to the value of the nodal gap. As the spectra shown in figure 9-09A line up not only within a sample but also across samples, we conclude that the nodal gap is uniform over the entire doping range shown in figure 9-09A (also see inset for expanded view).

Based on the simple analysis of the shape of the spectra near zero bias, our conclusions regarding the nodal gap can be put on a firmer footing by using the extraction procedure to determine the gap versus angle for each spectrum. The results of this analysis (figure 9-09B) show that our simple expectation for the nodal gap is correct; all the spectra for these samples follow a universal curve near the node. We find that spectra for the different samples break away from this universal line in a doping dependent fashion (marked by the arrows in figure 9-09B): the sample with the lowest $T_c$ breaks away at the smallest angle from the node, whereas the sample with the highest $T_c$ continues along this line for the largest angle.
Figure 9-09 – Fitting the Spectra with Our Model – (A) Average normalized $dl/dV$ spectra for different $\Delta$s on three underdoped samples with $T_s$ of 35 K (UD35), 58 K (UD58), and 74 K (UD74) taken at 8 K, 13 K, and 20 K respectively. The inset shows the low bias region, where the spectra follow a universal behavior. The normalization is done by averaging over the whole bias range. (B) Gap as a function of angle for the same samples as in (A). The low bias universal behavior can be seen at angles near the nodes in all samples, and agrees with a simple $d$-wave form. At different points marked by colored arrows, the spectra deviate sharply from the universal behavior, leading to the kinks in the raw spectra. (C) Average normalized $dl/dV$ spectra for different $\Delta$s on an optimally doped (OP91) and on two overdoped samples with $T_s$ of 76 K (OV76) and 65 K (OV65), all taken at 8 K. The inset shows the low bias region, where the universal behavior is lost. (D) Gap as a function of angle for the same samples as in (C). No universal behavior is seen at angles near the nodes. Extracted from [Pushp et al. 2009].
We contrast these results obtained for underdoped samples with the overdoped case. In the spectra obtained from an optimally doped sample ($T_c = 91$ K) and two overdoped samples with $T_c$s of 76 K and 65 K (figure 9-09C) we can see that there is a variation in the near zero bias slope among spectra obtained on these samples (expanded view in the inset of figure 9-09C). The results of the $\Delta(\theta)$ extraction procedure on these spectra (figure 9-09D) show that the universality of the nodal gap function is lost in these samples as anticipated. Instead, there is substantial inhomogeneity in the nodal gaps both within a sample as well as between dopings. The gap function in these samples is much closer to a $\cos(2\theta)$ form as compared to that observed for the underdoped samples, although very close to the anti-nodal region there is still some deviation from $\cos(2\theta)$ dependence. This high-energy behavior is most likely associated with deviations from a pure $d$-wave form caused by coupling to a bosonic mode [Damasceelli et al. 2003; Pasupathy et al. 2008]. This coupling causes the conductance to increase above the $d$-wave value at energies above the true anti-nodal gap, for which the fit compensates by adding a small weight for these oversized gaps.

### 9.5 Normalization Procedure

In this analysis, we have normalized the tunneling conductance measured on different samples to their average value over the entire range shown. It might be argued that this surprising universal nodal behavior is an artifact of the chosen normalization procedure. This is not the case. The agreement of the low-bias region
in the spectra is independent of the normalization. The tunneling differential conductance is proportional to the density of states only up to an arbitrary constant. Because spectra from samples with different doping must necessarily come from different junctions, we must normalize them to properly compare them. Ideally, we would take advantage of a sum rule and normalize over all voltages. However, the measurement is only carried out to 200 mV on either side of the chemical potential, so we normalize the spectra to the average over this range. Figure 9-10 shows spectra taken at 8 K on the same atomic location on the underdoped sample with $T_c = 35$ K with different junction conditions, in both raw (figure 9-10A) and normalized (figure 9-10B) conductance units.

![Normalized Spectra](image)

**Figure 9-10 – Normalizing the Spectra** – Spectra taken at an atomic location on a UD35 BSCCO sample at 8 K with different junction conditions. In A the raw spectra are shown, in B the spectra have been normalized over the whole bias range. Clearly, the effects of varying junction conditions are removed by normalizing the spectrum.

This demonstrates that normalization removes any junction dependent effects. To demonstrate that 200 mV is sufficiently far from the chemical potential,
we show in figure 9-11 a comparison between underdoped spectra analogous to figure 9-09A, only normalized to the conductance in the range -100 mV to 100 mV.

Figure 9-11 – Smaller Normalization Window – Average normalized $dl/dV$ spectra for different gap sizes on three underdoped samples with $T_s$ of 35 K, 58 K, and 74 K taken at 8 K, 13 K, and 20 K, respectively, as in figure 9-09A. The inset shows the low bias region, where the spectra follow a universal behavior. The normalization is done by averaging over only half of the full bias range, i.e., from -100 to 100 mV.

The agreement in the low bias region is still present, demonstrating that this phenomenon is not sensitively dependent on the normalization procedure. Furthermore, our procedure for determining the gap as a function of angle is totally
independent of normalization, and also demonstrates the universality of low bias excitations.

9.6 Nodal Gap Extraction

Figure 9-12 – Extracting the Nodal Gap – (A) The inverse nodal slope ($\delta_n$) extracted from a parabolic fit to the low bias region of the raw spectrum, plotted against the anti-nodal gap ($\Delta_0$) extracted from the maximum in $dl/dV$ on the positive side of the raw spectrum. For a $d$-wave gap the inverse nodal slope from a normalized $dl/dV$ measurement is equal to the gap. (B) The nodal gap ($\Delta_N$) extrapolated from the gap versus angle fits versus $\Delta_0$. The dotted lines indicate the behavior expected for $\Delta_N$ tracking $T_c$ or pseudogap temperature $T^*$. Note that both methods of determining the nodal behavior indicate a saturation at low doping and neither quantity tracks $T_c$ or $T^*$.

In order to compare results for the nodal gap across the phase diagram, we define two measures of the nodal gap. The first measure is the inverse slope of the normalized $dl/dV$ spectra near the Fermi energy, $\delta_n$, (figure 9-12A) as a function of the maximum anti-nodal gap $\Delta_0$ observed for each spectrum. Ideally we would determine the slope as close to zero bias as possible, but in order to avoid broadening effects we determine the slope at 10 mV bias from a parabolic fit. For
anti-nodal gaps smaller than $\sim 50$ mV (optimal and overdoped samples) the nodal gap increases along with the anti-nodal gap. However, once the anti-nodal gap increases beyond 50 mV, the nodal gap is essentially saturated. A more quantitative estimate of the nodal gap is obtained from our $\Delta(\theta)$ extraction procedure for each spectrum by extrapolating the shape of the near nodal gap following the universal $d$-wave $\cos(2\theta)$ curve to the anti-node. We refer to this as the universal nodal gap $\Delta_N$, which characterizes the strength of pairing experienced by excitations near the node. We plot this quantity as a function of the anti-nodal gap (figure 9-12B) and once again see that for optimal and overdoped samples there is a strong correlation between $\Delta_N$ and $\Delta_\theta$ (for a simple $d$-wave, $\Delta_N = \Delta_\theta$). However, as $\Delta_\theta$ increases into the underdoped regime, $\Delta_N$ saturates. Altogether, our results show that the evolution of the nodal gap with doping is very different from that of a simple BCS $d$-wave superconductor. On the overdoped side the nodal gap on average tracks the $T_c$ of the sample, although there is strong local inhomogeneity which gives rise to local patches of pairing even above $T_c$ [Gomes et al. 2007; Pasupathy et al. 2008]. The data on the underdoped side show that pairing associated with nodal excitations does not increase in strength beyond its value at optimal doping and does not track $T_c$, yet the angular range of universal nodal $d$-wave excitations is systematically suppressed as doping is reduced.
9.7 Temperature Evolution & Fermi Arcs

Examination of the temperature evolution of the tunneling spectra across $T_c$ demonstrates an important connection between the universal $d$-wave structure we find at low temperatures and the Fermi arc behavior that has long been the hallmark of underdoped cuprates [Kanigel et al. 2006]. The angular extraction procedure for $\Delta(\theta)$ previously used at low temperature can also be applied to determine the temperature dependence of $\Delta(\theta)$. Figures 9-13A and 9-13B show the temperature evolution of the extracted $\Delta(\theta)$ for two underdoped samples with $T_c = 58$ K (UD58) and $T_c = 35$ K (UD35) while the insets show the corresponding sample-averaged spectra.

![Figure 9-13 - Fermi Arcs](image)

Figure 9-13 - Fermi Arcs - Temperature evolution of the gap as a function of angle for the UD58 sample (A) and UD35 sample (B), obtained from the corresponding sample averaged spectra (insets), showing the collapse of the nodal gaps near $T_c$. The gap strength at the point of deviation from $d$-wave is not diminished with temperature.

We see that as the temperature is raised above $T_c$, the gaps around the node vanish leading to an arc of gapless excitations, while the anti-node is relatively
unchanged. The value of the inverse lifetime broadening, $\Gamma$, for these fits is determined at the lowest temperature. We note that the destruction of the gap can imply that either the amplitude of the gap is zero or the lifetime broadening exceeds the gap magnitude [Norman et al. 2007; Anderson 2008].

Although the nodal gaps disappear above $T_c$ in underdoped samples, the temperature dependence of the gaps is very different from that of a conventional $d$-wave BCS superconductor. As the temperature is raised, the nodal points expand into arcs whose length increases with increasing temperature rather than reduce continuously as a function of temperature and disappear at $T_c$. The observation of the Fermi arc above $T_c$ is in accord with previous ARPES measurements that ubiquitously show this phenomenon in the underdoped cuprates [Campuzano et al. 2003; Kanigel et al. 2006]; however, the $\Delta(\theta)$ from STM measurements shown in figure 9-13 provides a new perspective on the relationship between the arc and the $d$-wave nodal gap. For both underdoped samples, the angular region over which the arc occurs immediately above $T_c$ is the same as the universal $d$-wave region we observed at temperatures well below $T_c$. As the doping is reduced (the two dopings shown in figure 9-13), both the arc regions as well as the universal $d$-wave region decrease together.

9.8 Summary

Our measurements of the behavior of the nodal gaps with doping and temperature imply a new picture of superconductivity in BSCCO. In overdoped
samples, the nodal gaps on average increase with $T_c$, as one would expect for an inhomogeneous $d$-wave superconductor, and collapse at a range of temperatures above $T_c$ correlating with the local variation of the pairing interaction [Gomes et al. 2007; Pasupathy et al. 2008]. The anisotropic shape of the gap follows that of a simple $d$-wave order parameter, and it is reasonable to assume that the entire Fermi surface contributes to bulk superconductivity. Below optimal doping, the anti-nodal gap continues to increase with decreasing hole doping as has been measured in several previous experiments [Campuzano et al. 2003; Le Tacon et al. 2006; Tanaka et al. 2006; Gomes et al. 2007; Lee et al. 2007; Kondo et al. 2009]. However, our measurements demonstrate that the nodal gap does not change with reduced doping. The pairing strength does not get weaker or stronger as the Mott insulator is approached — it saturates. There are strong deviations from the universal $d$-wave excitation spectrum, which occur closer to the node with reduced doping. For each doping, the deviation point coincides with the Fermi arc observed above $T_c$. These observations are consistent with the hypothesis that only the areas of the Fermi surface that follow the universal $d$-wave spectrum contribute to bulk superconductivity. Such a reduction in the $d$-wave region also reduces the superfluid density, which in turn could make the systems susceptible to phase fluctuations [Emery et al. 1995], thereby reducing $T_c$. While the origin of the anti-nodal gap remains unclear, optimal $T_c$ is achieved when excitations follow the universal $d$-wave characteristic along the entire Fermi surface.
Chapter 10

Conclusions

This brings us to the last section of this thesis. We began with introducing the open questions in this hotly debated field of high temperature superconductivity. We then introduced the technique of STM and how we bring in the power of temperature variability to understand pairing on atomic scale in these systems, followed by an introduction to the BSCCO material system and its properties.

Using our technique of VTSTM to study BSCCO samples as a function of temperature and doping, we showed that for optimally doped to over doped samples of BSCCO, the gap in the excitation spectrum could be fit to a simple $d$-wave gap within the coherence peaks. As the temperature is raised, this gap ‘$\Delta$’ doesn’t close at the bulk $T_c$ of the sample; instead it decreases in size vanishing at a temperature $T_p$ following the relationship $2\Delta/k_B T_p = 7.9 \pm 0.5$ \cite{Gomes2007}. A very similar result exists for Bi-2201 material where $2\Delta/k_B T_p = 7.6 \pm 0.4$. We also introduced the inverse lifetime broadening in these fits, which kicks off near the bulk $T_c$ of the sample implying that the cooper pairs are short lived near $T_c$.

Outside the coherence peaks we saw signatures of electron boson coupling in the energy range 20 meV to 120 meV and we exploited this information to provide evidence against electron boson coupling being responsible for the inhomogeneous distribution of pairing gaps. Hence, we concluded \cite{Pasupathy2008} that the
bosons are parasitic in nature in these systems and not the driving force for superconductivity.

In search of a better candidate that could explain the origin of such inhomogeneous pairing gaps, we looked at the excitation spectrum of the normal state [Pasupathy et al. 2008] in the overdoped material where there was no gap and showed that the conductance values near the Fermi energy were also inhomogeneous in space with the same correlation length as the gaps in the superconducting state. In fact, the conductance maps near the Fermi energy were a very strong predictor (76% anti-correlation) for the pairing strength in the superconducting state despite the inhomogeneity in these BSCCO samples implying that strong electron-electron interactions are responsible for superconductivity in these materials. The anti-correlation between the normal state conductance near the Fermi energy and the local pairing strength also runs contrary to a BCS-like mechanism where the coupling to bosons is directly proportional to the density of states near the Fermi energy.

In the end, we discussed the underdoped regime [Pushp et al. 2009] in more detail and showed that the gap in the conductance spectrum in the deeply superconducting state could not be fit to a simple d-wave gap. The excitation spectrum, in fact, showed two features: 1) the lower energy feature near the nodes, which were remarkably homogeneous not only across the sample but also across doping (in the underdoped regime) and 2) the higher energy feature which remains inhomogeneous across the sample. These universal nodal excitations in samples with different $T_c$ values in the underdoped regime imply a doping-independent
nodal gap. Further, the $T_c$ of an underdoped sample instead correlated with the fraction of the Fermi surface over which the samples exhibited the universal spectrum. We hence concluded that optimal $T_c$ is achieved when all parts of the Fermi surface followed this universal behavior. Increasing the temperature above $T_c$ turned the universal spectrum into an arc of gapless excitations, whereas overdoping broke down the universal nodal behavior.

Based on the fits to the excitation spectrum, we concluded that near the nodes, all samples exhibit $d$-wave form. The nodal pairing strength is saturated on the underdoped side but decreases on the overdoped side. Moreover, in the underdoped samples, the anti-nodal gaps have a larger energy scale, which is perhaps related to the pseudogap physics. The higher energy feature seems to take away parts of Fermi surface and hence decreases its contribution to pairing thereby competing with superconductivity. Future experiments need to be performed to ascertain the origin and properties of the higher energy scale.

Our observations put stringent limits on any theory that aims to explain high temperature superconductivity. This thesis contains experimental results about the excitation spectrum in all the different regimes of the phase diagram of high temperature superconductivity. Our unique ability to correlate excitation spectra between different electronic states by tracking the same atomic location opens up new avenues to study other inhomogeneous correlated systems.
Appendix

A1. Experimental Setup

Figure A-01 – System Design – (top) Inside view through the viewport as shown in the (bottom) entire assembly of our Variable Temperature Scanning Tunneling Microscope (VTSTM). We have two such systems capable of performing experiments from 6 K up to room temperature in Ultra High Vacuum ($<10^{-10}$ Torr).
In this section, we will describe the home-built apparatus that we use to perform scanning tunneling microscopy. Figure A-01 shows the entire assembly of our VTSTM. The top figure shows the view inside the main chamber through the main view port as indicated in the bottom figure. Most of the components have been labeled. The entire chamber is made of stainless steel. Temperature is maintained by continuous Helium flow from the dewar pressurized at about 6.5 psi through the Helium transport line as shown in figure A-02.

**Figure A-02 – Setup** – tabletop STM 5’ high, 8’ wide. Temperature control via continuous Helium flow through the transfer line. UHV maintained via ion pump. Optical table for vibration damping.
Since the pressure in the dewar is always kept at 6.5 psi, our helium transfers are quite violent as we apply almost 10 psi to the reservoir source dewar. This way we can refill the dewar while maintaining the temperature of the STM. Care is taken to minimize noise while helium transfer so as not to crash the tip on the sample. The dewar is not directly connected to the assembly except for the transfer line, to minimize vibrations. The helium flow cryostat (see figure A-02 for label) is where the heat exchange takes place. It also has a small heater, which runs on a negative feedback loop to maintain any desired temperature from 6 K to 300 K.

Ultra High Vacuum (UHV implies pressure ~ $10^{-10}$ Torr) is continuously maintained by a non-mechanical Ion pump. In order to attain UHV, we bake the system up to 100 degrees Celsius with a turbo pump pumping on the setup. The heating facilitates the vacuuming of polar molecules (such as H$_2$O, CO) and other hydrocarbons which have an affinity to stick to the inside surface of the chamber. We avoid baking the system any hotter to preserve the piezoelectric tubes on the microscope stage from getting depoled. These piezoelectric materials typically have a depoling temperature of about 300 degrees Celsius. The entire chamber is wrapped with heating tapes and then covered with aluminum foil, as can be seen in figure A-02, to aid in uniform heating of the chamber. Typically the pressure reads in the $10^{-5}$ Torr range when baking is started. We bake at the highest temperature until the pressure has come down to low $10^{-7}$s to high $10^{-8}$s Torr. Typically for a system of this size, this can take up to 4-5 days. We then slowly cool down the system to room temperature and turn on the ion pump when the pressure has come down in the mid $10^{-10}$s Torr, which further lowers the pressure. We can also use a
Titanium Sublimation Pump (TSP) to lower the pressure even further. We speculate that cryocooling by the copper shields keeps the pressure in the $10^{-11}$ Torr range near the sample. We maintain UHV for as long as we can in order to avoid thermal cycling of our system. The load lock (which is being pumped on by the turbo pump) is used to transfer samples in and out while the main chamber is always kept under UHV by the ion pump. The load lock gate shown in figure A-01 separates the load lock and the main chamber. The load lock is the dirtiest part of the main assembly as it is frequently exposed to atmosphere in order to transfer samples. The load lock gate is opened only when the pressure is less than $3 \times 10^{-8}$ Torr in the load lock after a few hours of turbo pumping.

**A2. Acoustic Shielding & Power Conditioning**

The assembly is mounted on an optical table (figure A-02) for vibration damping. The entire setup is kept under specially designed acoustically shielded rooms as shown in figure A-03.

The power supply is also conditioned using Topaz isolator and the power conditioner as shown in figure A-04. Both machines have their own independent ground (see ground bar in figure A-04) and a UPS system than can give backup power for 6 hours in case of an outage.
Figure A-03 - Princeton Nanoscale Microscopy Lab - VTSTM facility. Acoustically shielded rooms.

Figure A-04 – Electrical Noise Reduction – Topaz filter and individual ground bars with UPS.
Our experiments require uninterrupted measurements for long duration of time (typically weeks even months). An STM tunnel junction requires a tip to be a few Angstroms away from a sample without ever touching the sample. Clearly, these experiments are ultra sensitive to noise and thus require such ultra low acoustic and electric noise facility.
**B1. The STM Head**

![STM Head Diagram](image)

**Figure B-01 – STM Head** – (Top) Cartoon showing sample placed on the stage, piezos layout show both in cartoon and real form. (Bottom) Offset ramps of two kinds- self-centering for small samples and non-self centering for exploring different parts of a sample.

Our STM is a Besocke design [Besocke 1987]. Figure B-01 shows both schematics as well as a real view of the STM stage. This is the heart of the entire setup. The offset ramps as shown in the figure B-01 change the tip-sample distance by rotating with respect to the STM head. We use self-centering sample holders to approach small samples and non-self centering sample holders to explore different areas of the sample. The self-centering holder has grooves in its offset ramps that
restrict sideways movement. The following section describes how the piezoelectric tubes (piezos) function and how the tip-sample distance is controlled. Details of the STM design and construction can be found in the PhD thesis by our former group member Michael Vershinin [Vershinin 2004].

**B2. The Pizza-Toss Approach Mechanism**

Piezoelectric materials deform (deformation ~ Å/V for an inch long piezo-leg at room temperature) when a voltage difference is applied across them. This is depicted in the figure B-02. Every piezo-tube is divided in four independent quadrants. Deformation in different directions can be obtained by applying different voltages to these quadrants. If all quadrants are given the same voltage whereas the inside is kept grounded, then the piezo can be stretched or contracted in the z-direction depending on the polarity of the voltage. We apply voltage in a special stick-slip fashion to mimic the motion of the hands of a baker while tossing a pizza up in the air. We hence call it the “pizza toss” approach.

![Figure B-02 - Piezos](image)

*Figure B-02 - Piezos* – Application of different voltages to different quadrants deform the piezos in different directions.
The sample approach mechanism is explained (figure B-03) with the help of cartoons.

At start

A zoomed in view of a part of the sample holder sitting on one piezo. The sample holder has inclined surfaces (ramps) that touch the piezo

Step 1

In the first step, the sample holder is lifted and rotated slowly by the offset piezos

Step 2

Next, the offset piezod are brought back to their initial position quickly before the sample holder has a chance to fall, as shown to the left.

Step 3

The sample holder then falls back onto the offset piezo. At the end of this process, the sample holder has rotated relative to its starting position. The inclined ramps thus bring the sample closer to the tip.

Step 4

The scanner piezo extends slowly looking for a tunneling current. If it is unable to find one before it reaches the end of its range, it retracts back and the entire process is repeated. Typically it takes several thousand steps over many hours to “find” a sample with the tip.

Figure B-03 – The “Pizza Toss” – Various steps in approaching a sample.
This is the *tip retract* mode (figure B-03), which is used to approach a test sample without ever touching the sample surface. Care is taken that the range of the scanner piezo is larger (4-5 times) than an average step size lest the sample crashes on the last step.

Alternately, we can do a fast approach (*feedback detect* mode), where we keep the tip extended to its maximum range looking for a current while performing the pizza-toss steps continuously with the leg-piezos. Once the feedback detects any current, it stops the walk and retracts the tip. We use this mode to approach a metal surface such as Cu 111 or Au 111 quickly. We are bound to "soft" crash on the sample with this approach, which is ok as we end up poking the tip on the metal surface anyway to make it sharp and stable. We describe the sample and tip preparation in the next section.
**C1. Metal Sample Preparation**

We usually prepare our tips on Cu 111 or Au 111 single crystals. When first inserted into the STM chamber, these samples are quite “dirty”. We out gas them for a few hours until the pressure goes back to normal. Surface sputtering in an Argon environment and subsequent annealing gives us clean surfaces with atomic steps, which is ideal to prepare the tips. As Argon is a non-reactive gas, fast moving sputter current of Argon ions bombards the dirt on the outer layers revealing a “badgered” yet metallic surface. Annealing in vacuum to about 400-500 degrees Celsius (sample holder looks red hot) smoothens the badgered surface giving atomically flat surfaces along with atomic steps. Temperature of the STM during this process is kept above 140 K to avoid Argon atoms getting stuck to the copper shields as Argon is introduced in the chamber for sputtering. After preparing the metal sample, it is put on the stage and the temperature of the stage is changed to the desired set point. By using the screw (figure A-01) the stage can be brought in contact with the shields for thermal conduction and fast equilibration- we call this locking the stage to the shields. It takes about 4-5 hours to equilibrate the metal sample at a given temperature good enough for a quick tip preparation.

**C2. Tip Preparation**

We use chemically etched tips that are ultra sharp on one end (100 Å radius). These Pt/Ir or W tips are cut from the blunt end and slid into a tube and then
crimped to appropriate height with a tolerance of 10 thousandths of an inch. This tip tube is then placed in the collet of the scanner piezo-leg. As the starting distance between the tip and the sample is on the order of a few mm, there is very little margin for error in the tip height.

We first approach a clean metal surface to make sure that the tip is sharp and metallic, suitable for a real experiment. Frequently, the STM junction is poor on first approach because of residue from chemical etching or “crap” stuck at the end of the tip from the previous experiment. We use field emission to get a stable current (Voltage = 200 V; Current = 20 μA). This melts the end of the tip and usually gives a blunt yet metallic tip. We approach a new area on the metal sample with this new field-emitted tip. We can make soft controlled pokes into the metal surface and then can image the end of the tip by imaging the “poke sites”. A good tunneling tip is one that is stable at 200 pA and 10 mV, images the steps without any “glitches” in the current, and gives a well rounded small poke cross-section (~50 Å), when poked 5 Å inside the metal surface. The real test of a tip being single is while tracing an atomic step- the trace should look like a step function. When all these requirements are met, we withdraw the tip (by applying a large voltage to the scanner piezo-leg), record the capacitance of the junction using the lock-in and “walk out” using inverse of the “pizza toss” making sure that there is no crash and then lock the stage to the shields.
C3. Sample Approach

Samples are usually attached to the center of the sample holders using conducting epoxy. The height of the samples with respect to the ramps can be adjusted by adding spacers. Using UHV compatible epoxy, we then glue small clean aluminum posts to the surface of the samples- BSCCO in our case. Prior to gluing the aluminum posts on the samples, the posts are cleaned by sonicating in acetone and then isopropanol. These samples holders are then transferred into the chamber via the load lock and kept in the carousel. After a desirable tip is prepared on a metallic surface, the sample is cleaved at room temperature by knocking the post off (the post is collected in a small trash can in the carousel) in UHV and if the sample shows a nice and shiny surface, we put it on the stage and wait 18-20 hours for it to equilibrate after changing the temperature to the desired set point. (We have modified one of the STMs to allow for cleaving at colder temperatures. This is useful for samples that cleave better when cold.) Then, using the screw, we unlock the stage from the shields and fast approach in feedback detect mode (discussed in Appendix B2), while keeping an eye on the capacitance of the junction. Once, the capacitance is in the vicinity of the capacitance recorded from the tip preparation on the metal surface, we use the standard slow tip retract method of careful approach to get within tunneling range (~10 Å) of the sample without ever touching the sample surface.

Even after so many precautions, there are times when we have a bad junction because of a flake on the sample or other unknown reasons. In such a situation, we
abort the experiment and start from the first step of preparing the metal surface (Appendix C1). If the current is stable at 40 pA and -200 mV, we call it a good junction and then we perform the standard measurements of topography and spectroscopy as discussed in chapter 2.

We use a lock-in amplifier to perform spectroscopic measurements. We apply a small ac modulation (~700 Hz) on top of the junction bias and adjust the phase of the lock-in to record the differential signal on the conductance channel. One can auto-phase the lock-in first when the tip is away from the sample (asking for zero current and then opening the feedback loop). This way the lock-in locks on the capacitive channel of the signal and then adding a 90 degrees phase makes it to lock on the resistive channel. Typical settings for our measurements are: 20-30 ms as the time constant of the lock-in, ac modulation on the order of 2-4 mV, sensitivity 5-10 mV. The entire spectrum measurement cycle is show in the figure C-01.

![Figure C-01 – Measurement Cycle – Color-coded steps in measuring a spectrum at a location.](image-url)
The modulation is smaller at low temperatures. Thermal broadening is of the order of $3.5 \ k_B T = 6 \text{ meV}$ at 20 K. Modulation should be a few factors smaller than the thermal broadening (we apply $\sim 2 \text{ meV}$ at such low temperatures) so as not to smear out the conductance signal and broaden the features in the excitation spectrum. At higher temperatures, we typically use 4 meV.
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Curriculum Vitae

Education

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