VISUALIZING COOPER PAIR FORMATION ON THE ATOMIC SCALE IN
HIGH TEMPERATURE SUPERCONDUCTORS

BY
KENJIRO GOMES

Bacharelado, Pontifícia Universidade Católica do Rio de Janeiro, 2001
Mestrado, Pontifícia Universidade Católica do Rio de Janeiro, 2002

DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Physics
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2008

Urbana, Illinois

Doctoral Committee:

Professor Lance Cooper, Chair
Professor Ali Yazdani, Director of Research
Professor Philip Phillips
Professor Paul Kwiat
Abstract

In the quest for a microscopic theory for the superconductivity in cuprates, one hotly debated issue is the temperature at which Cooper pairs first form. Do pairs form at the critical temperature $T_c$ or do they form at higher temperatures lacking phase rigidity? To answer the question, we have developed new techniques, based on scanning tunneling microscopy, to visualize the process of the pair formation on the atomic scale. The magnitude of the low-temperature superconducting gap measured in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ shows a large nanoscale spatial variation. These superconducting gaps evolve smoothly with temperature and close locally over a range of temperatures above the superconducting transition temperature $T_c$. Our results provide evidence that pairing first occurs in nanoscale regions above the bulk superconducting transition temperature. Using the ability to track the same atomic position while changing the temperature, we have examined the evolution of the electronic states from well below $T_c$ to above the temperature at which the pairs first form. Our technique allows us to investigate another fundamental question on the pairing mechanism: Is pairing mediated by a bosonic excitation, as in conventional BCS superconductors, or is pairing an unavoidable consequence of the strong Coulomb repulsion in these compounds? We quantitatively analyze the temperature evolution of the gap and the local electron-boson coupling for various atomic sites with different pairing strengths. We observe that the gap magnitude variation is not determined by the electron-boson coupling but instead it is strongly correlated to variations present in the normal (ungapped) electronic states.
Acknowledgments

I would like to thank my advisor Prof. Ali Yazdani for his contribution to my graduate education and research. I was lucky to have the opportunity to be a part of his research group at two different universities, University of Illinois at Urbana-Champaign and Princeton University. The staff and facilities of both universities made my life much easier. I own deep gratitude to my collaborators, Dr. Shimpei Ono, Prof. Yoichi Ando and Dr. Genda Gu. This research would never be possible without their knowledge and inputs.

I am grateful for the experimental training I received from Michael Vershinin and Shashank Misra in my first years as graduate student. I share all credits of this work with my labmates Abhay Pasupathy and Aakash Pushp who worked with me in every aspect of this research. I also thank the friendship and support of my labmates, Dale Kitchen, Anthony Richardella, Lukas Urban, Pedram Roushan and Colin Parker.

Finally and most importantly, I would like to express my gratitude to my family and specially to my girlfriend Muk, who has been the perfect companion for the last five years. They truly supported me and made a difference in my life.

The work at Princeton is supported by the U.S. Department of Energy (DOE) under contract DE-FG02-07ER46419 and NSF through the Princeton Center for Complex Materials.
Table of Contents

Chapter 1: Introduction ......................................................01

Chapter 2: High Temperature Superconductors .......03
   2.1 Classical Superconductors .......................................03
   2.2 Cuprate Superconductors .......................................06

Chapter 3: Scanning Tunneling Spectroscopy .......21
   3.1 The Tunneling Current ...........................................21
   3.2 Types of Measurements .........................................24
   3.3 Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ ....................................30
   3.4 Methods ..........................................................32

Chapter 4: Nanoscale Imaging of the Pair Formation ....34
   4.1 Pairing Above Tc ..................................................34
   4.2 The Inhomogeneous Pairing ....................................35
   4.3 Temperature Evolution of the Energy Gap ..................39
   4.4 Energy Gap Maps ..................................................48
   4.5 The Underdoped Regime ........................................56
   4.6 Concluding Remarks ..............................................62

Chapter 5: Study of the Single Layered
Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$ ...........................................65
5.1 Characterization of The Bi-2201........................................65
5.2 Statistical Study of the Gap Formation..................................71
5.3 How Many Gaps?.............................................................78
5.4 Concluding Remarks.......................................................83

Chapter 6: Bosonic Coupling and the Origin of the Pairing Inhomogeneity......................................................84

6.1 Strong Coupling Pairing...................................................84
6.2 Bosonic Modes in Cuprates...............................................92
6.3 Normal State Correlations.................................................99
6.4 Concluding Remarks.......................................................105

Chapter 7: Conclusion........................................................107

Appendix: Microscope Design and Operation.................109

A.1 Experimental Set Up.......................................................109
A.2 Operation Procedure.....................................................117

Bibliography.................................................................122

Curriculum Vitae.............................................................127
Chapter 1

Introduction

Our current understanding of the High Temperature Superconductors has been built from the strong interplay of theoretical ideas and experimental evidences. It is unimaginable that one could predict all the intriguing properties of the cuprate phase diagram without first having the experimental facts in hand. Even though many theories have been developed to explain the superconductivity in cuprates, ultimately they require experiments to give away more clues or to judge which predictions are valid. One of the major obstacles for the advancement of our understanding of high temperature superconductors is the lack of experimental answers to some of the most basic questions, such as “What happens at $T_c$?” or “What holds the Cooper pairs together?”. This thesis aims to provide experimental evidences that could help us to answer such hard questions that have been haunting condensed matter physicists for the last 20 years.

Understanding the nature of the superconducting phase transition at $T_c$ is a key step towards a theory for the high temperature superconductors. In traditional superconductors, the transition occurs when the superconducting order parameter goes to zero at $T_c$, breaking all Cooper pairs and bringing the system to a well understood metallic normal state [Tinkham 75]. Hole-doped cuprates present an unusual “normal” state above $T_c$, the pseudogap phase, characterized by presence of a gap in the density of states that exists between $T_c$ and $T^*$ [Timusk 99]. Despite many years of research there is not a consensus on the nature of the pseudogap regime and what happens at the superconducting phase transition at $T_c$. 


Scanning tunneling microscopy (STM) [Renner 98] and angle-resolved photoemission spectroscopy (ARPES) [Ding 96a] measurements have shown that the pseudogap evolves smoothly into the superconducting gap and both share many properties, such as d-wave symmetry. These experiments support the idea that the pseudogap state is precursor of the superconducting state, characterized by pairing correlations lacking long-range phase coherence [Emery 95]. The energy gap associated with the superconducting order parameter would be the only energy scale present in both states. In contrast to these measurements, other studies, such as the measurements of real space electronic ordering [Hanaguri 04, Vershinin 04] in the underdoped regime of cuprates, opened the possibility of another origin for the pseudogap. Recent ARPES experiments [Tanaka 06] also suggest that cuprates could have two different gaps: one gap associated with the Cooper pairing and another, possibly related to a competing order, dominating the spectra in the underdoped regime above $T_c$.

Low temperature STM measurements have shown that the superconducting state presents intrinsic spatial inhomogeneity [Howald 01]. Different from the traditional superconductors, the gap magnitude varies on the nanometer scale in cuprates, which obscures the results of spatially averaging techniques. The disorder found in the electronic states of cuprates presents a difficult challenge to overcome in order to reach a definitive answer for the nature of the pseudogap. For a more accurate description of the electronic states, we performed systematic temperature dependent STM measurements of the gap formation at the atomic scale [Gomes 07]. We present results demonstrating that the overdoped region of the phase diagram can be understood with a single energy scale, the pairing gap, that persists in an inhomogeneous manner above $T_c$. We show that the pair formation does not occur at $T_c$ but at higher temperatures $T_p$, which is determined locally following a simple criterion, $\frac{2\Delta}{k_BT_p} = 8$. 
The investigation of the superconductivity phenomenon is one of the main themes of solid state physics for almost one century. The search for new superconductors and their understanding motivate an enormous amount of research work, either due to the intriguing different mechanisms evolved or the possibility of new technological applications. Among all known superconductors, cuprates present the highest transition temperatures and also a set of unique phases that challenge our understanding. The main challenge to develop a microscopic theory for cuprates lies on a set of problems related to the wide variety of phases, phase transitions, crossovers that defy our standard basic paradigms, such as band theory, BCS superconductivity and Landau’s Fermi Liquid. This thesis focus in expanding our understanding of the superconducting transition in cuprates. In this chapter I present a few basic concepts of superconductivity and some of the most important properties of high temperature superconductors, in particular the superconducting and the pseudogap phases. I present an overview of some experimental work, specially those relevant for this thesis.

2.1 Classical Superconductors

In 1908, Kamerlingh Onnes prepared liquid Helium for the first time. Helium was the last known gas to be condensed. This achievement, extraordinary on itself, allowed research to be done into the properties of matter at temperatures which lie between 4.3° and 1.15° from absolute zero. While measuring the electric properties of very pure Mercury in helium baths, Onnes
made a stunning discovery: the electrical resistance below 4.2K completely disappears (Fig. 2-01) [Onnes 11]. At first, scientists expected that at absolute zero temperature, electrons would be strongly bound to atoms and therefore, metals should become insulators. Onnes found that at the lowest temperature the conduction electrons are not bound but instead the factors which hinder conduction actually disappear. This new state of matter was named superconductivity.

For many years, superconductivity was one of the most intriguing puzzles in solid state physics and it took almost 50 years to achieve a microscopic theory. J. Bardeen, L. N. Cooper and J. R. Schrieffer (BCS) proposed that electrons could overcome their mutual electrostatic repulsion to bind in pairs (Cooper pairs) due to the coupling to vibrations of the crystal lattice [Bardeen 57]. Unlike normal electrons, these pairs can condense to a single coherent ground state that due to its quantum rigidity forms a robust superfluid liquid that is insensitive to many perturbations and therefore carry current without loss of energy.

The pair formation leads to important experimental consequences. First, once the electrons bind in a pair they reduce their energy by a value $\Delta$. In other words, in order to break a Cooper pair and create a single particle excitation one needs to pay the binding energy $\Delta$. This leads to the opening of an energy gap at the Fermi energy in the single particle density of states (Fig. 2-02). Experimentally, the exponential decay of the heat capacity below $T_c$ hints at a
gapped fermi surface. Optical conductivity and later on tunneling would give the exact form of the gap. The pairing mechanism should also give us experimental signatures too. The phonon mechanism explains why the transition temperature changes with the isotope substitution [Maxwell 50; Reynolds 50]. If the mass of the ions is relevant to superconductivity, this means that their motion might be part of the mechanism.

Tunneling spectroscopy gives both a direct measurement of the pairing gap and details of the phonon modes relevant for superconductivity. Researchers from the Bells Lab extracted detailed tunneling spectroscopic data from Pb. By extracting detailed spectroscopy of the relevant phonon modes and electron-phonon interaction, they left no room for uncertainty on the mechanism of superconductivity. In latter chapters I will explain in details how this was
done and how we applied this technique to investigate a new type of superconductivity found in copper oxides.

2.2 Cuprate Superconductors

The understanding of the superconductivity turned upside down when in 1986 J. G. Bednorz and K. A. Müller discovered that under certain conditions, layered copper oxide (cuprates) superconduct [Bednorz 86]. It was quite surprising that a very poor conductor could become a superconductor and the $T_c$ was higher than any other known material. The pioneering material was La$_{2-x}$Ba$_x$CuO$_4$ (LBCO) (Fig. 2-03). For certain values of Ba substitution the material could go from an insulator to a superconductor.

![Figure 2-03 - The Discovery of the High-Temperature Superconductors - Bednorz and Müller discovered that under certain conditions, layered copper oxides, such as the one on the right, could superconduct and even surprisingly their critical temperature was higher than any other known material.]

The discovery of superconductivity in cuprates was the start of an avalanche of new superconductors (Fig. 2-04). Decades of work in traditional superconductors had pushed $T_c$ barely above 20K. In less than one year after the discovery of superconductivity in cuprates, the effort of hundreds of labs around the world pushed the transition temperature above the liquid Nitrogen temperature (77K) with the discovery of YBa$_2$Cu$_3$O$_{7-x}$(YBCO) [Wu 87], reaching
The discovery of cuprates initiated a revolution in the research of superconductivity. The highest known transition temperatures went from around 20K in 1986 to 130K in 1993. Interesting though, very little progress has been made since to elevate the critical temperature even more. Ultimately, we want to ask why is transition temperature so high and how can we make it higher?
as high as 130K in a mercury based compound [Sun 94].

Superconductivity was observed in various compositions of cuprates and the table in Fig. 2-05 [Eisaki 04] summarizes the most studied compounds. $T_c$ tends to increase for both increasing the number of neighboring Cu-O planes and reducing the disorder. This table also elegantly points out how structure effects, such as the dopant disorder, could influence the transition temperature. The only thing that all these high-$T_c$ superconductors have in common is the presence of lightly doped copper-oxide (Cu-O) planes, that serves as the stage for all the physics that we are interested. The Cu has a 3d orbital which is doubly ionized and hybridized with the O p-orbitals, forming a simple square lattice where the charge flows.

a. The Phase Diagram

The transport properties of cuprates change drastically by the introduction of charge carriers to the Cu-O planes. This is done by chemical doping that varies for each family of cuprates. In case of LBCO for example, the chemical doping is done by the substitution of some of the La$^{+3}$ atom by Ba$^{+2}$ which introduces holes to the Cu-O plane. The most studied cuprates are hole doped. Electron-doped cuprates have lower transition temperature and somewhat similar properties. In this thesis I will restrict to the discussion of hole-doped samples.

Interesting though, when undoped, the material is not a metal as would be predicted by simple band theory, but instead it is an insulator. When the band is half filled, each Cu site presents one free electron and therefore it should be a metal. Conduction though is suppressed because the strong Coulomb on-site repulsion prohibit two electrons to occupy the same site, leading to the so-called Mott insulator state (Fig. 2-06). In this state each electron is frozen in a lattice site because it cannot overcome the high energetic double occupancy price. The cuprates also present antiferromagnetism when undoped [Vaknin 87]. The second order process of virtual hopping between neighbor sites back and
Recent Y NMR experiments on yttrium barium copper oxide (YBCO) indicate that the spatial inhomogeneity in this system is much less severe than in LSCO or Bi2212. This is reasonable since the latter two systems exhibit a much higher degree of disorder located at the A site/La site and Sr site, whereas YBCO Ba site is thought to be free from such cation disorder. Indeed, recent penetration depth measurements on the YBCO variant Nd1xBaxCu3O7 with cationic disorder at the Ba site, demonstrate that the superconducting properties of this system change quite sensitively with the degree of Nd/Ba nonstoichiometry.

V. DISORDER EFFECTS IN THE CUPRATES

The two main lessons to be learned from our Bi2201 and Bi2212 case studies are that chemical inhomogeneity affects $T_{c,max}$ and that the effect of disorder differs depending on its location. In the following, we attempt to classify the various sites at which chemical disorder is possible and categorize other superconducting families on the basis of which kind of disorder is prevalent in each system.

In Fig. 3, we classify 25 cuprate superconductors based on the pattern of the chemical disorder and the number of CuO$_2$ planes in the unit cell. Materials belonging to the same family are indicated by the same color. Halogen family denotes (Ca, Sr)$_2$CuO$_2$A$_2$ (A/Cl, F-based materials. Bi family denotes Bi$_{22}$ ($n_1$1) ($n_1$=1,2,3). Pb family denotes Pb$_2$Sr$_2$Ca$_n$/H11002 1Cu$_{n_1}$/H11001 O$_{2}$, $n_1$. 1L Tl family denotes one-Tl-layer cuprates, TlBa$_2$Ca$_n$/H11002 1Cu$_{n_1}$/H11001 O$_{4}$, $n_1$. 2L Tl family denotes two-Tl-layer cuprates, Tl$_2$Ba$_2$Ca$_n$/H11002 1Cu$_{n_1}$/H11001 O$_{4}$, $n_1$. La family denotes La$_2$Ca$_n$/H11002 1Cu$_{n_1}$/H11001 O$_{2}$, $n_1$. YBCO family denotes LnBa$_2$Cu$_3$O$_6$, $n_1$. Hg family denotes HgBa$_2$Ca$_n$/H11002 1Cu$_{n_1}$/H11001 O$_{2}$, $n_1$. The transition temperatures are compiled from works listed in Ref. 21.

**Figure 2-05 - High-Temperature Superconducting Cuprates** - This table presents the most studied High-T$_c$ superconductors. It is organized by number of Cu-O layers and by the type of dopant disorder. Materials in the same families are displayed in the same color. This figure was extracted from [Eisaki 04].
forth leads to an overall reduction of the total energy of the state. This process is only possible if neighbor electrons have opposite spins, leading the material also into an antiferromagnetic order. The superconductivity, as well as other interesting properties, will arise once we remove some of the electrons, allowing then electrons to hop and therefore destroying the antiferromagnetic insulator (AFI) state. The best way to visualize the different phases that arise from doping the cuprates is through a phase diagram commonly plotted as function of temperature and doping level of the Cu-O planes (Fig. 2-07).

Superconductivity happens within a limited range of doping from $x \sim 0.04$ to 0.27. Not many of the cuprates allow to access all doping levels but the dome-shaped doping dependence of $T_c$ is universal across all families of superconducting copper oxides (even though the maximum value of the $T_c$ varies significantly). When the superconducting transition temperature $T_c$ is maximum we define this doping as optimal doping. Samples with doping lower than the optimal doping are referred as underdoped and samples with higher doping than optimal are referred as overdoped. Superconductivity is but one aspect of the unique and complex phase diagram exhibited by this class of materials.
At high doping the electronic states in the cuprates behave as a fermi liquid but in the underdoped regime, between the superconducting dome and the AFI phase, an unusual metallic state is present. The main signature of this state is the presence of a depression at the density of states near the Fermi energy which identifies it as the pseudogap phase. Near optimal doping, well above $T_c$, where no pseudogap can be measured, the transport properties also deviate from Fermi Liquid. This strange metal regime presents similar thermodynamics properties to a Fermi liquid but unique power law temperature dependence for most of the transport properties, such as linear temperature dependence of the resistivity [Batlogg 94], instead of the quadratic dependence expected for electrons scattering from one another.

Figure 2-07 - The Phase Diagram - The different phases of the cuprates can be observed in this phase diagram. The diagram is plotted as function of the hole doping in the Cu-O layer and temperature. At low dopings, the material is an antiferromagnetic insulator (AFI). Superconductivity (SC) happens within a limited range of doping (typically from 4% to 27%). Between the AFI and the SC phases the material is in a unusual normal state characterized by the partial gapping of the fermi surface (Pseudogap).
b. The Superconducting State

A common feature of all superconductors, both the low and the high-temperature variety, is that the electrons somehow form Cooper pairs. Evidence for Cooper pairing can be obtained from the observation of the magnetic flux quantization (the flux quantum being $h/2e$ instead of $h/e$ [Gough 87]) and other simple measurements. We also know that the main stage for paring is the copper oxide plane. Most models treat pairing to happen independently at each plane at first approximation. The high resistivity along the c-axis infers a high hopping price along the that direction. This justifies the treatment of the Cu-O planes as discrete and weakly coupled layers. Different from the superconductivity in metals, the carrier density is low whereas $T_c$ is high and coherence length is very short. The coherence length, 10–30Å, is almost as short as the distance between no more than few Cu-O planes.

\[ Gough 

Figure 2-08 - The d-wave Superconducting gap - The nodes in the superconducting gap can be directly measured with ARPES. (a) shows the gap measured at different locations of the fermi surface. The location of the nodes determine the d-wave symmetry. Tunneling lacks momentum resolution but the d-wave symmetry results in a V-shaped gap in the density of state as seen in (b). Plot in (a) was extracted from [Ding 96b]
The gap that opens in the density of states is unusual though. Instead of the simple symmetric s-wave gap found in conventional superconductors, the gap presents a d-wave symmetry (the orbital state is $d_{x^2-y^2}$). This means that the gap magnitude have momentum space dependence. It is maximum along the Cu-O bond and zero 45 degrees to it. This was shown by the magnetic flux modulation measurements of YBCO dc-SQUIDs [Wollman 93]. A direct measurement of the gap symmetry can be performed with angle resolved photoemission spectroscopy (ARPES) (Fig. 2-08). The intensity of the ARPES signal is a direct measurement of the single particle spectral function and it can be used to determine the gap value $\Delta$ for all directions (for a review of ARPES on cuprates, [Damascelli 03]). The biggest puzzle of the cuprates is what is the mechanism that binds the pairs together.

The phonon-based pairing mechanism present in the low-temperature superconductors has as the starting point the Landau-Fermi liquid theory that well describes the behavior of electrons in a metal. The single electrons and their coulomb repulsion are “renormalized” to form quasiparticles. In the absence of interactions, these quasiparticles would be reduced to bare electrons. In most cases though, they behave like electrons but have a different effective mass. Many of the metal properties can be described by the transport of these quasiparticles that only interact perturbatively. The heavily overdoped cuprates present a Fermi liquid behavior and many theorist have proposed a pairing model based on the phonon interactions but this was not easily established as the mechanism for high-$T_c$ superconductivity. First, there are predictions for the ceiling to $T_c$ well below the nitrogen boiling temperature. Also, there wasn’t a striking isotope effect measurement that could settle the importance of ion masses involved. This lead to the proposal of other models with different kinds of “glue” that bind the pairs. Because of the proximity to the antiferromagnetic regime, it has been proposed that instead of phonons, magnetically mediated interactions could act as the pairing glue [Scalapino 86]. There is a precedent for this kind mechanism in He$^3$, where spin fluctuations
mediate the pairing that leads to the superfluid state and a similar mechanism has been proposed for another class of materials, the heavy fermions.

The Fermi Liquid model breaks down above the superconducting transition temperature for large range of doping. Many theorist took a very different route to understand the physics of cuprates. Instead of the starting from the Fermi liquid scenario, one can start from the Mott insulator regime (for a review, [Lee 06]). The Hubbard hamiltonian, which presents a large on-site interaction, is the starting point for a lot of theories. For example, the central idea of the Anderson’s RVB theory [Anderson 87] could explain a lot of the physics behind these material: superconductivity arising from the doping of spin-1/2 particles singlets. In his proposal, quantum fluctuations would disorder the AF phase, resulting in a liquid of singlet pairs, a resonating valence bond (RVB) state. This provides a close link between the pairing for superconductivity and the magnetism in the sample and gives a broad description to the pseudogap phase.

The abundant number of different models for the pairing mechanism in cuprates is only surpassed by the proposals for the pseudogap state [Norman 05]. It is not the purpose of this thesis to build or evaluate any specific theory of the pairing in cuprates but instead I aim to provide a statement of experimental facts and give the best description of the data obtained, independent of any theory. In the next section, I will describe a few experimental results from various spectroscopic techniques on the pseudogap phase that will be relevant for the understanding and the analysis of our data. For a more general experimental review refer to [Timusk 99].

c. The Pseudogap Phase

The pseudogap phase gains its name from the presence of a gap in parts of the Fermi surface above the superconducting transition temperature $T_c$ (Fig. 2-09). The pseudogap persists up to a temperature $T^*$ where it can no longer be
The observation that in Bi2212 the gap magnitude is 44 meV, and $T^* = 83 K$, is a typical underdoped sample. The temperature where the pseudogap vanishes decreases with doping, and in the overdoped regime, $T^*$ merges with $T_c$. Moreover, the energy scale of the energy gap measured in tunneling follows the same doping dependence of the LDOS by STM is expected. The tunneling energy gap closes as the sample approaches $T_c$. In cuprates, by raising the temperature, the superconducting gap smoothly evolves into the pseudogap [Renner 98]. The gap measured doesn’t seem to change in magnitude as it crosses $T_c$ in an underdoped sample. The temperature where the pseudogap vanishes decreases with doping, and in the overdoped regime, $T^*$ merges with $T_c$. Moreover, the energy scale of the energy gap measured in tunneling follows the same doping dependence of the LDOS by STM is expected. The tunneling energy gap closes as the sample approaches $T_c$. In cuprates, by raising the temperature, the superconducting gap smoothly evolves into the pseudogap [Renner 98]. The gap measured doesn’t seem to change in magnitude as it crosses $T_c$ in an underdoped sample. The temperature where the pseudogap vanishes decreases with doping, and in the overdoped regime, $T^*$ merges with $T_c$. Moreover, the energy scale of the energy gap measured in tunneling follows the same doping dependence of the LDOS by STM is expected. The tunneling energy gap closes as the sample approaches $T_c$. In cuprates, by raising the temperature, the superconducting gap smoothly evolves into the pseudogap [Renner 98]. The gap measured doesn’t seem to change in magnitude as it crosses $T_c$ in an underdoped sample. The temperature where the pseudogap vanishes decreases with doping, and in the overdoped regime, $T^*$ merges with $T_c$. Moreover, the energy scale of the energy gap measured in tunneling follows the same doping dependence of the LDOS by STM is expected. The tunneling energy gap closes as the sample approaches $T_c$. In cuprates, by raising the temperature, the superconducting gap smoothly evolves into the pseudogap [Renner 98]. The gap measured doesn’t seem to change in magnitude as it crosses $T_c$ in an underdoped sample. The temperature where the pseudogap vanishes decreases with doping, and in the overdoped regime, $T^*$ merges with $T_c$. Moreover, the energy scale of the energy gap measured in tunneling follows the same doping dependence of the LDOS by STM is expected. The tunneling energy gap closes as the sample approaches $T_c$. In cuprates, by raising the temperature, the superconducting gap smoothly evolves into the pseudogap [Renner 98]. The gap measured doesn’t seem to change in magnitude as it crosses $T_c$ in an underdoped sample. The temperature where the pseudogap vanishes decreases with doping, and in the overdoped regime, $T^*$ merges with $T_c$. Moreover, the energy scale of the energy gap measured in tunneling follows the same doping dependence of the LDOS by STM is expected. The tunneling energy gap closes as the sample approaches $T_c$. In cuprates, by raising the temperature, the superconducting gap smoothly evolves into the pseudogap [Renner 98]. The gap measured doesn’t seem to change in magnitude as it crosses $T_c$ in an underdoped sample. The temperature where the pseudogap vanishes decreases with doping, and in the overdoped regime, $T^*$ merges with $T_c$. Moreover, the energy scale of the energy gap measured in tunneling follows the same doping dependence of the LDOS by STM is expected. The tunneling energy gap closes as the sample approaches $T_c$. In cuprates, by raising the temperature, the superconducting gap smoothly evolves into the pseudogap [Renner 98]. The gap measured doesn’t seem to change in magnitude as it crosses $T_c$ in an underdoped sample. The temperature where the pseudogap vanishes decreases with doping, and in the overdoped regime, $T^*$ merges with $T_c$. Moreover, the energy scale of the energy gap measured in tunneling follows the same doping
dependence as $T^*$, decreasing with increasing doping. This presents the first puzzle for the pseudogap: if the energy gap observed in tunneling correlates with $T^*$ and not $T_c$ does that indicate the presence of a different phenomena? If that is the case, is there any other energy scale that could be associated to $T_c$?

Raman Scattering experiments reveal two distinct quasiparticle dynamics between quasiparticles at the nodes (moving 45 to the Cu-O bonds) and antinodes (moving along the Cu-O bonds) [Le Tacon 06]. While electronic coherence persists along the nodes down to low values of doping, antinodal quasiparticles become incoherent in the underdoped regime. The Raman peaks $B_{1g}$ (antinode) and $B_{2g}$ (nodes) show that there are two different energy scales in underdoped regime.

ARPES measurements confirm the results found by Raman spectroscopy. The maximum gap measured along the antinodal regions behaves the same as the tunneling gap, getting larger with less doping. On the other hand, the gap measured near the nodes gets smaller the more underdoped the sample is,

![Figure 2-10](image)

**Figure 2-10 - Evidence for Two gaps in the Underdoped Regime** - The doping dependence of the symmetrized ARPES spectra show different behaviors for the gap measure at different regions of the Fermi surface in underdoped Bi-2212. While the gap measured close to the nodes (a) tend to get smaller for lower dopings, the gap measured close to the antinodes (b) gets larger a lower dopings. The inset in (b) shows the temperature dependence of the antinodal gap for the sample with $T_c = 30K$ by plotting the spectrum at 10K and 50K. (c) Illustrates the different behavior of the gaps measured at different locations of the fermi surface (inset) and compares it to behavior of $T_c$ and $T^*$. This figure was extracted from [Tanaka 06]
following better the superconducting dome (Fig. 2-10) [Tanaka 06]. Also in ARPES, the near-nodal regions present a larger coherence peak, indicating the presence of well defined quasiparticles. As the temperature is raised, the gap at the nodal regions closes [Ding 96a, Lee 07] while the gap magnitude in the antinodal regions remain mostly unchanged (Fig. 2-11), leading to the formation of an usual Fermi surface, referred as Fermi arcs [Norman 98].

The next question one must ask then is what phase is associated the pseudogap state or the antinodal gap? The obvious candidates are related magnetic order observed in the insulating regime. Muon spin relaxation (μSR) measurements indicate signs of the presence of local order on short length scales [Niedermayer 98]. μSR also suggests that vortex cores in YBCO are antiferromagnetic [Miller 02]. Further evidence for magnetic/charge order was found by neutron scattering experiments. When some of the La was replaced by Nd in La$_{2-x}$Sr$_x$CuO$_{4+δ}$ (LSCO) samples, a static ordered phase was found, in the form of one dimensional “stripes” [Tranquada 95]. This phase consists of series stripes where the charge must live, separated by antiferromagnetic regions. This stripe phase is particularly strong at 1/8 doping, and has been also been observed in LBCO samples at this doping [Fujita 04]. Signs of “melted” stripes correlations can also be found a different dopings [Kivelson 03]. There is little doubt that stripes excitations happen in cuprates but it is not clear whether they
provide a complete description for the pseudogap phase or if they have any relation to the mechanism of superconductivity.

One important aspect of the pseudogap and the superconducting energy scale is that they merge in the overdoped regime (Fig. 2-12). It is very difficult to distinguish the two energy scales in this regime. The gap measured in the nodal and antinodal regions lead to a single d-wave parameter. Also, close to the optimally doped regime, the gaps measured in the antinodal region present a well defined coherence peak. In these regions, ARPES measurements [Lee 07] show a very unusual temperature evolution for the gap. The gap magnitude hardly changes (Fig. 2-11) as the sample crosses $T_c$ but the coherence peaks disappear above $T_c$. The coherence peaks don’t seem to broaden up, but simply reduce in size, indicating an unusual normal state where quasiparticles are not well defined above $T_c$ [Deutscher 99]. This is unlike the normal metal, where the
Fermi liquid leads to the presence of quasiparticle peaks. In an unexpected manner, both STM and ARPES present coherence peaks that follow the same trend as the superfluid density.

Another important aspect to understand is that the unusual normal state above $T_c$ might be coming from the superconducting state itself. Fluctuations of the superconducting order parameter play a very important role in cuprates. In traditional superconductors, the order parameter is uniformly suppressed to zero as the sample approaches $T_c$. Fluctuations of the normal state below $T_c$ or the superconducting state above $T_c$ are unusual because the long coherence length makes these fluctuations very costly. Cuprates carry a large gap, short coherence length, of the order of 20Å, leading to a more relevant role for phase fluctuations. The low phase stiffness could also point out that the $T_c$ would be a the temperature at which the long range order is established instead of the temperature at which the magnitude of the order parameter becomes non-zero [Emery 95]. Experimental evidence of pairing above $T_c$ has been found from both Nernst effect [Xu 00, Wang 01] and susceptibility measurements [Wang 05]. The Nernst signal comes from the presence of mobile vortices in superconductor. Measurements in cuprates show that vortices are still present for a large range of temperatures above $T_c$, for many dopings in different cuprate families. Torque magnetometry shows that the diamagnetic response of the sample also survives far above $T_c$ consistent with the Nernst results (Fig. 2-13). It is important to notice that in both cases, the region of superconducting fluctuations does not cover the entire pseudogap regime, specially at very low dopings and therefore it is insufficient to describe the pseudogap regime. Terahertz spectroscopy has also shown evidence for the superconducting fluctuations far above $T_c$ in the underdoped cuprates [Corson 99].

The anomalously low phase stiffness, the short coherence length and the important role of the phase fluctuations have changed how we study these superconductors, requiring spectroscopic techniques with nanoscale resolutions. The use of scanning tunneling spectroscopy in the study of cuprates is one of the most promising candidates to bring new answers to this twenty
year-old puzzle. In the next chapter I will explain the methods of scanning tunneling spectroscopy that we implemented to study the cuprates.

Figure 2-13 - Evidence for Pairing above $T_c$ - (a) Shows the measurement of torque versus magnetic field realized with torque magnetometry on underdoped Bi-2212 ($T_c = 50K$). The diamagnetic contribution, coming from a proposed vortex state, grows rapidly below 120K. The vortex state can also be measured using the Nernst effect. The Nernst signal measures voltage generated by the motion of a vortex when a temperature gradient is applied to the sample (b). The phase diagram in (c) shows the onset of the Nernst signal. The contours indicate regions of the Nernst coefficient in $nV/KT$. by This figure (a) was extracted from [Wang 05], (b) and (c) were extracted from [Wang 06]
Chapter 3
Scanning Tunneling Spectroscopy

Tunneling spectroscopy is probably the most powerful technique to directly measure the electronic density of states in real space. When used in a superconductor, it provides direct signatures from superconductivity such as the pairing gap in the density of states. We use this powerful technique to extract the temperature evolution at the atomic level of the density of states. This can teach us when the Cooper pairs first form and what is the meaning of the transition temperature for the high temperature superconductors. One of the difficulties over the past twenty years in the study of cuprates comes from the lack of good experimental probes for short distance correlations, that could be very important at the Mott insulator proximity. Atomically-resolved tunneling spectroscopy is the best way to probe the electrons within this regime. This chapter introduces the experimental set up used in this work. I give a brief introduction to scanning tunneling spectroscopy, the basic experimental procedures and the materials studied.

3.1 The Tunneling Current

Almost 50 years ago, Giaever have observed the tunneling current flow between two metals separated by a thin insulating oxide layer [Giaever 1960]. The electrons could flow between the two conductors due to quantum mechanical tunneling. The simplest model to describe the tunneling current assumes independent electrons, obeying the Fermi-Dirac distribution \( f(\epsilon) = (1 + \exp(\epsilon / k_B T))^{-1} \) where \( \epsilon \) is the energy of electron to respect to the Fermi level. If metal 1 is biased by a voltage \( V \) with respect to metal 2, this effectively
raises the Fermi level of the electrons in metal 1 with respect to the electrons in metal 2. Electrons will tend to flow out of the filled states of metal 1, into the empty states of metal 2 (Fig. 3-01). The elastic tunneling current from metal 1 to 2 is assumed to be proportional to the density of occupied states of metal 1 and the density of unoccupied states of metal 2:

\[ i_{12} = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} |M|^2 \rho_1(\varepsilon + V) f(\varepsilon + V) \rho_2(\varepsilon)(1 - f(\varepsilon)) d\varepsilon \]

where \( e \) is the electron charge, \( M \) is matrix element, and \( \rho \) represents the density of states for each metal. Bardeen has shown that under the experimental conditions, it is plausible to treat \( M \) as a constant [Bardeen 1961]. For small energy differences, \( M \) is independent of energy and also unchanged as a metal becomes superconducting. The term \( i_{12} \) represents the dominant current but we should also add the current flowing from the occupied states of metal 2 to the unoccupied metal 1. Adding both currents we obtain the total tunneling current:

\[ I = \frac{4\pi e}{\hbar} |M|^2 \int_{-\infty}^{\infty} \rho_1(\varepsilon + V) \rho_2(\varepsilon)(f(\varepsilon + V) - f(\varepsilon)) d\varepsilon \]

From the equation above, it became clear that the tunneling current could be...
used as tool to measure the density of states. The next leap was to add spatial resolution to this measurement.

The scanning tunneling microscope, first developed at IBM in Zurich by Binnig and Rohrer [Binning 82] added the ability to investigate the electronic states with high spatial resolution. In Scanning Tunneling Microscopy (STM), a sharp conducting tip is brought within tunneling range to a sample. A bias voltage $V$ is applied between the sample and the tip and the tunneling current is measured as the tip scans the sample (Fig. 3-02). This way, one can measure the tunneling current as function of both the voltage $V$ and position $r$. We choose a tip material which has a flat density of states within the range of energies from the Fermi surface that we wish to study. If we add this simplification and differentiate with respect to the voltage $V$ the expression above for the tunneling current we obtain:

$$\frac{dI}{dV}(r,V) \propto \int_{-\infty}^{\infty} \rho_{\text{sample}}(r,\epsilon) \frac{df}{d\epsilon}(\epsilon + V) d\epsilon$$

The second factor in the integral is the derivative of the Fermi-Dirac distribution and it has a bell-shaped form. This means that the differential conductance of the tunneling current is a temperature-broadened measurement.
of the density of states of the sample. For low temperatures the derivative of the Fermi-Dirac distribution can be approximated as a delta function, leading to:

$$\frac{dI}{dV}(r,V)_{T=0} \propto \rho_{\text{sample}}(r,V)$$

3.2 Types of Measurements

STM is still today a golden standard for imaging the electronic states at the atomic level. We measure tunneling current as a function of 2 variables: the position in the surface of the sample $r$ and bias voltage $V$. The tip is mounted on top of a piezo tube scanner which provides motion resolution on the sub-Angstrom scale in all directions. The bias voltage is applied to the sample and the current measured through the tip, which is maintained in a virtual ground.\footnote{Details of the microscope design and operation can be found in Appendix A.}

a. Topography

The matrix element $|M|^2$ can be determined by assuming a square-shaped barrier for the insulating barrier. That leads to the wave function of electrons in both the tip and sample falling exponentially inside the insulating barrier, resulting to the tunneling probability through the barrier to drop exponentially with width of the barrier, that in the STM case is the tip to sample distance $d$:

$$I \propto |M|^2 = e^{-2d \sqrt{2m\gamma / h}}$$

where $\gamma$, the height of the barrier, acts as the work function between the tip and the sample. By measuring the slope of $\log I$ vs $d$ one can determine if we are in the tunneling regime and obtain the value of the work function. Typically, $\gamma$ is about 4 eV in our measurements. Notice that it is important to be in the limit of
the bias $V \ll \gamma$ to make sure that we are in the tunneling regime. Our measurements of $\gamma$ have shown that $|M|^2$ is energy-independent for bias voltage $V$ below 1eV.

The exponential dependence of the tunneling current with $d$ is exploited to image the surface of the sample. The topography is a measurement of the tip position $z$ as it scans the sample while keeping a constant current. The current is maintained constant by a feedback loop at a fixed bias voltage. As the tip scans the surface of the sample, the tip will move following the contours of the sample. The topography is a quick and powerful way to image the sample surface with atomic resolution. Actually, the constant current contours contain information from both the atomic contours and the integral of the electronic density of states between the fermi level and $eV$. For example, the topography of the surface of Ag-111 (Fig. 3-03) reveal both the atomic steps and the electronic surface states, that display waves patterns from the reflection off of the atomic steps and random impurities. The electrons occupying the surface
state bands of noble metals are very weakly coupled to the bulk bands and form a two-dimensional almost-free electron gas, leading to the formation of the standing-wave pattern observed in the topography [Crommie 1993].

b. Tunneling Conductance Spectrum

The tunneling differential conductance is a thermally broadened measurement of the density of states of the sample. The measurement of the differential conductance as function of the bias voltage provides the density of states spectrum. To obtain the differential conductance, one could perform the numerical derivative of a measurement of the tunneling current but more sensitive measurement can be performed using a lock-in amplifier technique. We employ a lock-in amplifier to modulate the bias voltage by \( dV \) around a voltage \( V \) of interest. As result of the modulation, we can measure a current modulation \( dl \) at the same frequency. We use the ratio \( dl/dV \) as the measurement of conductance. The measurement of \( dl/dV \) spectrum is made with constant tip-sample distance. For this it is required to open the feedback loop for the duration of the measurement.

The energy resolution of the spectrum is determined from both the temperature and the modulation \( dV \). Typically, we use a few mV for \( dV \) and we always try to keep it less than \( k_B T \). From the derivative of the Fermi-Dirac distribution, the thermal broadening width is about \( 3.5k_B T \), which leads to about

![Figure 3-04 - Tunneling Spectrum](image.png)

The tunneling differential conductance spectrum is proportional the density of states in the material. The measurement in Ag-111, reveals a sharp step starting at -100mV that corresponds to the bottom of the surface state band.
15mV for T=50K. A sinusoidal modulation in V introduces a smearing of about 1.4dV which is 5.7mV for a 4mV modulation.

The tunneling $dI/dV$ as function of the bias Voltage $V$ provides us the information from the local density of states spectrum as function of energy $eV$. Using again an example from the surface of Ag-111 (Fig. 3-04), one can observe that in the $dI/dV$ spectrum the bottom of the surface state band, about 0.1 eV below the Fermi energy.

c. Line cut

The line cut is simply a succession of conductance spectra taken along a line in the sample. The line cut is usually plotted as a 3D plot that presents the differential conductance as function of both energy and on direction in space. These plots are ideal to visualize the variation of the conductance spectra in space. The high-$T_c$ superconductors studied in this work, present nano-scale variations of the density of states spectra and the measurement of a line cut demonstrates this variation very well.

d. Conductance Map

The conductance maps are color map plots of the differential conductance at a given bias $V$ as function of the tip position $r=(x,y)$. This way, it provides a map of the local density of states for each measured energy.

We use open loop measurements of the conductance to plot the conductance maps. At each location $r$, the tip-sample distance is set by the feedback loop for a given setup bias $V_0$ and current $I_0$. Then, we open the feedback loop, and measure the conductance $dI/dV$ for all desired energies. To move to another location, the feedback loop is closed.

Conductance maps measurements are extremely time consuming. The time required for each measurement of $dI$ is set by the lock-in time constant. Typically to overcome the signal to noise, we use a lock-in time constant $\tau=20\text{ms}$. The measurement at each energy has to be delayed by about $6^\circ\tau$. This
Figure 3-05 - Conductance Maps

The tunneling differential conductance maps are a real space picture of the local density of states of the sample. The ripples in the image are quasiparticle excitations of the surface states scattering off steps and impurities. Notice that with increasing energy, the wavelength of the modulation decreases, corresponding to the higher momentum of the states at that energy. One can use this technique to extract the dispersion relation for the state.
way, a 256 pixels x 256 pixels map will take more than 2 hours for each energy. The very low-drift in our microscope design allow us to take data sets for days while keeping the spatial registry.

Measuring the conductance maps of the Ag-111 surface allows us to examine the dispersion of the surface-state band. One can use the conductance maps to image the quasiparticle scattering directly. Two dimensional quasiparticle excitations form a standing wave pattern in the conductance maps. The energy dispersion of quasiparticles $\varepsilon(k)$ determines the wavelength of the standing wave pattern at each energy. As seen in Fig. 3-05, the higher energy maps contains electrons with higher momentum and therefore shorter wavelength.

d. Temperature Dependent Measurements

The biggest challenge we faced was how to make all these measurements mentioned above, now for a wide range of temperatures. We realized that because of the nano-scale inhomogeneity of the density of states, the definite data would also have to present spatial registry for different temperatures.

For temperature variations of a few degrees Kelvin, the expansion of different parts of the microscope would be of the order of $\mu$m. This could easily lead to the loss of the spatial registry. A combination of thermally compensation design and careful analysis of the temperature drift allowed us to measure from 20K to about 100K while maintaining the spatial registry.

To track the same area for different temperatures, we take a topography of a large area, e.g. 200 nm x 200 nm. Then by doing a small temperature change we can determine how much it is drifting and which direction we need to offset the sample position to compensate the drift.

The temperature drifts are also very time consuming. We have to make sure that the temperature equilibrates before each measurement. Ideal conditions after a temperature change can take up to a whole day to be
obtained even after a small temperature change. We have performed several runs which last about 2 months of constant data acquisition while keeping the atomic scale spatial registry.

3.3 Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

Scanning tunneling microscopy imposes certain restriction in the choice of samples to study. The studied materials need to be conductors and present a flat and clean surface. STM, as most surface measurements, is very sensitive to the surface quality. This limits the number of families of cuprates that is accessible to STM. For this study we chose to use Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) because it presents the best surface quality among the most studied cuprates (Fig 3-06).

The samples used are single crystals grown with a floating zone method. The hole doping in the sample is controlled by adding interstitial oxygen atoms between the Sr-O and Bi-O layers. Annealing the sample under different oxygens gas pressures control the doping level. The doping level is

Figure 3-06 - Bi-2212 - The Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ is the most studied cuprate compound in STM and ARPES. This is because the cleave produces a very flat and stable surface that can be probed by these spectroscopic techniques. The picture above was obtained with a optical microscope. The cleave happens between two weakly bonded Bi-O planes (right) which preserves the charge doping for Cu-O plane that is closest to the surface.
characterized by the measurement of the superconducting transition temperature using a SQUID magnetometer.

The plane of interest are the Cu-O planes but Bi-2212 cleaves between two adjacent Bi-O layers. The topography reveals the positions of the Bi atoms (Fig. 3-07). The Oxygen atoms don’t appear in the our measurements [Kirk 1988]. The Cu atoms have the same position as the Bi atoms (Fig. 3-06). The predominant physics observed in the spectroscopical measurements originate from the Cu-O. This can be verified by the presence of the superconducting gap and imaging of the quasiparticle excitations. Also we also measured impurity resonances generated by the substitution of Cu atoms by known atoms such as Ni and Zn. The influence of the atoms Sr-O and Bi-O planes on the tunneling process, either by altering the density of states or the tunneling matrix elements, is still not completely understood.

The actual crystal structure is changed by the presence of an incommensurate supermodulation which extends throughout the bulk crystal.

Figure 3-07 - Topographic Image of Bi-2212 - The Topography of Bi-2212 is capable of revealing the atomic lattice of the Bi atoms. The O atoms are not visible in the topography. The Bi atoms are spaced by about 4 Å and are located straight above the Cu atoms. The topography reveals a bulk reconstructing normally referred as the b-axis supermodulation. The atomic lattice runs 45 degrees to this modulation. The image on the left is over a 500 Å field of view and the on left over a 150 Å area.
The period of the supermodulation is about 26 Å and it runs along the b-axis (crests are parallel to the a-axis) [Yamamoto 1990]. The supermodulation is easily seen in STM topographies (Fig. 3-07).

Our work would be impossible without the collaboration with outside research groups who are capable of producing the best quality samples to study. Our collaborators in Japan, in special Dr. Shimpei Ono and Prof. Yoichi Ando, and in the Brookhaven National Laboratory, in special Dr. Genda Gu, provide us with all the samples studied in this work and also taught us a lot about the nature of these materials. A lot of the progress in this research was the fruit of their effort and I am deeply grateful for their collaboration.

3.4 Methods

All the measurements presented in this thesis were taken with two almost identical variable temperature microscopes that are described in the Appendix A. The microscopes were home built and I personally assembled one of the machines. The operation and capabilities of both systems are very similar.

The tips used are commercially available STM tips produced by chemical etching. We use 2 types of tips, made of Tungsten (W) and made of a Platinum-Iridium (Pt-Ir) alloy. We did not notice any difference in the spectroscopic data taken with either type of tip. Before each measurement the tips are calibrated in a noble metal surface. Most of the time we used the Copper cut along the 111 surface. Other commonly used crystals are Cu-100, Au-111 and Ag-111. The tips are cleaned and sharpen by field emission onto the metal surface [Wiesendanger 94]. To check the tip quality, we image the metal surface. The topography of the metal surface will determine if the tip is atomically sharp. A quick measurement of the the current versus tip-sample (I-Z) can determine if we have the exponential tunneling current. The current versus bias voltage spectrum can tell if the tip has linear density of states (because Cu definitely has flat density of states).
After preparing the tip, we insert the Bi-2212 samples on the stage. The cleave is performed just before measurement in ultra-high vacuum and room temperature. The cleave generally produces a clean and very flat surface. Steps are extremely rare within our scanning field of view. After cleave, the samples are immediately inserted in the microscope stage for cooling and measurement. We have not observed degradation of the surface or change in our spectroscopic data even after months of consecutive measurements.

After cooling the samples to the desired temperature (a process that takes about 18 hours to avoid the thermal drift) we approach the sample. The approach is done carefully to avoid the contact between the tip and the sample. The tip needs to be brought within a few angstroms to the sample surface but the smallest touch to the delicate Bi-O layer could make impossible to establish the tunneling junction. Once in range, our instrument allows us to track at the atomic scale specific areas of the sample as function of temperatures. This is made manually by offsetting the sample position to compensate the thermal drift. We measured samples with diverse doping level and through large range of temperatures in order to cover a large area of the phase diagram of the cuprates. In the next chapter I start to present the experimental results.
Chapter 4
Nanoscale Imaging of the Pair Formation

In this chapter I will start to answer the question I first proposed in the beginning of this thesis: Do pairs form at the critical temperature $T_c$ or do they form at higher temperatures, lacking phase rigidity? To answer the question, we have used the scanning tunneling microscope to visualize the process of the pair formation on the atomic scale. The magnitude of the low-temperature superconducting gap measured in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) displays a large nanoscale spatial variation. We study the temperature evolution of these inhomogeneous superconducting gaps and we find that they close locally over a range of temperatures above the superconducting transition temperature $T_c$. Our study is done both through a local and a statistical point of view. Our results provide evidence that pairing first occurs in nanoscale regions above the bulk superconducting transition temperature. The results presented here were published in [Gomes 07].

4.1 Pairing Above $T_c$

The understanding of the nature of the superconducting transition at the critical temperature $T_c$ could be the key to reveal both the pairing mechanism and the physics behind the pseudogap. The superconductivity is characterized by a complex order parameter which contains an amplitude and a phase. In traditional superconductors, the sample becomes metallic once the amplitude of order parameter vanishes at $T_c$. The phase stiffness energy is very high, so
fluctuations of the order parameter phase don’t occur below $T_c$ [Fisher 91]. It has been proposed [Emery 95] that materials where the superfluid density is low, such as the cuprates, could present low phase stiffness and poor screening, resulting in the relevance of phase fluctuations for the superconducting transition. This means that the critical temperature $T_c$ would be controlled by the onset of long range phase order and would have little to do the temperature at which pairs first form.

Over the years there has been accumulating experimental evidence for the presence of paring above $T_c$, such as the results from Prof. Ong’s group [Wang 05 and Wang 06] presented in the Chapter 2. Our goal is to determine when Cooper pairs first form and unveil the nature of the pseudogap measured in tunneling spectroscopy above $T_c$. Is the pseudogap originating from pairing or from some other competing order?

4.2 The Inhomogeneous Pairing

The tunneling conductance spectrum in Bi-2212 (Fig. 4-01) taken at low temperatures (30K) show a clear energy gap, that is well characterized by the
Figure 4-02 - The Inhomogeneous Tunneling Spectrum - The figure presents 128 differential conductance spectra measured along a 250Å line across the sample, measure in the same conditions as Fig. 4-01. The variation in the position of the coherence peaks are result of the nanoscale variation in the magnitude of the superconducting gap.
presence of coherence peaks at the edge of the gap. The measured spectrum also presents an overall slope, giving it an unusual bias asymmetry. The asymmetry between the hole and the electron excitations is somewhat unexpected and not fully understood because breaking Cooper pairs produces excitations that are hole-electron symmetric. One explanation attaches the asymmetry to the Mott physics remnant in the sample [Anderson 06]. In a Mott insulator, the low energy tunneling current at positive bias, where electrons flow from the tip to the sample, would be forbidden because one would have have to pay the large price of double occupancy. On the other hand, by removing electrons while tunneling with negative bias, no such restriction would apply. The tunneling asymmetry could be come from the remains of such correlations present in the weakly doped samples, favoring the conductance at the negative bias over the positive bias.

One of the greatest difficulties of our study comes from the fact that the tunneling spectra varies greatly within nanoscale distances in the sample. By measuring the tunneling spectra across a 250 Å line in the sample (Fig. 4-02) we

![Figure 4-03 - Gap Map and Histogram](image)

- We use a color map of the gap magnitude as a way to visualize the spatial variation of the superconducting gap. The gap map plotted images a 400 Å square area of the overdoped Bi-2212 sample measured at 40K. The gap histogram plotted on the right contains the probability distribution of the gap values in the map.
can determine that the energy gap is varying by as much a factor of 2. This large spatial modulation of the energy gap can be better visualized in a gap map (Fig. 4-03). A gap map is color plot of the gap magnitude as function of position. To obtain a gap map we measure the tunneling spectrum at each location and determine the gap magnitude by the position of the coherence peaks. The position of the coherence peaks are a valid approximation for the gap size as long as \( T << T_c \). In our measurements, we have used the peak on the positive bias because it is easier to determine from the spectra at every doping and temperature due to the spectrum asymmetry bias.

The energy gap inhomogeneity was first studied by two other STM groups, one in Stanford [Howald 01] and another in Cornell [Pan 01]. It has been pointed out that the spatial disorder is in same scale as the coherence length of cuprates which is around 20Å. The Cornell group later correlated the gap variations with other signatures in the tunneling spectrum. They have shown that the gap maps are correlated to conductance maps taken at high negative bias (-960mV) [McElroy 05]. They argue that the high bias conductance maps unveil the position of the interstitial oxygen dopants and they associate them with the cause of the gap variations. They also investigate the impact of varying interatomic distances due to the super-modulation present in Bi-2212, and found a correlation between the dimension of individual unit cells and the local gap maximum [Slezak 08]. In general terms, we can summarize that the disorder present outside the Cu-O planes has a strong effect in the superconducting gap.

Eisaki et al. realized a beautiful study of the effect of chemical inhomogeneity in copper oxides [Eisaki 04]. They concluded that the maximum transition temperature can be obtained by minimizing the out-of-plane disorder. The enhancement of the inhomogeneity caused by out-of-plane disorder was also studied with STM probing the single-layer cuprate \( \text{Bi}_2\text{Sr}_2\text{CuO}_6+\delta \) (Bi-2201) [Sugimoto 06].

In traditional s-wave superconductors, the effect of adding non-magnetic disorder on the single-particle properties, such as the gap in the density of states, is very small, following the argument first used by Anderson.
To study the case of disordered d-wave superconductors, where even ordinary disorder is pair breaking, Franz et al. argue that the standard Abrikosov-Gorkov theory does not apply for short coherence length high-$T_c$ superconductors [Franz 97]. Instead, they use numerical calculations within the Bogoliubov-de Gennes formalism to show that to describe these systems correctly one must allow for the spatial variation of the order parameter. This way, they conclude that the suppression of $T_c$ due to disorder is found to be weaker than that predicted by the Abrikosov-Gorkov theory and in agreement with experiment. By introducing a modulation in the order parameter, Andersen et al. use the Bogoliubov-de Gennes formalism to self-consistently calculate the temperature evolution of the inhomogeneous gap maps [Andersen 06]. They predict the formation of superconducting islands above the bulk superconducting transition temperature which eventually overlap at a lower temperature. We performed this exact measurement, the mapping of the gap magnitude associated with the order parameter in real space as function of temperature, and I present it later in section 4.4. Before I show the statistical analysis of the gap maps, I will present the measurement of the temperature evolution of the energy gap in the density of states at individual locations in the sample. This will help us understand that the gap measured at all temperatures in the overdoped Bi-2212 samples is indeed the superconducting gap.

### 4.3 Temperature Evolution of the Energy Gap

While performing tunneling measurements, the almost immediate question that one can ask is how does the energy gap evolve with temperature? Early measurements performed with STM [Renner 98] have demonstrated the presence of a pseudogap above the critical temperature $T_c$. The precise quantitative analysis to extract the relation between the pseudogap and the superconducting gap was not obtained because of the gap inhomogeneity. To overcome this problem, we use our ability to keep track of the spatial registry for a large range of temperatures. This way, we can obtain the tunneling spectrum
for different temperatures at the same atomic location. This task is far from trivial as the temperature change involves thermal expansions of the order of microns. The compensated design of our variable temperature microscope, together with the ability to offset the sample to compensate the thermal drift, made possible to maintain the spatial registry from 20K up to 100K. The sample offset and the tracking of the spatial location is done manually, with successive topography scans, which requires a very careful procedure. More details of this procedure can be found in Appendix A.

We chose to start our measurements with highly overdoped samples of Bi-2212 (OV65). The samples are single crystals and present a doping level of $p = 0.22$ and $T_c = 65$K. This is the highest doping achieved for the pristine Bi-2212 compound. These overdoped samples transition to a Fermi liquid and the present a low value for $T^*$. In Fig. 4-04, we present the tunneling conductance spectra taken at different temperatures at the same lattice location. Notice that our procedure results in a very smooth evolution of the energy gap as function of the temperature. All changes observed in the spectra happened below 100mV and the spectra overlap well at high energies. This demonstrates that the opening of the gap conserves the density of state. In tunneling spectroscopy, the integral of the conductance spectrum is maintained constant due to the set point condition. Before each measurement, the tip-sample distance is set up by the bias and current set points. This means that every spectrum follows the normalization condition:\footnote{Strictly speaking, this normalization is not satisfied experimentally because of losses in the conductance signal due to the pre-amplifier bandwidth and frequency filters in the lock-in amplifier. The numerical integral of the measured conductance falls short of the actual current and it is the same for all spectra taken so this carries no consequences for any of the analysis performed in this thesis.}

\[
I_{set} = \int_0^{V_{set}} \frac{dI}{dV} dV
\]
Figure 4-04 - Temperature Evolution of the Superconducting Gap - The conductance spectrum was measured at the same atomic location for temperatures ranging from 30K to 86K. By tracking the same locations, we avoided effects of the gap inhomogeneity, obtaining a very smooth temperature evolution for the spectrum. We observe from (a) that all changes in the spectra are state conserving and happen below 100mV. In (b) we present the same data as in (a) but with a constant vertical offset for better visualization of the gap evolution. The spectra were taken with $V_{\text{bias}} = 200\text{mV}$ and $I = 40\text{pA}$ and $dV=3\text{mV}$,
As consequence, one cannot just measure the integral of the tunneling spectra to extract whether the density of states is being conserved because the set point conditions enforce an artificial normalization of this integral. If the opening of the gap was removing density of states to energies beyond the set point bias, the tunneling normalization would still enforce the integral of the spectra to remain constant but it would artificially enhance the conductance in the spectrum. Therefore the conservation of the density of states is not obtained from the integral of the conductance but from the actual proof is that the spectra overlap so well at high energies.

The second important observation is that this state conserving energy gap evolves smoothly as function of temperature and clearly survives above $T_c ( = 65K)$. The spectrum taken at 70K still presents a small but clear gap, which vanishes close to 80K. The measured gap value is also quite large when compared to traditional superconductors. In traditional weak coupling BCS superconductors, the ratio between gap magnitude and the transition temperature is $2\Delta/k_B T_c = 3.5$ [Tinkham 75], where $k_B$ is the Boltzmann constant. This ratio has also been extended to the d-wave superconductor case where $2\Delta/k_B T_c = 4.3$ [Won 94]. We can estimate the gap size by the coherence peaks position in the spectrum taken at the lowest temperature, $\Delta = 27mV$ and if we use the temperature that the gap closes $T_p = 80K$, we find a ratio $2\Delta/k_B T_p = 7.8$. This ratio is larger than any traditional superconductor and if we use of the bulk transition temperature $T_c$, it would only increase the ratio even more. The measurement made here in a single atomic site is not statistically significant but following a similar procedure, in chapter 4.4 I will extend the analysis to a large set of data.

This measurement was also performed at different locations with different gap sizes. In Fig. 4-05, we show the spectra taken on sites with both smaller and larger than the average size of gaps. Notice that both the larger and the smaller spectrum are state conserving. Also the temperature that the gap
vanishes is different at each case. The smaller gap ($\Delta=23\text{mV}$) vanishes around $T_p=72\text{K}$ and the larger one ($\Delta=33\text{mV}$) vanishes at higher temperature $T_p=90\text{K}$.

To extract a precise values of the temperature evolution of the gap magnitude, we apply a simple numerical model to our data. We realized that the asymmetric background the spectrum has no temperature dependence within the range of temperatures studied therefore is not associated with the pair formation. We can remove the normal state background by dividing the low temperatures spectra by the highest temperature one, when the gap is completely closed. Even though the normal state spectrum has no apparent feature, it is still different at each location so the division needs to be taken in a point-by-point basis. The division results in set of symmetric spectra and it eliminates the normal state slope and also possible matrix element effects. As mentioned in Chapter 3, the matrix element is assumed to be independent of energy in the range of interest and independent whether the material is superconducting or not. We found that we can fit the ratio spectra with a simple d-wave superconductor density of states model. The model includes only two
fitting parameters: The maximum gap magnitude $\Delta$ and a inelastic scattering term $\Gamma$ [Dynes 78], coming from the inverse of the quasiparticle lifetime. For a $d$-wave superconductor, the density of states is given by:

$$ \rho(E,T) = \frac{1}{\pi} \int_{0}^{\pi} d\theta \Re \left( \frac{E - i\Gamma(r,T)}{\sqrt{(E - i\Gamma(r,T))^2 - \Delta(r,T)^2 \cos^2 2\theta}} \right) $$

The integral over $\theta$ accounts for the momentum average nature of the our real space probing method. We assumed equal weight to all direction, not considering band structure effects. Besides the $\theta$ dependence of $\Delta$, this is the same formula used for $s$-wave superconductors [Tinkham 75]. Our spectra are measured at significantly high temperatures, making necessary to add additional broadening arising from the Fermi distribution $f(E,T)$. As shown in Chapter 2, this is done by using the derivative of $f(E,T)$. The conductance ratio will then be fitted to:

$$ \frac{dI}{dV}_{SC} (V) = \int_{-\infty}^{\infty} dE \frac{e^{E-V/k_BT}}{e^{E-V/k_BT} + 1} \rho(E,T) $$

This fitting model allows us the extract a set of $\Delta(T)$ and $\Gamma(T)$ for each location.

We applied the fit to multiple sets of spectra taken at different locations (Fig. 4-06). In this overdoped sample, the fit gives good results independent of the gap magnitude. We observe that a single energy scale is sufficient to describe the energy gap below and above $T_c$. The energy gap evolves smoothly across $T_c$ and eventually vanishes at a higher temperature $T_p$. The value of $T_p$ is different at each location, smaller gaps have a lower $T_p$ while larger gaps have a larger $T_p$ as can be seen in Fig. 4-07. The only aspect that is not enclosed by the
**Figure 4-06 - D-Wave Fit** - In (a) we present the conductance spectra taken at each energy divided by the conductance spectrum taken at 86K. The division results in symmetric spectra that can be them fit with a simple d-wave model. The dots are the data points and the solid lines the fitting. The values of $\Delta$ extracted from this fitting are plotted in (b). The fitting procedure can be applied to gaps of different size with equal success. In (c) we show another example for the fitting applied to spectra with a large size gap.

**Figure 4-07 - The Local Temperature Evolution of the Paring Gap** - The superconductor gap closes independently at each location of the sample. Smaller gaps close at lower temperatures while large gaps survive to higher temperatures. The gap values were extracted with a d-wave fitting model. Notice that for all measured points the gap closes at a temperature above the bulk transition temperature $T_c$ (gray line).
fitting are the “dip-hump” features, present at energies just higher than the coherence peaks. We will discuss the meaning of this feature later in Chapter 6.

Trying to understand the STM gap measured in this overdoped samples with a two gap model, as presented in Chapter 2, leads to incongruent results. The nodal region excitations are responsible for the low energy density of states while the high antinodal excitations would fall at the coherence peaks energies. The gap measure with STM would then follow the antinodal gap because one would intuitively follow the position of the coherence peak to determine the gap size. But our d-wave fit allows to extract the value of the gap at the nodal region also. The slope of the gap near the Fermi energy is mainly defined by the presence of the excitations near the nodal regions. In our data the slope at low energies and the position of the coherence peaks lead to the same value for the maximum gap. We conclude that in at this doping there is a single energy gap present in the spectrum.

The second parameter that we can extract from our fitting is the lifetime broadening $\Gamma(T)$ (Fig. 4-08). The values of $\Gamma$ are always much smaller than the

![Figure 4-08 - D-Wave Fit](image-url)

In (a) we present the conductance spectra taken at each energy divided by the conductance spectrum taken at 86K. The division results in symmetric spectra that can be them fit with a simple d-wave model. The dots are the data points and the solid lines the fitting. The values of $\Delta$ extracted from this fitting are plotted in (b). The fitting procedure can be applied to gaps of different size with equal success. In (c) we show another example for the fitting applied to spectra with a large size gap.
gap magnitude below $T_c$. We noticed that the value of $\Gamma$ is larger for larger gaps. It has been suggested [Fang 06] that quasiparticles present in regions of larger gaps could quickly decay because of the available excitation states found in the nearby regions with smaller gap. On the other hand, lower energy excitations found in regions of small gaps are not capable of penetrating the regions of large gaps. This results in a long lifetime for the smaller gap regions. Notice that the lifetime also drastically reduces (larger $\Gamma$) above the transition temperature. Again this can be understood using a similar argument due to the opening of regions without the pairing correlation, where excitation can happen at any energy.

A different approach to fit the data is also possible. Instead of fitting the data with an increasing $\Gamma$ as the temperature is raised, one could suggest that the temperature evolution gap follows an Fermi arc-like behavior [Lee 07]. As the sample crosses $T_c$, the gap in the nodal regions would close leaving only the antinodal regions gapped. Indeed, due to the lack of momentum resolution in the STM data, it is not possible to precisely distinguish whether the gaps are closing with increasing $\Gamma$ or if $\Delta$ is closing in a slower rate while an ungapped arc is opening. For example, a spectrum produced with our d-wave model and one

![Figure 4-09 - Fermi Arc model](image)

Figure 4-09 - Fermi Arc model - We contrast the d-wave model with large $\Gamma$ and a model with Fermi arc-like gap. In blue, we plotted the density of states calculated with a Fermi arc gap shown in the inset (also in blue). In orange the d-wave gap (also plotted in the inset) used in our fitting model. The parameters used were: arc: $\Delta = 36$ mV, $\theta = 22$ degrees and $T=70$K. d-wave: $\Delta = 30$ mV, $\Gamma = 10$ mV and $T=70$K.
with a simplistic Fermi arc model can almost trace each other. In Fig. 4-09, we plot a d-wave gap ($\Delta = 30\text{mV}$, $\Gamma = 10\text{mV}$ at temperature, $T=70\text{K}$) and a Fermi arc gap, produced with similar d-wave equation but with $\Delta = 0$ for around the nodes ($\Delta$ is plotted in the inset for both cases). A given $\theta_{\text{arc}}$ determines the angle from the antinodes where the arc starts. In the arc plot, we don’t use a $\Gamma$ broadening and we plot $\Delta = 36\text{mV}$, $\theta_{\text{arc}} = 22$ degrees and $T=70\text{K}$. This shows that the STM spectrum of a Fermi arc state is very similar to a spectrum of quasiparticles with short lifetime. Our data points out that the value for the gap at low temperatures follows a single energy scale but the precise temperature evolution, accounting to momentum space of this energy scale will be model dependent and is not uniquely determined.

4.4 Energy Gap Maps.

One very peculiar aspect of the pairing in cuprates is that, as shown in Fig. 4.07, each location of the sample presents its own value of $\Delta$ and it evolves independently from other regions. Each of the $\Delta(T)$ curves resembles the typical mean field evolution of $\Delta$ observed in traditional superconductors but it is only valid within a nanoscale region of the sample. We want now to give this analysis a statistical significance by extending the analytical method to a large ensemble of locations.

We measured the tunneling spectra in 128 by 128 pixels array over a 300 by 300 Å region of the sample. The region size was determined to be a representative statistics of the whole sample. The correlation length of the gap sizes is about 20 Å, so the 300 Å square field of view encloses a large statistics of the gap variation. The array size is just constrained by the measuring time (one single map takes 2 days of constant measurement to finish). With the spectrum map at hand, we extract the gap magnitude at each location.

The statistical analysis required us to simplify the way we determined the gap size. In our study we want to focus on two important pieces of information:
the gap magnitude at low temperatures and the temperature that it vanishes, which we refer as $T_p$. We will use the position of the coherence peak in positive bias as a way to determine the gap size and we will define the gap to be closed once the conductance at zero bias is higher than the conductance at the positive bias (Fig. 4-10). These approximations lead to a small error in the determination of the gap size. At low temperatures, where both the thermal and the lifetime broadening are small, we found this error to be less than 5%. Also the criteria for the closing of the gap actually results in a small under-estimation of $T_p$. These simplifications are necessary because we need a systematic and clear method for determining our parameters and a point-by-point division would just not be possible for such large data sets.

A color map of the gap magnitude, the gap map, is presented in Fig. 4-11, for four different temperatures measured. The data was obtained in a overdoped Bi-2212 sample, with $T_c = 65K$ and hole doping $p = 0.22$ (OV65). While maintaining the spatial registry, we measured gap maps for a range of temperatures around $T_c$. It is clear in the sequence that the gaps vanish inhomogeneously across the sample. Notice that the smaller gaps vanish first, being then followed the the larger ones. At 74K, the sample presents an interesting regime where, the paring gap can only be found nanoscale islands.

![Figure 4-10 - Method for Approximately Determining the Gap Magnitude](image)

Figure 4-10 - Method for Approximately Determining the Gap Magnitude - In order to produce a high sampling approach to perform a statistical analysis of the gap formation, we had to simplify the method to determine the gap locally. Instead of fitting to a d-wave model, we simply take the position of the coherence peak at positive bias as the gap size (bottom plot). The gap is considered closed once the conductance at zero bias is higher than the conductance at positive bias (top plot).
Figure 4-11 - Gap maps in the Overdoped Regime - We measured gap maps of the same 300x300Å area of the sample from 60 to 74K. The sample is an overdoped Bi-2212 with critical temperature $T_c = 65$K (OV65).
These islands are also about 20 Å in size. This enforces serious constraints in the size of the Cooper pair in the cuprates. This small size is just slightly larger than the distance between Cu-O plane and also put us close to the crossover between a BCS condensate and a Bose-Einstein condensate (BEC).

The maps in Fig. 4-11 and the plots in Fig. 4-07 lead us to search for a meaningful relation between the gap size $\Delta$ and the temperature it vanishes $T_p$. The distribution of the gap sizes of the sample can be plotted as a histogram as shown in Fig. 4-12. We can see from the histogram, the shift from finite size gaps to ungapped regions. In the search of a relation between $\Delta$ and $T_p$ we start off with the simplest possible relation, where $T_p$ is just proportional to $\Delta$. In that case, the percentage of the sample that would be ungapped at a given temperature $T$ would just be the percentage of the sample with a gap smaller than a corresponding value $\Delta(T)$. This percentage is just the integral of the gap histogram up to this value $\Delta(T)$ (Fig. 4-13). That means that for the linear relation between $\Delta$ and $T_p$ to be correct, the plot of the percentage of the ungapped regions as function of the temperature should be proportional to the plot of the integral of the gap histogram as function $\Delta$. We use the integral of gap histogram taken at the lowest temperature measured, 40K, and compare it to the plot of the percentage of ungapped regions as function of temperature. We
found that both plots trace which other well and the ratio between the Δ scale and the temperature scale is best fit by \(\frac{2\Delta}{k_B T_p} = 7.8 \pm 0.3\). The fit was performed with a standard least-squares fit routine and the error is the error from the fit. We have established that despite the strong variations of the gap magnitude, at each nanoscale region of the sample the gap collapses following a single local criterion.

We extend our analysis to study the temperature evolution of the gap in the density of states at different dopings. The statistical nature of this study eliminates the need to keep the spatial registry. As long as a large enough area is measured, it will be representative of the whole sample and our analysis will still be valid. Even if we tried to keep the spatial registry, samples with lower doping demand measurements at even higher temperatures, above 100K, so it becomes extremely difficult to measure the same area. Let’s start presenting results on another overdoped Bi-2212 sample with \(T_c = 83K\) and lower hole doping \(p = 0.19\) (OV83). The sample presented similar behavior but the energy

![Figure 4-13 - Simple relation between Δ and \(T_p\)](image)

- The integral of the gap histogram (a) represents the number of points that have a gap smaller than a given value of Δ. We compare this plot to the of how many points are ungapped at a given temperature (b). The ratio between the top and bottom x-axes is given by \(2\Delta/k_B T_p = 7.8\). The error bars are one standard deviation, calculated based on the finite statistics, due to the limited area covered by each map, and imprecisions in our conductance measurements.
gaps are larger than the ones found in the OV65 and survive to even higher temperatures (Fig 4-14). Again the lowest temperature measured was 40K and we used this histogram as our gap distribution for the integral plot. We found the same criterion between the gap distribution and the temperature that the gaps vanish also applies for this doping, $2\Delta/k_B T_p = 7.8\pm0.2$. Despite the differences in the samples, in both the transition temperature and average gap size, the temperature that the gaps vanish following the same simple criterion.

We extended our study to optimally doped samples where both $T_c$ and the gap sizes continue to increase. We have used optimally doped Bi-2212 sample with $T_c = 93K$ and hole doping $p = 0.16$ (OP93). The optimally doped sample are fully gapped even at 100K, emphasizing that from tunneling there is a very smooth transition through $T_c$ which does not determine that temperatures
that the gaps close. The gaps measured above \( T_c \) do show some differences when compared to the gaps measured below \( T_c \) (Fig. 4-15). First, they lack of coherence peaks. Similar to what happens to the quasiparticle peaks in ARPES (Fig. 2-11), the coherence peaks at the density of states gap edge are almost non-existent or very broad. This would lead us to either a very small quasiparticle lifetime or possibly to a more drastic conclusion that quasiparticles are not the correct way to describe this system. A second aspect is that even though the changes to the density of states that happened below \( T_c \) were state conserving, it is unclear whether the pseudogap closes in the same fashion. Notice that in overdoped samples, the spectral weight of the gap in the density of states is transfered to the coherence peaks. In optimally doped samples, even

**Figure 4-15 - Gap Maps of Optimal Doping** - The same statistical approach was applied for a less overdoped sample, with \( T_c = 83K \). The gap maps taken above \( T_c \) show a similar evolution and the same formation of nanoscale islands where pairing can be found. The maps were not taken at the area of the sample. The histogram statistics show offers the same scaling criterion, \( 2\Delta/k_B T_p = 7.8 \).
though the gap magnitude is larger, the coherence peaks are smaller. The trend continues towards the underdoped regime. This means that the pseudogap in the underdoped regime cannot close with simple transfer of spectral weights at low energies (<200mV), specially for gaps larger than 50mV.

The statistical analysis of the gap maps in the optimally doped samples reveal very similar results to the ones observed in the overdoped regime. In order to reach the regime with nanoscale islands of pairs, we had to reach 140K, but the evolution of the gaps in the density of states up to this temperature could again be captured with a very simple scaling, $2\Delta/k_BT_P = 8.1\pm0.2$. Within our error bars, all three dopings studied so far can be understood with the local criterion:

$$\frac{2\Delta}{k_BT_P} = 8$$

![Figure 4-16 - Single Local Criterion](image)

**Figure 4-16 - Single Local Criterion** - The data taken over 3 different dopings, 16 different temperatures, and more than 250,000 spectra are presented in this plot. The single scaling used in this plot between the temperature and $\Delta$ axes is $2\Delta/k_BT_P = 8$. The simple criterion is capable of summarizing all data taken in the optimal/overdoped samples.
This criterion has been used to produce the plot in Fig. 4-16. It is surprising that all the data taken across different doping and various temperatures, more than 250,000 spectra are all being represented in this single figure.

The criterion though has its limitations. Notice that we have not tested the criterion for gaps larger than 50mV, even though the OP93 sample presents regions with gaps larger than 50mV we did not raise the temperature enough verify if they vanish. In the underdoped regime, most gaps are large, and we will see that our criterion breaks down. In the next section we will cover some of the aspects of the underdoped regime in cuprates.

4.5 The Underdoped Regime

The criterion set to describe the density of states gap formation in the overdoped regime fails to describe the gaps in the underdoped regimes. We have repeated the same exact procedure (Fig. 4-10) to determine the gap sizes and the temperature they vanish. We realized that the linear criterion used in the

![Figure 4-17 - Gap Maps Statistics in the Underdoped Regime](image)

The same statistical approach was applied to underdoped samples, UD83 and UD73. The gaps show some ungapped regions but same scaling criterion, $2\Delta/k_BT_p = 8$, used in the plot on the right to scale the two x-axes, fails to describe how the gaps are closing.
other dopings does not apply to the underdoped regime. We studied two
different dopings of pristine Bi-2212, one with $T_c = 83K$ and hole doping $p = 0.14$
(UD83) and another with $T_c = 73K$ and hole doping $p = 0.14$ (UD73). The
deviation from the linear criterion is clear even at low temperatures on the UD83
sample and even more accentuated in the UD73. The gap maps do show the
presence of small ungapped regions (Fig. 4-17), but their percentage falls short
of the predicted value using the criterion. At 160K, the expected percentage of
ungapped regions following the local criterion $2\Delta/k_B T_p = 8$ would be roughly
50% for the UD83 sample but the measured value is less than 30%. In the UD73
sample at 180K, the criterion predicts 60% of the sample to be ungapped but
we measured only 15%. Unfortunately we have not been able to measure these
samples at higher temperatures to fully characterize the trend of the temperature
evolution of the large energy gaps.

This failure of the local criterion could originate from the inadequacy of
the method to determine the gap value or to the change in the behavior of the
electronic states in the underdoped regime. We have used the position of the
coherence peaks as a way to determine the gap size but we realize that the
spectra in the very underdoped regime fails to fit the simple d-wave model
proposed in Section 4.2. Unlike the overdoped regime, the temperature
evolution of the conductance spectrum in underdoped samples reveals an
unusual pattern.

The density of states spectrum found much above $T_c$ are different when
comparing the overdoped and underdoped regimes. While in the overdoped
regime, the conductance spectrum evolve to a smooth monotonic curve, in the
underdoped samples, the spectrum presents a loss of spectral weight that
forms a large V-shaped gap (Fig. 4-18). This V-shaped gap represents the
pseudogap that is measured by most thermodynamics and spectroscopic
techniques [Timusk 99]. In the overdoped regime, we have been able to
associate the gap measured above $T_c$ as having the same origin as the gap
measured below $T_c$ but in the underdoped regime it is unclear whether this V-
shaped normal states is arising from pairing.
We have also been able to identify an inner gap feature in the form of a "kink" that is present around 30 mV in the spectrum of the UD73 sample (Fig. 4-18). The feature could be observed in 30% of the probed area at 20K of the UD73 sample. The kink is more easily observed in heavily underdoped samples at very low temperatures.

We measured the temperature dependence of the kink in highly underdoped Bi$_2$Sr$_2$Ca$_{1-x}$Dy$_x$Cu$_2$O$_{8+\delta}$ samples. The Dy doping helps to underdope the sample further, allowing to achieve doping levels inaccessible with pristine samples. The measurements performed in Dy-doped samples present the same characteristics as measurements in pristine samples. We did not observe impurity states or extra disorder effects at the doping level studied. The sample with 30% Dy substitution, presented $T_c = 23K$. This low transition helps to avoid the temperature broadening effects that could smear the kink from the spectrum. We measured the conductance spectrum at a single atomic location as function of temperature. We observed that the kink feature at that

Figure 4-18 - Density of states in the Underdoped Regime - The left plot is a comparison between representative density of states found much above the transition temperature for underdoped samples and optimally/overdoped samples (offset for clarity). Notice that the underdoped samples transition to a V-shaped spectrum that almost does not change for the temperatures studied (below 180K). On the right, we present spectra measured at various locations in the UD73 sample at 20K. We point out the presence of an inner gap feature in the form of a "kink" in the spectrum.
location survives to temperatures slightly above $T_c$ (Fig. 4-19). The spatial
distribution and temperature evolution of the feature, just as the pairing gap in
overdoped samples, is inhomogeneous (Fig. 4-19, inset). The presence of this
second energy scale raises the possibility that the larger gap is not associated
to pairing and that this kink is the true signature of superconductivity in cuprates
[Boyer 07].

The understanding of the pseudogap spectra falls in two scenarios: (i) The large gaps are still originating from pairing and (ii) the V-shape gap is result from a different gap while the kink is the pairing signature, resulting in two competing orders present in the sample.

Relative success can be achieved to fit the underdoped gaps with a more elaborate d-wave model by adding an energy dependent inelastic scattering rates [Alldredge 08]. This can be justified by the observation that in STM the energy dependence from the gap is closely attached the angle that the excitations move. More specifically, the nodal quasiparticles dominate the features present in the STM spectrum at low energies while the antinodal quasiparticles dominate the contributions near the gap edge. The difference in the lifetime between nodal and antinodal quasiparticles, as it is measured by

Figure 4-19 - Temperature Evolution of the “kink” - We measured the conductance spectrum as function of temperature with spatial registry in a Dy-doped Bi-2212 sample with $T_c = 23$K. We can observe the smooth evolution of the kink, vanishing roughly 8K above $T_c$. The inset, shows a histogram of kink energy and gap energy obtained in a pristine Bi-2212 sample with $T_c=73$K.
ARPES, can incorporated in the STM spectra by allowing this energy dependent \( \Gamma \). For simplicity Alldredge et al. propose \( \Gamma \) that is proportional to the energy. The fit works well for lightly underdoped samples but it fails to capture the kink that is present in more underdoped regimes.

In a recent work, Hanaguri et al. have pointed out that the quasiparticle scattering modulations can only be observed in the conductance maps taken at low energies, up to the kink energy [Hanaguri 07]. The measurement was performed in the optimally doped \( \text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2 \) (Na-CCOC) and the analysis revealed that the quasiparticle scattering shows the same pattern as optimally doped Bi-2212 but terminating close to the kink energy (Fig. 4-20). The spectra
in Na-CCOC do not resemble the spectra of optimally doped Bi-2212, instead it shows similarities with very underdoped samples, presenting a large V-shaped gap and very visible kink feature. Despite that difference in the spectrum and three times smaller transition temperature ($T_c \sim 27$K) the modulations in Na-CCOC have the same dispersion as the modulations found in Bi-2212. The authors fit this dispersion with a d-wave gap of roughly 40mV. Oddly enough, the fit obtains a gap that is larger than the kink energy but much smaller than the large V-shape gap. The measurements performed at higher energies, present only a non-dispersive pattern associated with possible charge ordering [Kohsaka 07]. The authors proposed that this charge ordering is associated to the pseudogap energy scale (Fig. 4-21).

The evidence for two energy scales in the underdoped regime has been also accumulating from Raman measurements (Le Tacon 06) and photoemission

---

![Figure 4-21 - Two Different Behaviors in the Underdoped Regime](image)

The spectra shown are averaged by gap size over a 300 Å area of the sample. The spectra were taking in Dy-doped Bi-2212 with $T_c = 58$K. Conductance maps measured at different energy range reveal 2 distinct behaviors: The quasiparticle scattering patters can only be observed at low energies while at high energies, only an static charge ordering is measured. The image top right shows the static charge ordering while the bottom right image shows the Fourier transform of the scattering pattern, revealing scattering wave vectors present . The images on the right are from [Kohsaka 07 and 08].
It is important to remark though that the same measurements that identify two energy scales on the underdoped regime, indicate that the two gaps merge into a single gap in the overdoped regime. Recent Raman scattering study points out that gap observed in the antinodes in overdoped samples is a true superconducting gap [Guyard 08], in complete agreement with our conclusions. Further work is required to establish whether the kink is really related to the presence of pairing at low dopings and what is origin of the pseudogap. To extend our investigation of the nature of the pseudogap, in the next chapter we will study another sample from the Bi family of cuprates which also presents the same kinks in the similarities and other spectra.

4.6 Concluding Remarks

What is the temperature that pairs first form? Our measurements provide a microscopic picture containing key aspects of the pair formation in cuprates. We have been able to identify that the gap in the density of states measured above $T_c$ in the optimally/overdoped regimes is the pairing gap, that survives beyond the point where resistivity vanishes. At these dopings we can draw the
line where pairs first form (Fig. 4-22). A comparison between our results and the Nernst Effect data [Wang 06] shows that the onset temperature measured for the Nernst Effect falls close to the point where 50% of the sample has developed paring. Given that the Vortex response requires a certain amount of pairing to first develop in the sample, our measurements provide also the microscopic basis to understand these measurements. One can conclude that $T_c$ marks the onset of phase coherence in cuprates and not the formations of Cooper pairs.

The nanoscale pairing regions and the universal local criterion $2\Delta/k_B T_p = 8$, reveals an unusual kind of superconductor. The ratio between $\Delta$ and the pairing temperature is high even for strongly coupled superconductor and bring us close the BCS-BEC transition. A successful theory for paring has to explain how can pairs nucleate and the robustness of local pairing criterion.
Table 4-01 - Samples and Gap Map Statistics
The table below provides some of the statistics for the five dopings of Bi-2212 studied in this chapter.

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

* cannot be extracted from data
Chapter 5

Study of the Single Layered Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$

In this Chapter I extend our statistical study another member of the Bi-based cuprate family, the Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$ (Bi-2201) compound, which differentiates from the Bi-2212 for having a single Cu-O layer per unit cell. We will use the similarities between the two samples to trace a parallel with our results in the Bi-2212 compound and bring out the main differences found in the single layered samples. The most characteristic distinction between the two compounds is the much lower transition temperature found in the single layered samples, which results in a reduced dome and large pseudogap region even in overdoped regime. Our results indicate that the gaps measured in the pseudogap region found in overdoped regime follows the same statistical behavior as the gaps measured in the overdoped Bi-2212. A publication with the results from this chapter is still in preparation.

5.1 Characterization of The Bi-2201.

The Bi-2201 and Bi-2212 samples have a very similar chemical structure. The main difference is that Bi-2212 presents two neighboring Cu-O layers separated only by Ca atoms, while the Bi-2201 presents a single Cu-O layer instead. In both cases our studies are performed in high quality single crystals grown with the same floating zone technique and both samples expose the same Bi-O layered when cleaved. To reach the Cu-O layer, we tunnel through the Bi-O and Sr-O layers. All these similarities create the perfect scenario to
investigate and understand the differences in the physics occurring in these two cuprates. It is essential though to first understand the differences between the two compounds.

The main difference appears in the superconducting transition temperature. Bi-2201 has a much lower transition temperature than the double layered compound (Fig. 5-01). The optimally doped $T_c$ is 34K (94K for Bi-2212) and the overall superconducting dome follows the same shape, but restricted to a smaller doping region. Interesting though, the pseudogap region is delimited by almost the same scale $T^*$. The doping process in these samples also occur in a different way. As grown, Bi-2201 samples are very overdoped, with $T_c \sim 7K$. The pristine samples are not the most stable samples and the doping by change in the O content generates bad quality samples with a broad transitions. The better doping is

![Phase Diagram](image)

**Figure 5-01 - The Phase Diagram** - The phase diagram of Bi-2201 samples present similar temperature scales to the phase diagram of Bi-2212 but the superconducting transition temperatures are greatly suppressed. The doping in Bi-2201 is done through the La substitution, given by $x$ (replacing Sr, in Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$) and the resulting hole doping ($p$) is given in the table on the right, with the respective $T_c$. The data in the table is obtained from our collaborating sample grower Dr. Shimpei Ono.
accomplished by chemical substitution, replacing Sr with La, adding electrons to the sample. The table in Fig. 5-01 details the doping level information and respective critical temperatures. Details on the doping and the sample growth procedure can be found in [Ono 03].

The effect of a lower transition temperature in single layered samples is a general trend found in various cuprates, as seen earlier in Fig. 2-05. The highest transition temperatures are obtained in samples with three neighboring Cu-O layers\(^1\), where the influence of out of plane disorder is reduced [Eisaki 04]. Single layered samples present the lowest transition temperatures in cuprates and are very susceptible to disorder in the layers adjacent to the Cu-O planes.

The effect of the out-of-plane disorder has been systematically studied in Bi-2201 sample by modifying the introduced disorder through the chemical doping substitution in the Sr-O planes adjacent to the Cu-O planes (Fig. 5-02). The disorder can be controlled by changing the rare earth dopants (Ln) in Bi\(_2\)Sr\(_2-x\)Ln\(_x\)CuO\(_{6+δ}\) where Ln = La, Nd, Eu, Gd. It is found that \(T_c\) decreases by increasing the ion size mismatch between Sr and Ln [Fujita 05]. STM studies in

---

\(^1\) For even higher number of layers (>3) a reduction in \(T_c\) is observed due to a doping charge imbalance between the inner and outer Cu-O layers [Kotegawa 04].
the same compounds reveal that the increase of the out-of-plane disorder leads to an enhancement of the electronic inhomogeneity and the suppression of the coherence peaks [Sugimoto 06]. Recent photoemission results demonstrate that while the Fermi surface shape and the band dispersion is not affected by the increase of the out-of-plane disorder, the quasiparticle peaks are suppressed in both nodal and antinodal regions [Hashimoto 08].

We realized our study in samples that are only doped with La. These samples present the highest transition temperatures and the lowest disorder among the different Bi-2201 compounds. The surface topography of our Bi-2201 samples reveals the same b-axis super-modulation found in the double-layered compound (Fig. 5-03). The periodicity of the modulation and the atomic lattice also matched between the two compounds. We have found no features in the topography originating from the sites of the La atoms, located in the atomic layer underneath the exposed Bi-O plane. At optimal dope, 20% of the Sr atoms are substituted with La atoms.

A comparison between the spectra obtained in Bi-2212 and Bi-2201 reveals surprising similarity in the magnitude of the gap in density of states (Fig. 5-04). Both samples present the same hole doping level but the double-layered sample has a transition temperature almost three times a high. Clearly, the gap size is not scaling with the change in the transition temperature because the average gap is almost the same for both compounds. The gap size

![Figure 5-03 - Topography of Bi-2201](image)

- Our high quality single crystal sample cleave in the same manner as the Bi-2212 and expose the Bi-O plane. The topography of Bi-2201 reveals the same super-modulation found in the double layered compound, with the same periodicity. The La dopants don’t generate a clear signature in the topography. The image shows a 190x190 Å field of view and taken at 20K with V=-200mV and I=10pA.
Figure 5-04 - Bi-2212 and Bi-2201 Linecuts - Above we present the linecut spectra measured in optimally doped samples of Bi-2212 (top) and Bi-2201 (bottom). The line cuts are a sequence of 128 spectra measured along a 200Å line across the sample. The Bi-2212 spectra were measured at 40K (T_c = 93K) and the Bi-2201 spectra were measure at 20K (T_c = 34K). The samples present comparable gap sizes but the coherence peaks are suppressed in the single layered sample. The arrows, points out the presence of a “kink” inside the larger gap. This feature is observed in the underdoped regime of Bi-2212.
inhomogeneity is also present in Bi-2201 but the most striking feature is the considerable reduction of the coherence peaks at the gap edge. The spectra in Bi-2201 resemble the spectra found in the underdoped regime in the Bi-2212. In special, we call attention to the presence of an inner gap “kink” that is visible in the Bi-2201 spectra, and also found in the underdoped regime of Bi-2212. The kink feature is not observed in optimally doped Bi-2212.

The stronger disorder does not affect the average gap size but it does have consequences in the gap inhomogeneity. In Fig. 5-05, the gap distribution measured at 20K, which is 14K below the transition temperature for optimally doped Bi-2201 is contrasted with the gap distribution of optimally doped Bi-2212, also measured 14K below $T_c$. We interpret the broader gap distribution in the single layered compound as a result of the larger disorder.

The role of the disorder is a key element to understand the nature of the superconducting transition and the origin of the pseudogap. The features observed in Bi-2201 can be understood again in two different scenarios: (i) The disorder does not change the pairing strength, as the average gap size remains unchanged but it reduces the temperature that the pairs lose their global phase coherence to lower temperatures. This way, the gaps observed in Bi-2201 should vanish in the same manner as the gaps observed in Bi-2212. (ii) The disorder enhances the pseudogap and depresses the superconducting order.

Figure 5-05 - Histogram Statistics from Bi-2212 and Bi-2201 - The average magnitude of the gap found in Bi-2201 and Bi-2212 is very close but the distribution of the gaps across the sample is quite different. We plot the histogram of the gaps measured at 14K below the transition temperature for optimally doped Bi-2212 ($T_c = 94K$) and optimally doped Bi-2201 ($T_c = 34K$). The broader histogram in Bi-2201 indicates as stronger disorder effects.
The presence of the “kink” signals for the reduction of the superconducting gap while the larger gap is result of the enhancement of the effect of pseudogap, which is characterized by the gap lacking coherence peaks, as seen in the underdoped regime of Bi-2212. We will investigate the nature of the density of states gaps and by doing the statistical study of the how the gaps vanish with the raising of temperature, in the same manner of the work described in Chapter 4, establishing a single local criterion that describes the gap evolution. At the same time we will also take a more detailed look that signatures originating from competing phenomena in these samples.

5.2 Statistical Study of the Gap Formation.

As it was done in the previous statistical analysis, we start our investigation in the overdoped regime with the sample Bi$_2$Sr$_{1.8}$La$_{0.2}$CuO$_{6+\delta}$

![Figure 5-06 - Low Temperature Gap Map in Bi-2201](image)

*Figure 5-06 - Low Temperature Gap Map in Bi-2201* - We measured the gap map for the overdoped Bi-2210 compound (T$_c$ = 19K) at 12K. Even 7K below its transition temperature, the gap map presents gapless regions. The gap histogram reveals a broader distribution than the one observed in Bi-2212 and that 10% of the spectra measured are gapless.
(nominal formula given by sample grower) with $T_c = 19K$, as measured with a SQUID magnetometer. To obtain the gap maps we once again use the position of the maximum in positive bias conductance but we have to acknowledge that this procedure could lead to larger errors in Bi-2201 due to the small coherence peaks in the spectra. Keeping that in mind, this was the most reliable and systematic way we found to characterize the gaps measured in this sample.

We start by measuring the overdoped Bi-2201 sample at 12K, below its transition temperature. The gap map shows a significant part of the sample (10%) already presents a gapless spectrum (Fig. 5-06). We observed a similar effect in OV65 samples but in a much smaller scale, with less than 1% of the sample being gapless 5K below $T_c$. The gap histogram is broader in the mono layer compound, with a long tail that extends beyond 50mV. The increase in the inhomogeneity is another aspect that reinforces the fact that the Cu-O layers are more susceptible to disorder in the mono layered compounds.

The measurement of the temperature evolution of the gap map shows that the gaps vanish inhomogeneously as the temperature is raised (Fig. 5-07), replicating the behavior observed in the Bi-2212 samples. Comparing the maps taken at 12K, 20K (just above $T_c$) and 30K we take no notice of the bulk critical temperature, as most of the sample remains gapped at 30K. The data obtained at 40K and 100K were measured in a different cleave, using the same sample. We also measured the sample at 25K and 35K and included that data sets in the statistical analysis.

From the gap maps statistics, we obtain the scaling plot comparing the magnitude of the density of state gaps and the temperature that they vanish ($T_p$). In Fig. 5-08, the solid line represents the integral of the gap histogram measured at the lowest temperature 12K as function of the gap magnitude. This curve represents the percentage of the sample with a gap smaller than that given size. The data points represent the percentage of the ungapped regions as function of the temperature (plotted in the top x-axis). The scaling between the gaps sizes and the temperature they vanish is given by $2\Delta/k_BT_p = 7.6\pm0.2$. The error is the deviation from a least-squares fit between the curve and the data points.
Figure 5-07 - Gap Map Temperature Evolution in Bi-2201 - We measured the gap map for the overdoped Bi-2201 compound ($T_c = 19$K) at various temperatures. We observe the same temperature evolution found in the overdoped Bi-2212 samples. There is very little notice of the transition temperature and gaps vanish inhomogeneously. The two top maps were taken at the same region as of the map shown in Fig. 5-04. The measurements taken at 40K and 100K were taken in different regions of the same sample.
Despite the high agreement in our criterion, we must note though that our measurements contains errors in the gap estimations not accounted by the fit deviation. The error bars in the plot estimate better these expected errors in the measurement of the ungapped regions. Ideally we would like to have measured a gap map at lower temperature, where the gaps may be better formed.

The local criterion ratio found is slightly lower than the one measured in Bi-2212. We have no a priori reason to predict that both samples should present the same ratio, but it is interesting that the ratios are so close. It is more important to establish whether this local criterion persists for different dopings. To that end we measured the optimum doped sample, Bi$_{2}$Sr$_{1.6}$La$_{0.4}$CuO$_{6+\delta}$ with $T_{c} = 34K$.

The gaps found in optimally doped Bi-2201 vary from 20mV to more than 100mV. As mentioned before the gap distribution is wider than Bi-2212 and most gaps resembles the gaps found in the underdoped regime. So it is not surprising that at 60K, 25K above $T_{c}$, just 1% of the sample is ungapped. At 100% this ratio increases to 21% (Fig. 5-09). Up to this temperature, our scaling plot describes well how the gaps close, following the ratio $2\Delta/k_{B}T_p = 7.5$. From our measurements gaps that are smaller than 40mV seem to behave in the same

![Histogram Statistics in Overdoped Bi-2201](image-url)
Figure 5-09 - Gap Maps in Optimally Doped Bi-2201  - We measured the gap map for the optimally doped Bi-2201 compound ($T_c = 19$K) at 20K, 60K and 100K. The gaps ranging from 20mV to 100mV at 20K survive to temperatures much above the critical temperature ($T_c = 34$K). On the top we present the gap maps at 20K and 100K. Even at 100K, only a small portion of the sample is ungapped (21%). The two top maps were taken at different regions of the same sample. On the bottom left, the gap histogram is presented for all three temperatures measured. The plot on the bottom left represents our usual scaling plot. The ratio between the x-axes results in the local criterion, $2\Delta/\kappa_B T_p = 7.5$. 

$\Delta$ (mV)
manner as the gaps in the overdoped regime. Despite our efforts, we have not obtained a complete data set for higher temperatures and we cannot infer if the local criterion works for larger gaps. Among other difficulties in obtaining data in these samples, we faced a variation in the doping level of different crystals which does not permit the comparison between the data taken with different samples. To obtain a complete data set in one sample has proven to be challenging and time consuming.

The behavior of the gaps in Bi-2201 and Bi-2212 seem to follow the same trend. Gaps that are found in the overdoped regime, generally smaller than 50mV are formed according to a simple local criterion. This indicates the common origin for the gaps measured in both compounds. The disorder in Bi-2201 reduces the transition temperature by reducing the temperature at which the pairs lose the global phase coherence. The pairing strength, characterized by the gap size and the ratio in the local criterion, is the same in both compounds but the phase stiffness is different. The optimally doped regime represent cross over where other effects are present. The larger gaps present multiple features and are harder to characterize.

It is worth to mention the work of the Hudson Group (MIT) in overdoped Bi-2201 because it presents data that compliments our results and an alternative view of what are the pairing gaps [Boyer 07]. Their measurements of overdoped Bi-2201 with $T_c = 15K$ display a similar gap inhomogeneity, as found in our data, with gaps from 7mV to more than 50mV. They observe that between 6K and the superconductor transition temperature the changes in the spectra only occurs at very low bias. By diving spectra measured at 6K by the spectra measured at 16K, they obtain a uniform small gap $\Delta_{\text{kink}} = 6.7 \pm 1.6$ mV (Fig. 5-10). They identify this gap as the superconducting gap, and claim that it closes right at the transition temperature, relating this to the gap found in nodes in ARPES. In their interpretation, the large inhomogeneous gaps are not associated with the pairing gap and independent of the superconductivity. Their interpretation is consistent with the idea that the gaps vanish forming the arc-like feature observed in ARPES.
The energy of the kinks are uniform within an absolute scale when compared to the larger gaps but even in the Hudson Group measurements, their “kink gap” vary by a factor of 2 (from 4.1mV to 8.3mV), which is roughly proportional to the variation found in the gaps of Bi-2212. The plot of spectra that are average by the large gap size, such as the one presented in Fig. 5-10, give the impression that the kink is more uniform that it actually is. Individual spectra such as the ones presented in Fig. 5-04 allow to visualize that the low energy conductance is also varying in real space. Also, by using the normalization temperature to be right at $T_c$, it would difficult to determine whether the kinks would survive to higher temperatures. Actually their own data shows that the spectra taken at 16K displays a larger gap and a kink feature (Fig. 5-11).

Figure 5-10 - Spectral Survey in Bi-2201 - In (a), each curve is an spatial average of spectra with the same gap size, representing gaps varying from 7mV to 40mV. These were obtained by measuring the spectra over a 180 Å square area on the overdoped Bi-2201 sample ($T_c=15K$) at 6K. By keeping track of the spatial registry, the spectra at 16K at the same locations were obtained. In (b) is a plot of the conductance spectra at 6K divided by the conductance spectra at 16K, revealing uniform smaller gap. This gap is an identification of the temperature evolution of the kink featured. Notice that it also shows that almost not change happens above the kink energy. Both plots were extracted from [Boyer 07]
As correctly pointed out by Boyer et al. and also by our own work in the underdoped regime of Bi-2212, most of the changes below $T_c$ happen at low energies and they are correlated to the formation of the anomalous Fermi arc. While this could strongly suggest the presence of 2 independent gaps in the problem, the nature of the two gaps seem closely related. The fact that the two gaps merge into a single gap behavior in Bi-2212 and the same local criterion found for the gaps in Bi-2201 strongly impose a close connection between the superconductivity and the pseudogap phenomena.

The next section is a small appendix to the discussion of the nature of the pseudogap where I model how to obtain the different spectra using various d-wave models.

5.3 How Many Gaps?

In our work presented in Chapter 4, we introduced a simple d-wave model where the density of states is fitted with two simple parameters, the gap maximum magnitude $\Delta$ and the lifetime broadening $\Gamma$ following the equation:

**Figure 5-11 - Local Conductance Spectra in Bi-2201** - In (a), each curve is the differential conductance spectrum taken at different locations of the sample. The data was obtained on the overdoped Bi-2201 sample ($T_c=15K$) at 6K. By keeping track of the spatial registry, the spectra at 16K at the same locations were obtained. In (b) is a plot of the conductance spectra taken at 16K on the same location as the spectra presented in (a). The arrows point out the remnant inner gap kink. The division leads to mostly uniform gap, even though the original spectra are quite different. These plotted were extracted from [Yi 07].
The integral over $\theta$ is averaging the momentum dependence of the d-wave gap which we write in its simplest form:

$$\Delta(\theta) = \Delta \cos 2\theta$$

This simple gap is capable of reproducing the spectra observed in the overdoped regime in Bi-2212 and the angle dependence of the gap measured by ARPES [Ding 96b]. The temperature evolution is captured with a steady reduction from of $\Delta$ and an increase of $\Gamma$ (Fig. 5-12). The model starts to fail in the underdoped regime, where additional parameters are required to describe all features in the the gaps measured and to capture the quasiparticle dispersion.

$$\rho(E,T) = \frac{1}{\pi} \int_0^\pi d\theta \text{Re} \left| \frac{E - i\Gamma(r,T)}{\sqrt{(E-i\Gamma)^2 - \Delta(\theta)^2}} \right|$$
In the underdoped regime, ARPES measurements found a change in the gap anisotropy from the simple d-wave model proposed above. For samples with less doping, the enhancement of the long-range interaction requires additional terms to be added to the gap angle dependence [Mesot 99]. To fit the ARPES data in the underdoped regime, Mesot et al. add the next harmonic that is compatible with the d-wave symmetry, resulting in:

\[
\Delta(\theta) = \Delta [B \cos 2\theta + (1 - B) \cos 6\theta]
\]

where B is determined from the data.

In Fig. 5-13(a), we plot different density of states curves for various values of B. We notice that the addition of the second harmonic does not change the position of the coherence peaks (still located at the gap maximum \(\Delta\)) but it modifies the low energy spectrum. The presence of a kink in the spectrum is only observed once B is low enough to generate extra nodes in the gap (Fig. 5-13(b)). The ARPES results do not display this extra node so we cannot describe the origin of the kink as arising from the second harmonic contribution. The second harmonic does add a new aspect to the doping dependence of the gaps near the nodes. The lower the value of B the lower the value of the gap near the nodes. So even if the antinodal gap is increasing with lower doping, the nodal gap may have the opposite behavior because of the increase of long range interactions due to the proximity to the insulating regime (Fig. 5-13(c)).

The quasiparticle interference patterns as visualized in STM were used to extract the value of the gap in momentum space for many different doping levels of Bi-2212 [Kohsaka 08]. The results are better fit with the addition of the second harmonic even for the overdoped samples. The extracted values of \(\Delta\) from the quasiparticle dispersion are in good agreement with the values of the average gap in the density of states spectrum derived from the coherence peaks in each sample. This implies that the dispersion of the excitations is linked to the large gap and not to the kink energy. At the lowest doping studied, with \(T_c = 20K\), the interference patterns disperse very little and require a low value of B.
Figure 5-13 - Single d-wave gap - Long range interactions requires the addition of the the second harmonic to the gap angle dependence, \( \Delta(\theta) = \Delta [B \cos 2\theta + (1-B) \cos 6\theta] \). In (a) we plot the resulting density of states originating from different values of \( B \), with \( \Delta = 30 \text{mV}, T=4\text{K}, \Gamma = 2\text{mV} \). The curves in (b) represent the resulting \( \Delta(\theta) \) for the same parameters used in (a). Notice that a low value in \( B \) results in the presence of an extra node in gap and a kink in the density of states. (c) shows the ARPES extracted \( \Delta(\theta) \) in underdoped Bi-2212 (\( T_c = 73\text{K} \)) and 2 fits, using different values for \( B \). In (d) the curves represent the \( \Delta(\theta) \) fits from the dispersion of the quasiparticles as measured in the STM conductance maps. Each curve represents a different doping of Bi-2212 ranging from overdoped (\( T_c = 83\text{K} \)) to heavily underdoped (\( T_c = 20\text{K} \)). The inset shows that the gap extracted from the quasiparticle fit and the average gap in the tunneling spectra are almost the same. (c) was extracted from [Masot 99] and (d) from [Kohsaka 08].
for the fit. This results in a $\Delta(\theta)$ curve that reaches zero before $\theta = 45$ (Fig. 5-13(d)). The data from photoemission does not present multiple nodes so it is likely that the gap value deviates from the fitting model near the nodes and it is very small (or non-existent).

The addition of the second harmonic is not capable of generating a good fit to the kinks observed in the tunneling spectra and it does not offer a good explanation for the formation of the Fermi arcs above $T_c$. A kink in the density of states spectrum points out to the presence of another “kink” in $\Delta(\theta)$. The simplest way to introduce a kink in $\Delta(\theta)$ is to have two different angle dependences. It is easy to show that two independent gaps leads to the appearance of a kink in the density of states spectrum. Around the nodes, I will model a simple $d$-wave gap $\Delta(\theta) = \Delta_1 \cos 2\theta$. Around the antinodes, I introduce $\Delta(\theta) = \Delta_2 [B \cos 2\theta + (1-B) \cos 6\theta]$, where $\Delta_1 < \Delta_2$. In the intermediate region, $\Delta(\theta)$ is determined by which ever gives the largest gap. For a low enough $B$, the

![Diagram of normalized DOS and gap vs. angle](image)

**Figure 5-14 - 2 Gaps and the Fermi Arc** - The presence of a kink in the density of states is better captured with the addition of a kink in $\Delta(\theta)$. In (a) the blue curve represents the density of states normalized by the normal state of a superconductor with 2 different gaps: $\Delta_1 = 20\text{mV}$ near the nodes and $\Delta_2 = 80\text{mV}$ everywhere else (Shown also in blue in (b)). The orange curves are the density of states spectrum and the angle dependence of gap using a model for the Fermi arc. The gap is $\Delta_1 = 0\text{mV}$ near the nodes and $\Delta_2 = 80\text{mV}$ everywhere else. The blue curve was calculated with $T=20\text{K}$ and the orange one with $T=60\text{K}$. 

82
two curves cross at a given \( \theta \) and we obtain a kink. One example of \( \Delta(\theta) \) is plotted in Fig. 5-14 with the respective density of states spectrum. We can model the temperature dependence of this gap into a Fermi arc state by bringing the nodal gap to zero. The resulting density of states preserves the same aspect at high energies but loses the kink at low energies. This model fits best the data we obtained in underdoped Bi-2212 and also in Bi-2201 and Na-CCOC.

Future work in our lab will concentrate to study very underdoped Bi-2212 samples to better understand the nature of the kink and the pseudogap state. Statistical measurements of the temperature evolution of the density of states spectra and the quasiparticle scattering are currently being performed. The amounting experimental results pointing out to the presence of two energy scales in the underdoped regime does not discount the strong evidences that these two energy scales are intimately connected. The use of microscopic spectroscopy tools are fundamental to untangle this puzzle.

5.4 Concluding Remarks

The inner gap kink is present in all dopings studied in Bi-2201. This kink is a strong evidence for the presence of two different energy scales. In contrast, our statistical measurements of the large gaps, defined by the position of the coherence peaks in the overdoped and optimally doped regimes, point out to a common origin between the gap found in Bi-2201 and Bi-2212. The gaps in Bi-2201 form inhomogeneously according to a similar local criterium, \( 2\Delta/k_B T_p = 7.6 \). The origin of the kink and the its connection to the main gap could hold the key to understand the physics of the pseudogap.
Chapter 6

Bosonic Coupling and the Origin of the Pairing Inhomogeneity

In this chapter I will address the microscopic origin of the pairing inhomogeneity and analyze the implications for the pairing mechanism. In conventional superconductors, the gap in the density of states is determined by the coupling between electrons and phonon modes. It has been proposed [Lee J 06, Balatsky 06] that the gap inhomogeneity is arising from variations in the energy of the phonon modes or in the coupling between the electrons and these bosonic modes. The strong coupling between electrons and bosonic modes generates deviations in the density of states from the BCS-like fit used in Chapter 4. We have analyzed the spectral features associated with a low energy bosonic coupling and determined that they are unlikely to cause the gap variations. In our measurements [Pasupathy 08], we have used our newly developed technique of lattice tracking spectroscopy to reveal the normal state properties, measured much above Tc, that is strongly correlated and possibly causing the spatial variations of the pairing gap. The results in this chapter were published in [Pasupathy 08].

6.1 Strong Coupling Pairing

The BCS theory describes the superconducting state as a condensate of electron pairs, Cooper pairs, that are held together by the attractive interaction through the lattice via phonons. The most direct evidence of this mechanism comes from tunneling experiments [McMillan 65] that provided a clear picture of
the underlying electron-phonon interactions, in agreement with the phonon spectrum measured by inelastic neutron scattering [Brockhouse 62].

The coupling between electrons and phonons can be characterized by the ratio between the superconducting transition temperature and the Debye temperature. The BCS theory as originally stated in the weak-coupling limit, explains in remarkable manner many of the physical properties of superconductors, relying only in a single parameter, the transition temperature $T_c$. While it applies very well to some materials, such as Al or Sn, other materials, such as Pb and Hg, present larger electron-phonon interaction and fall in the class of the strong-coupling superconductors. The strong-coupling superconductors deviate from the BCS predictions in various ways. For example, the ratio $2\Delta/k_B T_c = 3.53$ predicted by BCS is usually higher (4.3 for Pb [Giaever 62]) and so is the jump in the specific heat at the transition temperature [Neighbor 67]. The tunneling spectrum of these materials (Fig. 6-01) also show structures that deviate from the BCS dependence [Giaever 62] and in fact, it motivated the development of the theory that accounts for the details of the electron-phonon interactions in these materials. Notice that the crossover for the

---

**Figure 6-01 - Normalized Conductance in Lead** - The tunneling conductance ratio between the superconductor and normal states was obtained in a superconductor-insulator-normal metal junction (Pb-MgO-Mg). Beyond the gap edge there are clear divergencies from the BCS density of states, in the form of "bumps". The figure was extracted from [Giaever 62].
deviations in the conductance spectrum is comparable to the Debye energy (~9meV).

The role of the electron-phonon interaction in superconductors has been made clear by the work of Eliashberg [Eliashberg 60] and others (a good collection of review articles of the theory for strong-coupling superconductors can be found in [Parks 69]). The recent theoretical developments in the understanding of the phonon interactions in metals [Migdal 58] were extended to the case of superconductors to construct the equations for the electron self-energy, from which a number of physical properties can be determined. It was found that the effective interaction between electrons is local in space and retarded in time [Morel 62], in contrast to the instantaneous and nonlocal effective potential from the original BCS model. This powerful formalism also goes beyond the BCS quasiparticle description and it can also be applied to the case where the damping rate is comparable to the excitation energy. This is specially important for the case of strong-coupling superconductors where the lifetime of the quasiparticles with energy close to the Debye energy is very short.

Before we proceed to review the experimental results, it is useful to start with a simple example of what are the parameters present in the tunneling data, to obtain a rough but more intuitive physical picture of the effects from the electron-phonon coupling in the experiments. Consider a phonon mode with the density of states $F(\omega)$ given by a single peak at $\omega_0$ (Fig. 6-02a). At excitation energies $\omega$ less than $\omega_0$, the lattice will be driven at frequencies below its natural frequency so positive ions over-respond, creating a net attractive interaction between the electrons. For frequencies $\omega$ larger than $\omega_0$ the response will be out of phase and it creates a repulsive interaction. The solutions for the gap equations, following the Eliashberg theory, are plotted in (Fig. 6-02b). The real component of the gap $\Delta(\omega)$ measures the strength of the electron-electron interactions therefore it presents a resonance at $\omega_0$. The imaginary component of the gap has a peak at $\Delta_0 + \omega_0$ which originates from the damping caused by the emission of real phonon. The energy is offset by $\Delta_0$.
because the lowest energy level available for electrons is $\Delta_0$. From the obtained values of the complex $\Delta(\omega)$ one can extract an effective density of states as:

$$\frac{N(\omega)}{N(0)} = \text{Re} \left[ \frac{\omega}{\sqrt{\omega^2 - \Delta^2(\omega)}} \right]$$

In Fig. 6-02c, the resulting density of states is plotted for this single phonon model. Notice the sharp decrease at the energy, $\Delta_0 + \omega_0$. This sharp slope corresponds to a negative peak in the derivative of the density of states, or in tunneling measurements, a negative peak in the second derivative of the
Another important feature in the plot in Fig. 6-02c is that the total density of states dives below even the normal metal density of states (it dives below 1 in the normalized plot). This is result of having an imaginary component in the gap.

On the experimental side, improvements on the tunneling data [Rowell 63] and the determination of the phonon dispersion curves by neutron scattering [Brockhouse 62] brought out new details to the phonon coupling structure. Using the results above, Schrieffer et al. [Schrieffer 63] undertook a solution of the gap equation and were able to model the density of states with remarkable precision. They built an effective phonon density, modeled with simply two Lorentzian peaks, and used it to calculate the complex gap parameter $\Delta(\omega)$ (Fig. 6-03). The calculated effective density of states from this model is in very good agreement with the measured tunneling conductance ratio. Even though it

![Figure 6-03 - Conductance Ratio in Lead](image)

**Figure 6-03 - Conductance Ratio in Lead** - In (a) the gap function $\Delta(\omega)$ is obtained from a model with two lorentzian peaks representing the phonon modes present in Pb. The plot shows both the real ($\Delta_1$) and imaginary ($\Delta_2$) components of the gap. The plot in (b) compares the effective density of states calculated using the gap function displayed on (a) and the simple BCS density of states (short dash). The experimental data on lead of the conductance ratio is also plotted (long dash), displaying good agreement with the effective density of states. The figures were extracted from [Schrieffer 63] and the experimental data was originally published in [Rowell 63].
provides a good estimate of the phonon density of states, their method of
guessing a simplistic phonon structure is not able to extract all the details
contained in the tunneling data.

The next step to test the accuracy of the superconductor theory was
taken by McMillan and Rowell [McMillan 65] who were able to extract the
parameters entering the Eliashberg gap equation directly from the tunneling data
itself. These parameters are the phonon density of states times the average
square of the electron-phonon matrix elements ($\alpha^2 F$) and the coulomb pseudo-
potential ($\mu'$). With the aid of a computer, these parameters were adjusted until
the computed electronic density of states fitted the density of states measured
in the tunneling experiment in Pb (Fig. 6-04). Their fit added details never
measured before to the phonon density of states and is very close to the density

\[ \alpha^2 F(\omega) \]

Figure 6-04 - Phonon Coupling in Lead - Curve (a) is the derivative of the normalized conductance presented in (b). (b) was obtained by the ratio of the conductance in the superconducting state and the normal state in a Pb-I-Pb junction at 0.8K. Curve (c) is the extracted density of states for the phonons, $\alpha^2(\omega)F(\omega)$. Figure from [McMillan 65].
of states calculated from first principles. One can also identify the phonon energies through the plot of the second derivative of the current which provides a good estimate for the location of the phonon modes in Pb. The extracted parameters have been used to calculate other physical properties, which were not used in the fit, with good agreement.

In traditional superconductors, gap size is tightly connected to the energy of the phonon mode. In the weak coupling BCS limit, the gap at zero kelvin $\Delta_0$ is determined by the energy of the phonon mode $\omega_0$ and the pairing potential $N(0)V$, where $N(0)$ is the electronic density of states at the fermi energy, and it is given by [Tinkham 75]:

$$\Delta_0 = 2\hbar\omega_0 e^{-1/N(0)V}$$

Clearly a variation in phonon density of states could cause the gap size to vary. In this chapter, we will explore this possibility to understand if the spatial inhomogeneity observed in the gap in cuprates is originating from the variation of the phonon frequency. Other aspect that we need to account is whether, if the mode is homogenous, maybe the coupling between the mode and the electrons is changing locally. In a BCS-like approximation of the Eliashberg equations, one can obtain the same result by substituting $N(0)V = (\lambda - \mu^*)/(1+\lambda)$ [Carbotte 90], where $\mu^*$ is the coulomb pseudo potential and $\lambda$ is the electron-phonon coupling constant, that can be obtained from the phonon density of states $\alpha^2F$.

The study of series of similar superconducting metallic alloys have shown that even though the energy of the phonon mode was constant across the different alloys, the gap size and transition temperature would change, due to the variation in the coupling constant (Fig. 6-05b). As an effect of this variation, the phonon mode signature in tunneling conductance would enhance even though its position in energy would not vary (Fig. 6-05b). In Fig. 6-05c, the plot shows the deviations from the BCS density of states as function of the gap size.

To summarize, the magnitude of the superconducting gap is determined by both the phonon energy and the strength of the electron-phonon coupling.
Figure 6-05 - The Effect of the Change in the Bosonic Coupling - The set of curves in (a) present the normalized tunneling density of states divided by the BCS density of states. They show the deviation caused by the coupling of electrons to phonons. The different alloys present various different transition temperatures and gap sizes but the phonon mode is found almost at the same energy. (b) plots the phonon energy for each compound as function of the normal density of states at the fermi energy. The culprit for the different gap sizes and $T_c$ is not the energy of the phonon mode but how strongly the mode couples to the electrons in each system. As result, the deviations rms deviations from the BCS density of states follows a almost linear dependence with the gap size (c). All results from [Dynes 75].
The location in the spectrum of the mode signature is determined by the energy of the phonon mode, dislocated by the gap edge. The magnitude of the deviation from the BCS density of states is determined from the coupling between the electrons and the phonon mode.

6.2 Bosonic Modes in Cuprates

In high temperature superconductors, no boson mediating the electron pairing has been clearly identified. One of the difficulties that has been impeding the progress is the gap inhomogeneity that makes these materials hard to characterize. We have used our ability to track the atomic lattice to overcome this difficulty and obtain spectra that permit a quantitative analysis of one of the bosonic modes candidate to mediate pairing.

Various spectroscopic measurements have shown signatures of the coupling between the electrons and some bosonic mode (Fig. 6-06). Early tunneling measurement obtained in Bi-2212 with a SIN (superconductor-insulator-normal metal) junction revealed a dip in the differential conductance beyond the gap edge [Huang 89]. This feature is similar to the structure ascribed to the coupling to phonon modes in conventional superconductors. Later, the same feature was also observed in scanning tunneling spectroscopy (STS) [Renner 95] and superconductor-insulator-superconductor (SIS) junctions [Zasadzinski 01]. Photoemission measurements also display a similar “dip-hump” structure in the spectra [Shen 97, Norman 98a]. The energy range for both the tunneling and the photoemission signatures are very close. It was therefore argued that some form of strong coupling analogous to the conventional superconductor case described above is taking place [DeWilde 98]. The ARPES data also displayed a kink in the electronic momentum dispersion that has been associated with the change of the electron velocity arising from the coupling to phonon modes [Lanzara 01]. Strong evidences have associated this feature to phonon modes, such as the measurement of an isotope effect in the feature measured in tunneling [Lee J 06].
Figure 6-06 - Bosonic Coupling Features - The coupling between the electrons and a bosonic mode produces clear signatures in tunneling and photoemission spectra. In tunneling a “dip-hump” feature is seen beyond the gap edge in the spectrum [Zasadzinski 01]. In ARPES the same dip-hump structure is observed in the spectrum [Norman 98a] and a kink in the dispersion relation is also observed [Lanzara 01].
An alternative explanation identifies the bosonic mode as a spin-fluctuation mode [Eschrig 03] observed in inelastic neutron scattering experiments. At similar energies, neutron scattering reports a spin resonance excitation for various dopings and across different families of cuprates [Fong 96, Dai 99]. Other spectroscopic measurements such as optical conductivity also reveal that carriers are coupled to a bosonic mode, which also have been many times associated with the spin resonance [Carbotte 99]. Even with the enormous number of experiments performed, there is no unambiguous evidence on the nature of the bosonic modes or more importantly, whether they are responsible for the pairing.

The bosonic mode can only be correctly characterized if one obtains the measurement in both the superconducting and normal states. In cuprates this cannot be done with the aid of a magnetic field, like in traditional superconductors, because the field required would be too high (>50T). It is required to do a temperature evolution study. As mentioned before, we overcame the gap inhomogeneity difficulty by tracking the same atomic location, from deep within the superconducting state up to temperatures where the density of states presents no gap. This is better done in the overdoped regime where the gaps close a lower temperatures. This way we avoid the complications arising from the nature of pseudogap in the underdoped regime. The mechanism for the Cooper pair formation should be the same, independent of doping. For this study we used pristine overdoped Bi-2212 samples with \( T_c \) from 62K to 68K (OV65).

We measured the tunneling conductance spectrum for 13 different locations with gap sizes varying from 15mV to 32mV and we tracked these locations from 30K up to temperatures where the density of state is no longer gapped. We follow the same procedure done with classical superconductors and take the ratio between the low temperature superconducting data (30K) and the normal state gapless spectra. I reemphasize that this is done through measurements in a location-by-location basis and not through averages or estimations of the normal state. The resulting conductance ratio spectra can be
seen in Fig. 6-07. All spectra gaps follow a d-wave fit well. The biggest deviation is the “dip-hump” feature, associated with the bosonic coupling, observed beyond the edge of the gap.

The analysis of the energy of the bosonic mode cannot be obtained from directly from bias value as it requires to be referenced to the gap edge. In Fig. 6-08, we replot all 13 spectra referenced to their respective gap value. Surprisingly, it became impossible to distinguish which spectra has the larger gaps and which have the smaller ones. After referencing to the gap edge, the “dip-hump” features in all 13 spectra are identical within experimental errors, independent of gap magnitude. We observe that a change on either the coupling

Figure 6-07 - Normalized Conductance Spectra - We present the conductance ratio between the superconducting and the normal states, measured in 13 different location of the sample with gaps varying from 15V to 32mV. The dots represent the data and the solid line the d-wave fit. Our interest is concentrated at the “dip-hump” deviations from the fit found beyond the gap edge.
constant or the energy spectrum of the boson would cause a change in the “dip-hump” feature. If the boson presented an inhomogeneous mode, the feature would have to offset in energy. No correlation between the position of the feature and the gap sizes was observed. Also, if the coupling between the mode and the electrons was inhomogeneous than the magnitude of the feature would be varying. Again, no change was observed for different gap sizes. We have established that the gap inhomogeneity is not correlated to the bosonic feature, which is fairly uniform across the sample.

Our results are in direct conflict with the conclusions from another tunneling experiment performed by the Davis group in Cornell [Lee J 06]. They performed a statistical study correlating the gap maps with the maps of the

![Figure 6-08 - Uniform Bosonic Signature](image)

Figure 6-08 - Uniform Bosonic Signature - All 13 spectra present the same bosonic signature. After referencing to the gap edge, the energy dependence of each spectra is identical. The horizontal line clearly shows that the conductance ratio dips below 1, implying that the gap has an imaginary component at that energy. The deviation from the d-wave fit also presents no correlation with the gap magnitude. The inset shows the RMS deviation for both positive (red) and negative bias (blue).
peak in second derivative of the tunneling current measured beyond the gap edge. The measurement of the peak in the derivative of the conductance is motivated as a way to find the energy of the boson mode, using the same idea behind measurements presented in Fig. 6-04. In their results, after referencing to the gap edge, they found an anti-correlation between the gap size and the energy of the mode, which means that the larger gaps present a bosonic mode with lower energy than the smaller gaps. This is a surprising result because contradicts the prediction from the BCS theory.

We need to point out a few aspects of their analysis. First, the measurement of the positive peak in second derivative of the tunneling current, even though backed by a theoretical model [Balatsky 06], is quite different from the measurements in classical superconductors, where a negative peak in second derivative is identified with the position of the modes. Second, they did not normalize their data with the measurement of the normal state. The normal states in cuprates present a spatial inhomogeneity which could change the location of the second derivative peaks. Lastly, the presence of the pseudogap or the smaller lifetime in regions with larger gaps could certainly affect the measurements too. It is likely that the energy variations in the bosonic mode are originating from a systematic error in the method instead of physical causes.

All things considered, the measurements presented by Lee et al. [Lee J 06] can still teach us a lot and present strong evidence that the magnitude of the gap is not being controlled by the energy of the bosonic mode. The energy distribution of the mode presents no dependence with doping. For the five different dopings of Bi-2212 measured, from overdoped to underdoped samples, the gap averages are varying by a factor of two and the transition temperatures are varying significantly too but all samples presented the same energy distribution for the bosonic mode (Fig. 6-09a). This means that mode is not linked to the big changes that occurs in the gap magnitude and Tc due to doping. Also the lack of doping dependence is used by the authors as an argument that this mode is not the spin fluctuation resonance observed in neutron scattering (which does have a doping dependence) but instead it is a
Figure 6-09 - Evidence for the Phonon as the Boson - (a) presents the gap (Δ) distribution for five different dopings and the corresponding distribution for the energy of the bosonic feature in tunneling (Ω). Ω by the position of the peak of the second derivative of the tunneling current, measured from the gap edge. In (b), we can observe the effect of the isotope substitution from the O dopants in the sample. The thick lines are the spatially average differential conductance spectra in each sample and the slim lines their derivative. Notice that with the isotope substitution, the gap did not change (Tc also did not change) but a small change is observed in the bosonic feature, which indicates the connection between the mode and the lattice. (a) can be found in [Lee J. 06] and (b) can be found in [Slezak 07].
phonon mode.

Lee et al. [Lee J 06] also performed the measurement of the isotope effect in these materials. They substituted the O dopants from the O\textsuperscript{16} by O\textsuperscript{18} and observed the changes in the spectrum. The authors show that the change did not affect the gap size or the transition temperature of the sample but it did affect the bosonic feature in the spectra (Fig. 6-09b), which strengths their argument to identify the bosonic mode as a phonon. In further investigation, the authors specify the phonon as a vibrational mode consistent with the B1g buckling mode, but find no evidence that it plays a direct role in the pairing mechanism [Slezak 07].

Although the low energy bosons may not be the source of the variations in the gap magnitude, the boson structure does present evidence that it is strongly coupled to the superconducting excitations. Notice that the superconducting differential conductance “dips” below the normal state conductance (in the normalized spectra, this means that the ratio between the superconducting and normal states is lower than 1, as shown in Fig. 6-08). This implies that we need to introduce a complex component to the gap in order to fit correctly the feature, just like it was shown in for the classical superconductors. We estimate that the interaction with bosonic excitations within the range of 20mV to 120mV results in a substantial imaginary component for the gap, up to about 25mV at V=40mV.

6.3 Normal State Correlations

After discarding the bosonic coupling as the source of the variations in the magnitude of the pairing gap, we focus our attention the the normal state excitations and their correlations with the superconducting inhomogeneity. We realized that, during consecutive processes of warming up and cooling down the sample, the gaps always form with the same spatial configuration. We decided to search for some indication in the normal state of which areas will develop the larger gaps and which area will develop the smaller ones.
Figure 6-10 - Superconducting and Normal State Inhomogeneity - We compare the inhomogeneity found in the gap magnitude much below $T_c$ (65K) with the inhomogeneity found in the normal state, much above $T_c$. On top, on the left the spectra showing fully formed gaps present at all locations and on the right the gap map taken at 50K. While tracking the same exact area, we measured the gapless spectra (bottom left) present in all locations at 90K. Even though there are no gap, the inhomogeneity of the conductance is still present, and can be visualized by conductance maps, such as the one presented on the bottom right, taken at $V$=0mV (Fermi Energy).
We studied the overdoped sample at temperatures high enough such that the sample presents gapless spectra in every location. At 90K, the OV65 sample presents less than 1% of gapped regions. Even though the spectra are gapless, they still present a strong spatial inhomogeneity in the local density of states. The inhomogeneity in the local density of states can be mapped through the conductance maps taken at each voltages. The conductance map measured at V = 0mV (Fermi level) shows a strong spatial inhomogeneity (Fig 6-10). We can use our lattice tracking technique to compare this inhomogeneity with the one found in the superconducting state. Comparing the conductance maps at V = 0mV with the gap map measured at the same exact area, at low temperatures (50K), we notice a very similar spatial inhomogeneity, both maps presenting similar correlation lengths, 10–20Å. One can numerically determine how correlated two maps are by measuring the cross correlation between the maps, through:

$$\text{correlation} = \frac{\sum_{m,n}(A_{mn} - \bar{A})(B_{mn} - \bar{B})}{\sqrt{\sum_{m,n}(A_{mn} - \bar{A})^2 \sum_{m,n}(B_{mn} - \bar{B})^2}}$$

The cross correlation index between the conductance map and the gap maps is -0.75, showing that the maps are extremely anti-correlated. This means that the regions where the gaps are very large are originating from the regions of low conductance at V=0mV, while the regions with small gaps are originating from the regions with high conductance. This anti-correlation can be better visualized if we invert the color scale from one of the maps (Fig. 6-11).

The anti-correlation between the gap size and the density of states at the Fermi energy is quite unique. In the BCS theory, the higher density of states at the Fermi energy leads better superconductors with larger gaps. In cuprates, we
found that the higher density of states is linked to smaller gaps. The same pattern can be observed with the doping dependence of the gap magnitude. The more underdoped samples present less carriers and larger gaps. With the addition of dopants, and therefore adding more carriers, the average gap size in cuprates decreases.

We investigated the energy dependence of the normal state inhomogeneity and examined to what extend it correlates to the gap inhomogeneity. This can be done by measuring the conductance maps at different bias voltages (Fig. 6-12) at the same area. We found that even at high-energies, for both the positive and negative bias, the normal state is still inhomogeneous but the anti-correlation with the gap decreases with increasing energy. The conductance maps taken below 200mV present a significant

![Gapmap](image)

Figure 6-11 - Correlation between the gap map and normal state excitations - The strong similarity between the gap map and the map of normal state excitations at the Fermi level can be better seen if we invert the scale from one of the maps. The maps on the left are the same ones presented in Fig 6-10 but the color scale for the gap map was inverted. Numerically, the self-correlation of both maps present a similar behavior while the cross correlation has a high 75% index. The negative value implies that the larger gaps happen at areas of low conductance and vice versa. The plot on the right shows how the correlation changes by translating the maps by a certain distances (averaged over all directions)
Figure 6-12 - High Energy Excitations - The energy evolution of the normal state inhomogeneity is captured by the conductance maps measured at various bias voltages. We show maps taken at 0mV, -100mV, -200mV, -300mV with set point at V=1V and I=40pA. The color scale of each map is normalized by the spatial average conductance of the map. The cross correlation between maps taken at different dopings and the gap map is plotted. Notice that the correlation is maximum at the Fermi Energy. The asymmetric curve is result of the asymmetry in the spectrum and a set point condition with positive bias.
correlation the the gap maps. The variations found in maps taken at higher energies (>200mV) mostly reflect the structural variations found in topographic images.

We used the information contained in the gap maps combined with the spectra measured at 93K to obtain the average spectra that generates each gap value. We measured the conductance spectra at 93K for a 128 pixels square array in the sample. We use the information from the gap maps to determine the gap size that each spectra generates, then we selectively average the spectra from locations with the same gap size. The plot in Fig. 6-13 shows the average spectrum that generates each gap size displayed in the legend. We observe systematic variations in the spectra that anticipate the gap value in the superconducting states. In particular, there is a systematic change in the high energy “hump” structure responsible for the bias asymmetry. Similar changes in high energy features have been observed by McElroy et al. in the spectrum taken at low temperatures [McElroy 05]. We speculate whether this feature could be tied to remains from the Mott physics dominant in very low doping samples, as the asymmetry in the spectra have previously been associated to the strong local Coulomb repulsion [Anderson 06]. Recent calculations using a strong correlated electrons model presents a similar high energy hump structure that

Figure 6-13 - The High Energy Conductance Spectra - The spatially averaged conductance spectra are shown on the plot. We combine the information from the gap maps measured below Tc, with the gapless spectra measured much above Tc to find the normal state spectrum that generates each gap size. Each curve represents the spectrum measured at 93K, spatially averaged over regions that develop the same gap size.
correlates with the gap size [Haule 07]. Our experiment does not provide enough evidence to support a specific model, so more measurements at different dopings are necessary to determine the origin of this “hump” structure and its relation with the gap magnitude.

6.4 Concluding Remarks

We have determined the presence of a link between the excitations found in the normal state and the modulation found in the pairing gap. It is not possible to pinpoint a single source for the disorder found in these states, but

Figure 6-14 - The Origin of the Microscopic Disorder - The disorder in the electronic states may be arising from many different sources. The correlation between the variations of the gap and lattice disorder has been observed. In (a), the Slezak et al. [Slezak 08] have shown that the gap modulation traces the b-axis super-modulation of the lattice. The plot shows the value of \( \Delta \) as function of the position in the lattice (measured as function of the phase in the super-modulation). In (b), McElroy et al. [McElroy 05] have shown a correlation between the location of the O dopants and the regions which present larger gaps. The map is the conductance map taken at -960mV showing in bright spots the location of atomic O dopants. The inset shows the spectrum measured at the O locations, showing the -1V resonance and a large gap and a typical spectrum, off the O location.
various experiments have pointed out the structural effects [Slezak 08] and dopant disorder [McElroy 06] to the superconducting states (Fig. 6-14). It is clear that these sources of disorder affect both the normal and superconducting states but most importantly we need to establish why both states are so tightly correlated. Our results dismiss the importance of the bosonic modes as the source of the gap modulation and it establishes the electronic origin for the pairing inhomogeneity.
Chapter 7

Conclusion

The experimental results presented here have important consequences for our understanding of the electronic correlations responsible for the superconductivity and the pseudogap state in cuprates.

We have measured the pair formation in overdoped Bi-2212 that happens inhomogenously over a range of temperatures above $T_c$, following local simple criterion, $2\Delta/k_BT_p = 7.9 \pm 0.5$. Our observation of the insensitivity of the large ratio 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 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 reported here.

Our study of the underdoped regime on cuprates and the single copper oxide layer Bi-2201 have shown two different energy scales in the density of states spectrum, signaling the presence of another phenomenon besides pairing. Even though we have not been able to fully understand the nature of these features, our result provide relevant information on their energy and temperature dependence and demonstrate an important link between the two phenomena.

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 the 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. In contrast, we find that the high-energy (up to ~ 300 mV) 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.

We address the question of the underlying cause of the 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. Our measurements show that structural and chemical inhomogeneity affects both the excitations of the normal state and the superconducting gap. As is common to several correlated systems, many structural and electronic features can influence the onset and strength of collective phenomena. 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.
Appendix

Microscope Design and Operation

Scanning tunneling microscopy revolutionized our ability to probe surfaces and electronic properties at the atomic level. In an effort to study temperature dependent phenomena, many different designs of variable temperature microscopes have been developed. In this appendix, I will detail the design and performance of the variable temperature scanning tunneling microscope (VTSTM) used in this work. Our work was realized in two VTSTMs that combine variable temperature operation with the extreme stability found in fixed low temperature STMs. This makes this system ideal to study electronic phase transitions at the atomic scale.

A.1 Experimental Set Up

The Princeton Nano-Microscopy Laboratory is located in the basement of Jadwin Hall at Princeton University. The experimental area is situated in an isolated section of the building underlying solid foundation, helping to isolate from the floor vibrations. The electrical power for each microscope is independently backed up and isolated by an UPS system (commercially available by APC). Further power conditioning is provided by a Topaz Isolator (MGE). Each system also has an individual rod to earth, serving as ground to the instruments used (Fig. A-01). All the instruments, the electronics, the computer and the metal components of the system, such as the main chamber, are grounded to the rod ground and isolated from the standard building ground. Each VTSTM is enclosed in an individual acoustic room with eight-inch thick walls. There no special measure for shielding the electromagnetic radiation but
Figure A-01 - Princeton Nanoscale Microscopy Laboratory - The low noise conditions for the VTSTMs are obtained by individual acoustic enclosures and floating optical tables. Each system also has their own power back-up system (UPS) and power conditioning (Topaz Isolator) and rod to earth that serves as ground for the measurement equipment.
both the acoustic rooms and the VTSTM chamber are grounded to reduce the electromagnetic noise pick-up. The control room, containing most of the electronics and computer, is located just outside each room.

The cryostat (made by ARS) consists of a liquid helium dewar (Cryofab) connected through a flexible transfer line to the cold finger where the microscope is attached. The System runs on constant helium flow during operation. The temperature in the cold finger can be controlled by calibrating the helium flow and finely tuned with the help of a resistive heater. To maintain a constant flow, we maintain the dewar pressurized to 6 psi, through a relief valve. A simple set of valves allows us to refill the dewar while maintaining the 6 psi pressure and therefore, maintaining the constant liquid helium flow to the cryostat. This is an simple and yet fundamental requirement for the variable temperature experiments we performed. The ability to refill the dewar without any temperature drift makes possible to remain in same area of the sample for month long runs. The full dewar capacity (125l of liquid helium for one system and 150l for another) allows about 10 days of constant operation at 100K. At 20K this number is reduced to about 7 days. The system operates at any temperature down to 6K. Even though it is possible to run the systems with liquid nitrogen for temperatures above 77K, we found it to be very difficult to equilibrate the temperature due to erratic flow of the coolant. The liquid helium provide a much quieter flow and it has been used for all data taken in this thesis.

The microscope is home built but all controllers are commercially available. The temperature is tuned with the used of a resistive heater which is controlled by a temperature monitor with a simple PID loop (Lakeshore). The microscope controls are done with a commercial scanning probe controller system (RHK). The system provides the high voltage amplifiers and also the software to control all operations in the microscope. The tunneling current is amplified with a Femto Preamplifier with $5 \times 10^9$ V/A gain and 1kHz bandwidth. The Spectroscopic data was obtained with the aid of lock-in amplifiers. We have used both digital (Perkin-Elmer) and analog (PAR) lock-in amplifiers. All models used are capable of equivalent results with minor differences in the performance
and operation. All these instruments are located in the control room, outside the acoustic enclosure.

The ultra-high vacuum (UHV) chamber (custom made by MDC) is mounted on top of an optical table, with a vibration isolation system (TMC). The pneumatic table legs allows us to float the table while taking measurements. Also, all connections to the main chamber are made as flexible as possible to reduce the vibration coupling. We also have full control over the air flow ventilation to the rooms.

a. The Main Chamber

The microscope is inclosed in an UHV chamber (Fig. A-02). The vacuum in the main chamber is maintained by an ion pump (Physical Electronics) and can monitored by an ion gauge (Varian) and a residual gas analyzer. The pressure in the chamber is less than 1x10^{-10} Torr during measurements. The samples are inserted in the chamber through a load-lock chamber. The load-lock can be pumped down to 1x10^{-8} Torr through a turbo molecular pump (Pfeiffer Vacuum) before inserting the sample in the main chamber to reduce contamination. All sample manipulation inside the chamber is done through a wobble stick manipulator. Our design also allows us to perform both sample and tip exchanges with the wobble stick. Samples and tips can be stored in a carousel of shelves located inside the chamber.

Most sample studied are single crystals that are cleaved in the main chamber but for the preparation of metal surfaces, we have an e-beam heater and sputter system (Physical Electronics). To calibrate our tips we use metal crystals, usually Cu-111, that are cleaned before each measurement. To clean the metal surface we use Argon ion sputtering. To obtain a flat surface, the samples are annealed using the e-beam heater system. Successive cycles of sputtering and annealing improve the surface quality drastically.
Figure A-02 - VTSTM - The microscope is located at the center of the main chamber (center of the figure). On the left side, there is a loadlock that is used to insert samples in the main chamber. The vacuum in the main chamber is maintained by an Ion pump while in the loadlock we use a turbo pump. The ion gauges and mass spec (RGA) are used to monitor the vacuum. The cryostat is cooled by a constant flow of liquid Helium through a transfer line (not pictured). The frontal wobble stick allows for sample manipulation and tip exchange.
b. The Microscope

The microscope is located at the center of the main chamber inside a couple of OFHC copper radiation shields (Fig. A-03). The radiation shields are attached directly at the end of the cold finger cryostat. The radiation shields serve to keep the sample cold but also helps to improve the vacuum at the microscope area through cryo-pumping. Notice that the temperature variation of our system is done through changing the temperature of the entire ensemble of sample, microscope and shields. In many systems the heater is attached directly to the sample but we have the heater attached to the cold tip. During measurement the microscope temperature drift is less than 0.01K.

The scanner base is suspended inside the radiation shields by springs to provide vibration isolation from the cryostat. The springs are made with Inconel wire. For further vibration damping we use three Samarium-Cobalt magnets attached in a cross piece at the bottom of the microscope. The proximity of the magnets to the shield walls result in Eddy currents damping of the microscope motion. Molybdenum was used in the microscope base for being a good refractory metal. Also, its low thermal expansion coefficient and high thermal conductivity makes it a good choice for the base.

The scanner is based on the Besocke design [Besocke 87]. The design is a thermally compensated design consisting of 4 dimensionally identical piezo-electric tubes (made of pzt-8 by EBL), the scanner and 3 sample supporting legs (Fig. A-03). While imaging, the x-y scanning motion is performed by the scanner. The legs are used for a controlled offset and for the coarse approach. The motion of the tubes is controlled by applying appropriate voltages between the inside and outside of the piezo tubes. The tubes present 4 external gold-plated electrodes that allow independent x-y motion. Application of a differential voltage across two opposing quadrants produces a deflection of the tube along that axis, and the application of a voltage between the outer and inner electrodes produces an extension of the tube.
Figure A-03 - Microscope - The microscope is located at center of a UHV chamber. On the left, a carousel is used to store samples and tips. On the right, an e-beam heater and an ion gun are used to clean metal samples through cycles of sputtering and annealing. The microscope is enclosed in double shields of Cu that help to maintain a stable temperature and cryo-pump for better vacuum. The stage is suspended by inconel springs that provide vibration isolations. The magnets at the bottom of the stage provide extra damping through Eddy currents in the shields. The stage has one piezo tube at the center holding the tip and is responsible for the scanning the sample. The three peripheral tubes are used for approach and the coarse motion of the sample.
The scanner tube carries a tip socket where the tip is inserted. We have used W and Pt-Ir electric-chemically etched tips. The legs carry Tungsten carbide spheres that allow the sample motion and also allow the electrical contact for the sample bias voltage. Sapphire ring spacers provide the electrical isolation from the piezo voltages. Sapphire is used for electrical insulation whenever possible because it is both a great electrical insulator and good thermal conductor.

The sample are mounted at the center of sample holder (Fig. 3-04). The sample holder presents 3 helical ramps that are used for coarse motion. The sample approach motion is accomplished by rotating sample holder by repeated “toss and catch”. The piezo legs move in coordinated directions and at each step quickly slip to a lower point of the ramps. The approach steps are accomplished with sawtooth wave form voltage to legs in both x-y and z directions.

We have 2 different ramp designs. In one, the ramps form a channel that assures that the sample holder remain centered as it rotates. This centering design permits to approach samples as small as 1 mm of diameter. The second design uses flat ramps that permit the x-y motion. This way we can offset the sample holder to explore different regions of larger samples. Guard skirts are attached outside of the ramps to avoid the sample holder from falling off the

Figure A-04 - Sample Holder - The sample holder is composed of 3 helical ramps and a center cavity where the sample is mounted. The ramps allow the coarse approach motion and also coarse in-plane offset. All motion is done by 3 supporting piezo tube legs. The sample is mounted at the center of the holder with the aid of 3 holding clips and spacers that help to adjust to the correct height.
legs. The ramps are made of either Molybdenum (resistant to very high temperatures) or Titanium (easier to machine and clean).

The precise details of the construction of the VTSTM can be found in the thesis of our former group member Michael Vershinin [PhD thesis, University of Illinois at Urbana-Champaign 2004]. Design considerations can also be found at [Stipe 99].

A.2 Operation Procedure

The first stage of preparation before any STM measurement is to obtain a sharp and clean tip. One simple procedure to clean the tip is to field emit the tip onto a metal surface. We use our metal single crystals (typically Cu-111) to that end. We apply roughly 200~300V between the tip and the sample and bring the distance between the two such that the current is of the order of $10^{-5}$ A. This procedure removes possible oxides or debris remain from previous measurements from the apex of the tip. The motion of atoms at the end of the tip results in jumps in the current. The field emission procedure is carried out until the emission current is stable and does not present large jumps.

The tip quality is checked on the metal surface afterwards. We move to a new area of the sample (as the area where the field emission is performed is likely to be disordered and dirty) and we perform our usual tunneling scanning. By scanning the sample with a low voltage (10mV) and high current (200pA) we make sure that the tip is stable even when scanning close to the sample. If necessary, small change to the tip can be made by lightly “poking” the surface with the tip. We move the tip ~10 Å into the surface which allows the tip to change the apex atoms. Randomly we end up with a more stable tip ready for measurements. The measurements of the current versus the voltage and the current versus the z-position is used to identify that the tip is metallic and vacuum tunneling. The preparation procedure parameters are rather arbitrary but it lead to good success rate at establishing a good tunneling junction for measurements.
All measurements presented in this thesis were preformed with single crystal samples. The sample are cut to about 2mm square size and mounted with to the sample holder with the aid of a metallic epoxy. After mounted in the sample holder, we glue a post to the top of the sample. The post is used to cleave the sample, once the sample is in the main chamber. The cleaves are made after the tip is prepped. We knock off the post which cleaves the sample and exposes a flat clean surface. The quality of the surface is assured by visual observation only. Right after we cleave the sample, the holder is introduced into the microscope stage to cool down. The cooling process is around 18 hours to guarantee low thermal drift during the experiments. One of the weakness of our design is that the cooling is preformed only through the piezo legs which conduct heat poorly.

The next step after the cooling is the coarse approach. The approach is performed through a coordinated motion of the piezo legs. The tungsten carbide balls at the end of the legs is in contact with the sample holder ramps that are sloped 3°. The leg move in a “slip-stick” motion through the ramps in the sample holder. Each step moves the sample down about 100 Å. The approach is performed in two stages. We use the measurement of the capacitance in the tip line to approach within ~10 μm from the sample. This is done by comparing the sample capacitance to the value of the capacitance obtained when in range in the metal sample. Then we use a slow approach to reach the sample without ever touching the surface. For each step that is given we extend the tip to search for the sample. If the sample is not found, the tip is withdrawn and another step is taken. This is a very time consuming procedure but it is essential to study sample that present a delicate or non-metallic surface. While poking in Cu-111 can help to improve the tip quality, poking into the Bi-O surface of Bi-2212 has disastrous effects, forming an insulating tip. The slow approach is our only way to guarantee that the tip does not touch the surface during this coarse motion. Each step take roughly 8 seconds and the total approach can extend for many hours.
After the approach, still many times we are not able to obtain good measurements because of the difficulty to establish a quiet tunneling junction, either because of a change in the tip quality or because of problems with the surface quality. Any impurity in the surface could cause the tip to change. Also, because of the unfriendly and delicate Bi-O surface to recover the quality of the tip is very difficult and forces us to restart the experimental procedure cycle. Pulses to the tip bias has proven to be capable of changing the quality of the tip but the results are unpredictable, they could either improve or ruin your tunnel junction.

The procedure to change the temperature and keep the spatial registry of the sample is rather simple. We first scan a large area, roughly 2000 Å. Then we change the temperature slightly, by roughly 1K, and let the temperature stabilize again. The position drift in our microscope is roughly 200 Å after the change and it can occur at any direction. The fact that we are changing the temperature of the whole microscope and the match of the materials and the dimensions in the design help to minimize this thermal drift. With visual inspection, we locate our new position in the large scanned area and we can apply a constant voltage to the piezo legs to compensate the drift. We also need to correct the offset along the z-direction in the same manner. This first step allows us to predict the drift pattern allowing larger temperature changes. We repeat the procedure, now with large steps, typically 5~10K, predicting the drift direction and the adjusting the legs voltage. All tracking procedures are done through visual inspection and the offsets applied manually. The range of temperature that we can keep the spatial registry will be limited by the offset voltage that we can apply to the microscope. The range of our high voltage amplifier allows for ±450V to be applied at the piezo legs which provide us roughly ±1μm square offset.

The higher quality topographic scans and spectroscopic data are taken typically taken with V = -200mV and I = 40pA. While tracking the area, the set point used for scanning the surface are set to a minimum value to avoid tip changes during scan. Typical gap maps are taken over 300Å square with the
resolution of 128 pixels square. Conductance maps require measurements with a lower energy resolution than gap maps so they can be taken with a 256 pixel resolution. The time of each measurement is set by the cycle described in Fig. A-05. The modulation in the bias for the measurement of the differential conductance is about 2mV for the lower temperatures and 4mV for measurements around 100K. We use lock-in amplifier time constant at 20ms and the sensitive at 10mV. All setting are determined by equating the following factors: the energy resolution, the signal to noise ratio, the stability of the junction and the protection of the tip quality.

---

**Figure A-05 - Measurement Cycle** - A conductance map or a gap map are taken over a grid of locations where at each point we repeat the cycle plotted above. After arriving at each position we measure the conductance spectra by opening the feedback loop and measuring dI/dV using a lock-in technique. The voltages are ramped at 20V/s (4 and 8), and typically the largest delay is caused by the spec delay (5). The spec delay is determined by the lock-in time constant. A large time constant in the lock-in allows better average of the conductance and a more precise measurement. Typically we use 20ms as the time constant. To avoid the error arising from the lock-in averaging while the voltages are ramped, we have to introduce a delay of at least 80ms before we can record the conductance. As this delay has to repeated at each energy that we measure the spectrum, it constitutes the highest impact factor in the duration of our measurements.
While the plot of topographies, conductance maps and conductance spectra are straightforward from the raw data, the gap maps require a small amount of data processing analysis. To find the maximum in the conductance (which defines the gap magnitude), we use a polynomial interpolation to avoid errors caused by random noise. Each spectrum is individually interpolated using a polynomial up to the 10th degree. The maps determined from this fit and the maps obtained from the raw data are almost identical. The fit simply helps to avoid small spikes in the conductance which could wrongly trigger the location of the maximum in the conductance.

The fits of the conductance spectra to the d-wave model used a simple least squares fit procedure to find the best values of $\Delta$ and $\Gamma$. The fit is only applied in the inner gap energy range to avoid errors arising from the deviations that occur mostly beyond the gap edge.
Bibliography

[Onnes 11] Onnes. Communications from the Physical Laboratory of the University of Leiden (1911)


Curriculum Vitae

Education

University of Illinois at Urbana Champaign — Ph.D., 2008 (expected)
Pontifícia Universidade Católica do Rio de Janeiro - M.S., 2002
Pontifícia Universidade Católica do Rio de Janeiro - B.S., 2000

Experience

Visiting Student Research Collaborator, Princeton University, 2005-present
Research assistant, University of Illinois at Urbana-Champaign 2003-2005
Teaching Assistant, University of Illinois at Urbana-Champaign 2002-2003
Graduate Fellowship, CAPES - Pontifícia Universidade Católica, 2000-2002
Undergraduate Research Fellowship, CAPES - Pontifícia Universidade Católica, 1997-2002

Publications

[1] Gomes K. K., Pasupathy A. N., Pushp A., Ono S., Ando Y. & Yazdani A. Visualizing pair formation on the atomic scale in the high-Tc superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, Nature 447, 569 (2007).
Interaction in the High-Tc Superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, *Science* **320**, 196 (2008).


[5] Pasupathy A., Pushp A., Gomes K. K., Gu G., Ono S., Ando Y., Yazdani A. Gap Formation at a Lattice Site in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. SCES’07 conference proceedings. Accepted for publication in *Physica B* (Elsevier).

Talks and Presentations

May 2008 - Invited talk at RIKEN, Japan.

March 2008 - Invited talk at MICuO: Metal Insulator Transition in Cuprates workshop, Parma, Italy.

March 2008 - APS March Meeting.

August 2007 - Poster presentation at SNS: Spectroscopies in Novel Superconductors, Sendai, Japan.

March 2007 - APS March Meeting.

December 2006 - Seminar at CRIEPI, Tokyo Japan.

March 2006 - APS March Meeting.

March 2005 - APS March Meeting.