Scanning Tunneling Microscopy Studies of an Electron Doped High-$T_c$ Superconductor $Pr_{0.88}LaCe_{0.12}CuO_{4-x}$

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SCANNING TUNNELING MICROSCOPY STUDIES

OF

AN ELECTRON DOPED HIGH-T $\text{c}_1$ SUPERCONDUCTOR Pr$_{0.88}$LaCe$_{0.12}$CuO$_{4-\delta}$

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Abstract

It has been more than two decades since the first high temperature superconductor was discovered. In this time there has been tremendous progress in understanding these materials both theoretically and experimentally. Some important questions however remain to be answered; one of them is the temperature dependence of the superconducting gap which is in turn tied to question of the origin of the pseudogap and its connection with superconductivity.

In this thesis, we present detailed Scanning Tunneling Microscopy (STM) spectroscopic studies of an electron doped superconductor, Pr_{0.88}LaCe_{0.12}CuO_{4-\delta} (PLCCO). The electron doped compounds form an interesting venue for STM studies for many reasons. In the hole-doped
In the first part of the thesis, we investigate the effect of temperature on the superconducting gap of optimally doped PLCCO with $T_c = 24$K. STM spectroscopy data is analyzed to obtain the gap as a function of temperature from 5K to 35K. The gap is parameterized with a d-wave form and the STM spectra are fit at each temperature to extract the gap value. A plot of this gap value as a function of temperature shows clear deviations from what is expected from BCS theory. We find that similar to the hole-doped superconductors a fraction of the surface still shows a gap above $T_c$. The implications of our finding to the pseudogap phase are discussed.

In the second part of the thesis, STM spectra are analyzed to determine the effect of impurities or vacancies on the local density of states. Electron doped superconductors require a post-annealing process to induce superconductivity. It is claimed that Cu vacancies in the CuO$_2$ planes which suppress superconductivity are healed by this process. This implies that for the same doping, a
sample with higher $T_c$ should have fewer impurities compared to a sample with lower $T_c$. We studied two PLCCO samples with 12% Ce doping; one with higher $T_c$ (24K) and the other with lower $T_c$ (21K). Through quasiparticle scattering study we find that there are more impurities in 21K samples than 24K sample, consistent with the picture of Cu vacancies in as grown samples. Finally, we present a discussion of the bosonic modes observed in the STM spectra and their connection to the spin excitations measured by neutron scattering.
DEDICATED TO MY LATE FATHER

WHO MADE THIS POSSIBLE

AND

TO MY SON WHO WILL CONTINUE THIS TRADITION OF LEARNING.
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Chapter 1

Introduction

This chapter provides an introduction to the basic properties and facts about conventional superconductors, followed by a discussion about hole-doped high-T_c cuprates and our current understanding about them. This chapter forms the background for chapter 2, which has a basic introduction to PLCCO, the primary material being investigated in this thesis.

1.1 Conventional Superconductors

In 1911, Kamerlingh Onnes was looking for the best residual resistivity [1], \( \rho_0 \) of Hg metal by purifying it through multiple distillations. However, to his great surprise he ended up finding that the resistivity drops down to zero at 4.15K. This was a completely new physical phenomenon at the time and he named it as superconductivity. The temperature at which metal enters into the superconducting phase is called transition temperature (T_c).

1.1.1 Conditions for Superconductivity

A material is considered to be a superconductor if it exhibits two distinctive properties:

a) No resistivity [2]

\[ \rho = 0, \text{ for all } T < T_c \]
Zero resistivity i.e., infinite conductivity, is observed in a superconductor at all temperatures below a critical temperature, known as the superconducting transition temperature $T_c$. Metallic resistivity is temperature dependent which increases with temperature because of the scattering with lattice vibrations. The residual resistivity, $\rho_0$ is defined as the resistivity to which the sample resistivity “tends” if the temperature approaches absolute zero. Residual resistivity depends on the degree of perfection and composition of the sample. The sharp drop of resistivity is shown in figure 1.2 (a).

![Graph showing variation of metallic resistivity with temperature](image)

Figure 1.1: variation of metallic resistivity with temperature

*Zero resistivity was the first hallmark of superconductivity.*

b) **No magnetic induction**

$B = 0$ inside the superconductor
Until 1933 superconductivity had been thought of as merely a disappearance of electric resistance. In 1933 two German physicists, Walter Mesissner and Robert Ochsenfeld discovered a surprisingly new phenomenon in superconducting phase: superconductors screen out applied magnetic field.

*Repulsion of magnetic field is the second hallmark of superconductivity.*

Hence, to test for superconductivity one has to make sure that the resistance vanishes and a magnetic field is forced out. Following the discovery of superconductivity in Hg many other metals or metallic alloys were found superconducting at different transition temperatures and their properties were studied with different experimental techniques. Great attempts were made to understand this strange phenomenon theoretically.
1. 1. 2 Theoretical Description

For decades after the discovery of superconductivity theorists struggled to find the microscopic origin of a superconductivity. The London theory [3] (1935) and Ginsburg–Landau theory (1950) can be considered milestones in this field. However, a universally accepted microscopic theory was given by Bardeen, Cooper and Schifer in 1957, a whole 46 years after Kamarlingh Onne’s discovery.

Bardeen Cooper Schrieffer (BCS) theory

The origin of superconductivity remained mystery until 1957 when Bardeen, Cooper and Schrieffer successfully explained the phenomenon microscopically. This theory is popularly known as the BCS theory of superconductivity, named after the first letter of their last names.

The basic idea of this theory is that two electrons (fermions), that have natural tendency to repel each other, feel an attractive force towards each other (mediated by phonons for example) and form a pair known as a cooper pair [4]. Unlike electrons, which are fermions, these cooper pairs are Bosons and they condense into a single coherent ground state, which allows the electrons to move cooperatively through the crystal without losing their forward momentum.

In BCS theory, the attractive force between two electrons on opposite sides of the Fermi surface, no matter how small, leads to a bound state for those electrons. By constructing a
wavefunction of the correct combination of these pairs they could stabilize a state with the gap in the density of states.

They proposed a trial, ground state wavefunction of the form

$$\mid BCS \rangle = \prod_{k} (u_{k}^{r} + v_{k}^{r}c_{k}^{*}\overline{c}_{-k}^{*}) |0\rangle$$

where $u_{k}$ and $v_{k}$ are the variational parameters, $c_{k}^{*}$ is the creation operator for an electron of momentum $k$ and spin $\uparrow$ and $|0\rangle$ is the vacuum state. In order for this state to be normalized the condition $|u_{k}^{2}| + |v_{k}^{2}| = 1$ is needed. By minimizing this ground state energy using this wavefunction it was found that
\[ |u_k|^2 = \frac{1}{2} \left( 1 + \frac{\varepsilon_k}{E_k} \right) \quad \text{and} \quad |v_k|^2 = \frac{1}{2} \left( 1 - \frac{\varepsilon_k}{E_k} \right) \]

\[ |E_k|^2 = |\varepsilon_k|^2 + |\Delta|^2 \]

where \( \varepsilon_k \) is the electron dispersion above the transition, \( \Delta \) is the size of the gap that opens to single particle excitations, and \( E_k \) is the quasiparticle dispersion below the transition temperature.

**The major points of the theory are as follows:**

- The Fermi surface becomes unstable against the infinitesimal attractive force which is caused by bosonic interactions. Therefore, the total energy of the system can be reduced by allowing electrons to get paired up, which causes an increase in kinetic energy but much larger decrease in potential energy [5].
- The paired electrons have equal and opposite spin and momenta.

### 1.1.3 Some key experiments that lead to BCS theory

**Specific heat measurement**

As the temperature increases below the transition temperature, the specific heat increases exponentially. This implies that the thermal energy is being used to bridge some kind of gap in the energy [6]. As the temperature increases there is an exponentially increase of
particles which would have enough energy to cross the gap. This experiment further emphasizes the existence of a coherent gap for single particle excitations. The gap was later confirmed by electromagnetic absorption in metals like aluminum and lead [7, 8].

Isotope effect

This experiment reveals that the superconducting transition temperature depends on the isotopic mass [9, 10] by $T_c \propto \sqrt{1/M}$; where M is the mass of the nucleus; indicating the involvement of lattice vibrations i.e. phonons in pairing.

Key achievements of BCS theory

1) Superconducting gap: BCS theory explains the gap in the quasiparticle density of states and gives and expression for how the gap grows with the strength of the attractive interaction. Furthermore, it describes how the density of states changes on entering the superconducting states, where there are no electronic states in the Fermi surface. The energy gap is most directly observed in tunneling experiments and the microwave reflection measurements.

2) BCS theory predicts the dependence of energy gap $\Delta$.

$$\Delta(T) = 3.2 K_B T_c \sqrt{1 - \left( \frac{T}{T_c} \right)}$$

3) The ratio of the specific heat at $T_c$ and just above $T_c$ is given by a universal constant 2.5.

4) $2\Delta / K_B T_c = 3.5$
5) It matches the experimental result of isotope effect.
6) It correctly predicts the Meissner effect.
7) It predicts the variation of the superconducting gap with the external magnetic field.
8) It can also predict the transition temperature in terms of electron phonon coupling potential and Debye cut off.

From 1901 to 1986 great progress was made in understanding superconductivity. The subject was extensively explored both experimentally as well as theoretically. However, there was sluggish progress in increasing the transition temperature $T_c$, which is important from the application point of view. The maximum $T_c$ reported till 1986 was 23K for Nb$_3$Ge [11]. The $T_c$ graph versus the time is shown in figure 1.4.

![Figure 1.4: Superconducting $T_c$ versus the year of discovery of conventional superconductors.](image)
Though the superconductivity has been widely used for different applications such as MRI, its cost has been high because of the low transition temperature. It has to be cooled down by liquid helium which is quite expensive. After decades of long hard work and extensive studies, the transition temperature couldn’t exceed 23K. Additionally BCS theory didn’t provide any clues to increase the transition temperature significantly. So, everybody thought the mystery that was started in Onne’s lab in 1911 came to the dead end. However, a new superconducting mystery had yet to come.

1.2 High Tc Superconductors

Three decades after BCS theory, a completely new family of superconducting materials was discovered. These materials are very complex multilayered ceramics but all of them consist of CuO2 planes. This is the reason they are known as cuprates. These materials have relatively high Tc s compared to conventional superconductors and are therefore called high-Tc cuprate superconductors. Until 2008 when the new iron-arsenic based superconductors came into the picture, the word high Tc superconductor was used mainly for cuprate superconductors. The cuprates are quite different from conventional metallic superconductors and are sometimes referred to as unconventional superconductors.

Historical Background

In 1986, Johannes Brdronz and Karl Muller, working at IBM Switzerland discovered a new material LaBaCuO [12] (LBCO) with Tc up to 30K, for which they were awarded a Noble prize in 1987. At first they were not sure about their discovery that’s why the title
of their paper was “Possible high $T_c$ superconductivity in the Ba-La-Cu-O system.” The major reason for their doubt was the material itself. No oxide had been previously found superconducting.

![Superconducting $T_c$ vs. Discovery Year](image)

Figure 1.5: Superconducting $T_c$ versus the year of discovery diagram right from the beginning 1991 to till today

This remarkable discovery stimulated material scientists all over the world and they started to cook ceramics in their lab. Within a year, YBa$_2$CuO$_4$ (YBCO) [13] with $T_c$ 90K was discovered which crossed the liquid nitrogen temperature 77K. Soon after this, Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (BSCCO) [14], the highly studied high $T_c$ superconductor was discovered and $T_c$ was extended up to 135K.
Unlike conventional superconductors, that are mostly metals or metallic alloys, the parent compounds of high-Tc cuprates are Mott insulators. Mott insulators are special type of insulators in which carriers in the uppermost occupied band feel strong Coulomb interaction from the neighboring electrons and get localized. These materials become superconducting when the localized electrons are given flowing path by doping with holes or electrons. We first discuss the hole doped cuprates briefly here because the electron doped cuprates being the principle material under investigation in this thesis, will be discussed thoroughly in other chapters.

1.2.1 Hole-doped Cuprate Superconductors

LBCO, the first discovered high-T_c cuprate is a hole-doped cuprate superconductor. These are the most studied family of cuprate superconductors. They have the highest T_c reported so far and they make the largest superconducting family. They have a very rich phase diagram. Based on doping and temperature they can undergo transition from antiferromagnetic mott insulator to the superconducting phase, pseudogap phase, Fermi liquid phase, strange metal phase, non-fermi liquid phase etc. These materials undergo a superconducting transition below the transition temperature (T_c) if 3 to 33% holes are doped. Holes can be doped with two ways: 1) by replacing some of the tetravalent atoms in the charge reservoir with trivalent atoms, 2) by adding some extra oxygen. This phase is shown as a red dome in the phase diagram in the figure 1.5(b).

Extra holes break the deadlock of localized electrons in the Cu sites of CuO_2 planes and
provide a channel for electrons to flow. Enough hole doping turns the material from Mott insulator to conductor and finally superconductor with exotic other phases shown in the phase diagram.

**Few facts about high \( T_c \) superconductors**

- High \( T_c \) cuprates have very complicated unit cell. However, the unit cell can be divided into two parts: the charge reservoir and the CuO\(_2\) planes. Though the charge reservoir may differ all cuprates consist of CuO\(_2\) planes. These CuO\(_2\) planes are the source of superconductivity. It has been found that the higher the number of CuO\(_2\) planes higher the transition temperature.

![Figure 1.6 (a) The first discovered high Tc superconductor LBCO. (b) Phase diagram of the hole doped high Tc cuprates.](image)
- It is generally agreed that electrons are paired. It was shown unambiguously by measurement of $\hbar/2e$ flux quanta [15], which indicates that the charge carriers have charge $2e$. Though the super current in these materials is also caused by paired electrons, but it is not clear so far what causes these electrons to get paired up. If the pairing mediator is a phonon, there is the question: which phonon? The unit cell is very complicated; these materials are composed of more than the four elements and the atoms of all these elements and their vibration is extremely complicated. Another fact is that in these materials there could be another source of mediator i.e. magnetism. This will be discussed in greater detail in Chapter 6.

- Though their $T_c$ is higher, these superconductors have shorter coherence lengths compared to conventional superconductors. In other words they are “dirtier” than the conventional superconductors. Since the superconductivity arises in the CuO$_2$ plane the coherence length is higher in the plane but an order of magnitude smaller in the direction perpendicular to the plane. So, we can consider them quasi-2D superconductors.

- Unlike conventional superconductors which have symmetric s-wave pairing, the order parameter of these materials has d-wave pairing. Due to this reason there exist quasiparticles well inside the maximum superconducting gap energy. This was shown by flux modulation measurements in a YBCO DC-SQUID [16] and then more unambiguously by flux quantization in a tri-crystal YBCO junction [17]. In simple terms, this $d$-wave gap means that electrons traveling different directions in the crystal feel a
different pairing potential.

1.2.2 Theory of High Tc superconductors

High Tc superconductors are highly sophisticated for BCS theory. It has no explanation for very strange phases present in these materials such as the pseudo gap. There are many proposed theories of high-Tc superconductor but none of them seem to be complete and sufficient. Some of the popular theories are listed below:

1. Resonating valance bond (RVB) state by Anderson (1987)[18]
2. Staggered flux phase (SFP) by Affleck and Marston (1988) [19, 20, 21]; later work relating to SFP as a “spin gap” phase by Wen et al. (1996) [22]; and SFP in vortices by Kishine et al. (2001) [23]
4. Multiple “stripe” and “checkers” phases of various periodicities by L’ow et al. (1994) [28]
5. SO(5) theory by S.-C. Zhang (1997) [29]
6. Spin density wave (SDW) by Vojta and Sachdev (1999) [30]; coexisting SDW + superconductivity by Demler et al. (2001) [31]
8. d-density wave (DDW) phase by Chakravarty et al. (2001) [33]
9. Fractionalized nodal liquid (superconductivity without pairing) by Senthil et al. (2001) [34]
10. QED3 phase by Franz et al. (2002) [35]

1.3 Summary

We started this chapter with conventional superconductors and ended with hole-doped high-$T_c$ superconductors. However, we haven’t mentioned that there is another type of high-$T_c$ cuprate superconductor as well i.e. an electron doped cuprate superconductor. From next chapter we will be discussing PLCCO, an electron doped cuprate, which is the principle material of investigation in this thesis.
References


Chapter 2

Electron Doped high-$T_c$ superconductors

The copper oxide plane of the cuprates, where the high-$T_c$ superconductivity is believed to occur, can be doped either by holes or by electrons. Though most of the work has been focused on the hole-doped materials, the understanding of their electron doped counterpart is essential to obtaining a universal picture of the high $T_c$ superconductors. In addition to possessing interesting physics in their own right, the $n$-type materials, with their different normal state properties and phase diagram, offer an alternative venue to test various theories of high-$T_c$ superconductivity. One such material is Pr$_{0.88}$LaCe$_{0.12}$CuO$_{4-\delta}$ (PLCCO), which is the subject of investigation in this thesis.

This chapter will discuss the following major points:

1. Introduction of an electron doped superconductors.
2. Doping and superconductivity.
3. Why the phase diagram is different from its hole-doped counterpart

2.1 Structure of electron doped cuprates:

The new superconductors are Ce$^{4+}$ doped compounds with the formula R$_{2-x}$Ce$_x$CuO$_4$, where R stands for one of the Lanthanides Pr, Nd, Sm, La and so on. R$_{2-x}$Ce$_x$CuO$_4$ will be
referenced as RCCO for the sake of simplicity. The compound has R$_2$CuO$_4$ (T'-phase) structure where R which is composed of sheet of Cu-O squares [1,2]. Unlike T-phase structure with Cu-O octahedra as observed in La$_{2-x}$Sr$_x$CuO$_4$, this structure has no apical oxygen figure (2.1) [3].

![Diagram](image)

Figure 2.1 (a) unit cell of an electron doped cuprate NCCO. (b) unit cell of a hole doped cuprate LSCO. The Cu-O in NCCO makes T'-structure, a rectangular shape shown with green sheet where as Cu-O in LSCO makes a octahedra shown in green.

Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ (NCCO) is one example of an electron doped high $T_c$ superconductor that precedes PLCCO and it has been a poster child of the electron doped superconductors for a long time. However, in this research the material under investigation is PLCCO. Therefore this analysis will focus on PLCCO. PLCCO has the
same structure as NCCO, except NCCO has (Nd,Ce)$_2$O$_3$ [4] as an impurity phase which is magnetic, whereas PLCCO has (Pr,La,Ce)$_2$O$_3$ as a non magnetic impurity phase. This is one of the great advantages of PLCCO over NCCO for studies that go through magnetic probes. However it doesn’t make big difference with respect to the issues being studied here. [5]

As shown in the figure box 2.3 (b), adding 12% tetravalent Ce in PLCO produces ~10$^{20}$ carriers/cm$^3$. Why are the extra electrons necessary? What do these extra electrons do to the material to induce superconductivity? The real answer of these questions lies in the understanding of the Mott insulator and superconductivity.

![Figure 2.2](image)

Figure 2.2 (a) Unit cell of PLCO, an undoped parent compound of superconductor (b) Calculation of its electronic configuration and showed that the compound has no extra mobile electrons.
2. 2 Mott insulators

The traditional theory of metals would predict that the CuO$_2$ plane in the parent compound PLCO would have a half filled band at the Fermi energy. With one hole per unit cell it would be considered metallic. However, it is a special insulator known as Mott insulator. In Mott insulators the insulation is caused by a strong on-site correlation energy that discourages double occupation, are frequently described by the single-band Hubbard Hamiltonian:

$$H = \sum_{ij} t_{ij} c_j^\dagger c_i + \sum_i U n_{\uparrow i} n_{\downarrow i}$$

Here, the first term of the equation is exchange interaction between neighboring sites and the second term is coulomb interaction. If $U \gg t$; the single band is split into two, the so-called upper and lower Hubbard bands that are respectively empty and completely full at half-filling. Hence the strong coulomb repulsion opens a band gap and confines the electrons (one electron per unit cells) in the lower Hubbard band forming an insulator. The system lowers the total energy of this configuration by forcing neighboring sites to have anti-aligned spins. Hence, Mott insulators are characterized by a strong Anti-ferromagnetic exchange in CuO$_2$ plane and static long range AF order as shown in figure 2.4 (a). By doping PLCO with Ce we are adding electrons into the CuO$_2$ planes. The addition of small amount of electrons suppresses the static AF order and introduces itinerant states at the Fermi level. Doping suppresses the ordering much more quickly than would be expected from a simple dilution of the spin lattice.
Anti-ferromagnetic ordering in the undoped compounds is well understood theoretically, however, we have a poor understanding of the relationship between short range (10-100 Å) in-plane antiferromagnetic correlations which survive the suppression of global Anti-ferromagnetic order and these electronic states.

2.3 Doping and superconductivity

To understand the relationship between doping and superconductivity it is necessary to know how superconductivity occurs in conventional superconductors. In conventional superconductors at temperature below $T_c$, lattice vibrations create an attractive potential...
for the Fermi surface electrons of opposite spins and momenta and they get paired up. Having integer spin, the pair behaves like a boson. Many such bosons condensate into a single energy state which is inaccessible to the scatterers and flow without any resistance. So, for superconductivity, in the microscopic level we have two pre-requisites: firstly a Fermi surface electrons i.e. mobile electrons; and secondly a suitable mediator to pair up the electrons.

![Figure 2.4](image)

Figure 2.4 (a) Schematic diagram of CuO₂ plane with half filled band forming an antiferromagnetic Mott insulator. (b) Doping destroys the antiferromagnetic order and allows the electron hopping.

For a material to be superconductor, it must also be a conductor. Therefore, doping creates mobile electrons and hence fulfills one of the two conditions for superconductivity. Now there are mobile electrons in the sample and if right mediator to pair these electrons up is present, superconductivity can be attained. However, in the case of electron doped cuprates mere doping is not sufficient.
2.4 Post Annealing

For the hole doped cuprates low doping levels (about 5%) entirely suppress Anti-ferromagnetic order and superconductivity appears over a wide range of whole concentration (6% to 30%). However, in case of electron doped cuprates doping alone is insufficient. In these materials superconductivity (maximum $T_c = 27\text{K}$) is achieved only when samples within a narrow dopant range (10% to 18%) are annealed in a oxygen reducing atmosphere.

This means that the phase diagram of electron-doped copper oxides is three dimensional as a function of both Ce and oxygen concentration Fig. 2.6. There are, therefore, two distinct ways to traverse the phase diagram of PLCCO: samples can be prepared at a fixed annealing condition but grown with variable Ce doping levels [6] or, alternatively, samples can be grown with a fixed Ce concentration but with variable annealing treatment [7, 8, 9].

The samples under investigation in this thesis is $\text{Pr}_{0.88}\text{LaCe}_{0.12}\text{CuO}_4\delta$ single crystal which was grown by using the travelling solvent floating zone technique and annealed it to obtain optimal superconductivity with $T_c = 24\text{ K}$ [10] and 21 K. The as grown compound for both of these samples is same but their different $T_c$ is the result of different post annealing process.
Two major consequences of post annealing

The post annealing process makes these compounds superconducting but it creates the patches of some impurity phases. The quantity of these impurity phases increase with $T_c$. In addition to the formation of impurity phases it is noticed that the oxygen content in the compound gets reduced. There are many theories and claims regarding the post annealing process. This analysis presents the one that appears to be the most convincing.

A small amount (~1%) of Cu vacancies was reported in as grown NCCO [11, 12] and PLCCO possibly as a result of the evaporation of some Cu atoms during the high...
temperature synthesis process. These Cu deficiencies act like non magnetic impurities in the CuO₂ plane and scatter off the electrons so that no pair formation could take place (a more detail study of these impurities is provided in Chapter 5). If these vacancies can be repaired such that the samples have intact CuO₂ planes, the electron-doped superconductors should be equivalent to the hole-doped ones.

Figure 2.6 (a) Schematic diagram of doped PLCCO, with Cu deficiency. (b) Repaired CuO₂ planes (top and bottom) with impurity phase in the middle (Ref. 13).

During the annealing, some of oxygen atoms will be evaporated. To understand the process examine figure 2.6. Figure 2.6 (a) shows many Cu defects in the crystal but the neighboring oxygen atoms of the defect are bound to one side only. During the repairing process, the R atoms and Cu atoms get displaced from their original position until they have the position as shown in figure 2.6 (b). To come to the position of figure 2.6 (b) some oxygen atoms needs to be removed and the impurity phase appears between the repaired CuO₂ planes. The non-defective CuO₂ planes are pre-requisite for the
superconductivity in the cuprates. The annealing process fixes the CuO$_2$ plane and makes the sample equivalent to the hole doped cuprates. [13]

The Cu deficiency in as-grown electron-doped materials provides a natural explanation of its electronic properties, effectively weakening the electron-doping effect of Ce by increasing number of oxygen atoms and therefore adding holes per Cu atom. In this model, the annealing process diminishes any Cu deficiency and therefore promotes the electron-doping effect of Ce, which also suppresses the AF Néel temperature ($T_N$).

Differences in the phase diagrams [1, 2] and the electronic properties [14, 15] of the electron- and hole-doped cuprate superconductors have been obscured by the ‘materials issue’ surrounding the annealing process in the electron-doped samples. The microscopic oxygen-reduction process presented here removes much of the mystery and will need to be taken into account to resolve any intrinsic differences between electron- and hole-doped superconductivity.
References


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Chapter 3

Experimental Techniques

This chapter introduces the use of the scanning tunneling microscope, the principle instrument employed in this research and its application on PLCCO. It also includes a brief explanation of the Angle Resolved Photo Emission Spectroscopy (ARPES) and Neutron Scattering, two other experimental techniques widely used to study the high $T_c$ cuprates.

3.1 Scanning Tunneling Microscopy (STM)

The scanning tunneling microscope was invented by Binning and Rohrer\(^1\) in 1982 and implemented by Binning, Rohrer, Gerber, and Weibel. It is an instrument in which a sharp conducting wire (tip), attached to the piezoelectric drive, is brought close enough to a flat surface (sample) so that the electrons can tunnel between them. When the bias voltage ($V$) is applied between the wire and the surface, there will be a current known as tunneling current ($I$). This current can be measured as a function of ($x$, $y$) and as a function of $V$. The schematic diagram is shown in fig 3.1.

3.1.1 STM Components

i. Samples

A sample is the material to be studied or under investigation. The sample under
Investigation in this thesis is an electron doped high-T\textsubscript{c} superconductor PLCCO. STM being a surface sensitive probe, sample preparation is very crucial. There are two important components of the good sample. 1) sample surface must be kept ultra clean; 2) sample surface should be flat. To get an ultra clean sample it is cleaved inside the ultra high vacuum ($10^{-9}$ torr) and immediately take down to the 5K. Even though the cleaved surface looks rough, there exist microscopic atomically flat surfaces good enough for investigation.

Figure 3.1 (a) Schematic diagram of STM with major components. (b) Schematic diagram of STM with electronic control and display.
Figure 3.2: (a) optical image of typical cleaved PLCCO. (b) Magnified portion. (c) 10 μm sq SEM image shows that even though the patches looks rough with eye, there are enough flat surfaces in microscopic level.

ii. Tip

It is a sharp conducting wire usually made up of Tungsten or Platinium Iridium or Platinum Rhodium. All the data reported in this dissertation is taken by Platinium Iridium tip. For atomic resolution, the tip should also be atomically sharp. Since the atomic surface in PLCCO couldn’t be observed, the tip was tested on Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (BSCCO). Once the atomic resolution and typical d-wave superconducting spectra are seen in BSCCO surface, the BSCCO is replaced with PLCCO.

iii. Piezoelectric walker

The piezoelectric walker in our STM has six piezo stacks which acts like six legs to take tip forward to the tunneling range and to bring it back from the tunneling range.
iv. Scanner

Scanner piezo in this STM is a tube which is electronically divided into four sections outside which are responsible for xy motion and an undivided part inside which takes care of the z motion.

v. Electronics

Current Amplifier: The tunnel current measured in STM is very small, typically from 10 pA to 1 nA. Current this small is hard manipulate without the addition of noise. Hence, the tunneling current is amplified by a current amplifier and is converted in to a voltage. The performance of the current amplifier, to a great extent, influences the performance of STM. Performance of amplifier is influenced by electronic noises.

Feedback Loop: This is the brain and the sense organ of the STM. The feedback loop keeps the value of tunneling current constant. It commands the piezos whether to extend or to contract depending on the amount of tunneling current.

3.1.2 Tunnel Current

When the tip is brought to within 1Å to 4Å of the sample, electrons tunnel between them until they share a common Fermi level. As a result the net current will be zero in steady state as shown in figure 3.1.1 A. But if the sample is biased with voltage V, there will be a net tunneling current flow from sample to the tip, which is demonstrated in the figure
3.1.1 B. For the simplicity we can consider only elastic tunneling, i.e., tunneling of sample electron of energy $E$ tunnels only to the same energy state of tip.

Following Bardeen’s transfer Hamiltonian approach [3, 4] to tunneling, the sample and tip can be considered as two separate subsystems. In other words, tips and samples have their own independent density of states. This is Bardeen’s first assumption. The electronic states of the separate subsystems are obtained by solving the stationary Schrodinger equations. The rate of flow of electrons from sample to the tip can be calculated by perturbation theory. The tunnel current from sample to tip is given by the equation (3.1).

\[
\mathcal{I}_{\text{sample} \rightarrow \text{tip}} = -\frac{2e^* 2\pi}{h} |M|^2 \rho_s(\varepsilon) \cdot f(\varepsilon) \cdot \rho_t(\varepsilon + eV) \cdot (1 - f(\varepsilon + eV)) \cdot \delta \varepsilon - - -(3.1)
\]

Where,

\[
f(\varepsilon) = \frac{1}{1 + e^{\frac{\varepsilon - \mu}{kT}}}
\]

$|M|^2 = \text{Tunneling Matrix Elements}$

$\rho_s(\varepsilon) = \text{Sample density of states (DoS)}$

$\rho_t(\varepsilon + eV) = \text{Tip density of states}$
Figure 3.3 (a) Bardeen’s first assumption: Tunneling between two independent electrodes tip (left) and sample (right). A- unbiased sample tip combination, B- biased sample tip combination. (b) Bardeen’s second assumption: the wavefunction decays exponentially in the barrier. (c) Bardeen’s third assumption: the overlap between the tip and sample wave functions are small enough to consider the matrix element constant.

Though the dominant current flow will be from sample to tip, there will also be a smaller current in the reverse direction which is given by the following equation.

\[ \delta I_{\text{tip \rightarrow sample}} = -\frac{2e}{h} \frac{2\pi}{\hbar} |M|^2 \rho_t(\varepsilon + eV) * f(\varepsilon + eV) * \rho_s(\varepsilon) * (1 - f(\varepsilon)) \delta \varepsilon \] (3.2)

\[ \text{# of filled tip states to tunnel} \quad \text{# of empty sample states to tunnel from} \]

The net current can be calculated by integrating over all energies

\[ I = \int_{-\infty}^{\infty} (\delta I_{\text{sample \rightarrow tip}} - \delta I_{\text{tip \rightarrow sample}}) \]

\[ I = -\frac{4\pi e}{h} \int_{-\infty}^{\infty} |M|^2 \rho_t(\varepsilon + eV) * \rho_s(\varepsilon) * \{ f(\varepsilon)(1 - f(\varepsilon + eV) - (1 - f(\varepsilon))f(\varepsilon + eV)) \} d\varepsilon \] (3.3)

\[ I = \frac{4\pi e}{h} \int_{-\infty}^{\infty} |M|^2 \rho_t(\varepsilon + eV) * \rho_s(\varepsilon) * \{ f(\varepsilon + eV) - f(\varepsilon) \} d\varepsilon \] (3.4)
Most of the time metallic tips like PtIr or W are used, since these are considered to have flat density of states for the energy range being used here. This is because Fermi liquid theory, for all intents and purposes, gives a constant for $\rho$ in conventional metals.

Hence assuming, $\rho_t = \text{constant}$

$$I = \frac{4\pi e}{h} \rho_t \int_{-\infty}^{\infty} |M|^2 \rho_s(\epsilon) \{ f(\epsilon + eV) - f(\epsilon) \} d\epsilon$$

According to Bardeen’s theory of tunneling the amplitude of electron transfer or the tunneling matrix element $M$, is determined by the overlap of the surface wave functions of the two subsystems at the separation surface. In other words, the tunneling matrix element $M$ is determined by the surface integral on a separation surface between the two electrodes.

$$M = \iint \left( \chi^* \frac{\partial \psi}{\partial z} - \psi \frac{\partial \chi^*}{\partial z} \right) \partial x \partial y$$

Where, $\chi$ and $\psi$ are wave functions of two electrodes separated by $z_0$.

The matrix element comes from the assumption that both tip and sample wave functions fall off exponentially into the square barrier, the vacuum gap. One of the major assumptions on which Bardeen’s theory is based is that the tip sample wave function overlap is small enough (i.e. tip sample separation is large enough) so that each side is insignificantly influenced by the tail of the wavefunction from the other side. Therefore the matrix element for tunneling will be virtually independent of the energy difference between the two sides of the barrier. The matrix will remain unchanged even if one side
transitions from the normal state to the superconducting state. Hence the matrix element can be taken as a constant.

\[ I = \frac{4\pi e}{h} \rho_t |M|^2 \int_{-\infty}^{\infty} \rho_s(\varepsilon) \{ f(\varepsilon + eV) - f(\varepsilon) \} d\varepsilon \quad (3.6) \]

From the WKB approximation, the tunneling probability through a square barrier will be

\[ |M|^2 = e^{-2\gamma} \]

Where,

\[ \gamma = \int_0^s \sqrt{\frac{2m\varphi}{\hbar^2}} dx \]

\[ = \frac{s}{\hbar} \sqrt{2m\varphi} \]

Where \( m \) is the mass of the electron, \( s \) is the width of the barrier (tip-sample separation), and \( \varphi \) is the height of the barrier, which is actually some mixture of the work functions of the tip and sample.

Thus,

\[ I = \frac{4\pi e}{h} \rho_t(0) e^{-\frac{s}{\hbar} \sqrt{2m\varphi}} \int_{-\infty}^{\infty} \rho_s(\varepsilon) \{ f(\varepsilon + eV) - f(\varepsilon) \} d\varepsilon \quad (3.7) \]

Since most of the data was taken at 5K, we can approximate the Fermi Dirac distribution function to be a step function. With this assumption,

For \( \Rightarrow 0 < \varepsilon, f(\varepsilon) \approx 0, f(\varepsilon + eV) \approx 0 \Rightarrow (f(\varepsilon + eV) - f(\varepsilon)) = 0 \)

For \( \Rightarrow \varepsilon < -eV, f(\varepsilon) \approx 1, f(\varepsilon + eV) \approx 1 \Rightarrow (f(\varepsilon + eV) - f(\varepsilon)) = 0 \)
But, $\gamma \Rightarrow 0 > \epsilon > -eV, f(\epsilon) \approx 1, f(\epsilon + eV) \approx 0 \Rightarrow (f(\epsilon + eV) - f(\epsilon)) = 1$

Hence the significant region is only $0 > \epsilon > -eV$

Therefore the tunneling current can be approximated as,

$$I \approx \frac{4\pi e}{h} \rho(0) * e^{-\frac{2e}{h}\sqrt{2mq}} \int_{-eV}^{0} \rho(\epsilon)d\epsilon$$

(3.8)

The tunnel current that measured through STM depends on the barrier size and the integrated DOS of the sample.

3.1.3 Types of Data Sets

i. Topography

One of the major functions of an STM is to obtain atomically resolved surface images of a sample. A topographical image is obtained by measuring the intensity of the tunneling current as a function of position which is stored as a square matrix, or a two dimensional array of numbers, $N(x, y)$. Lateral resolution $r = (x, y)$ plane represents the lateral resolution of the data recording device. For example, if a 100 x 100 matrix is assigned to 100 x 100 Å$^2$ image, the lateral resolution is limited to 1 Å. For a given bias, the physical quantity measured by the STM is the tunneling current, which is function of $r = (x, y)$ and the separation between tips and the sample $z$. 
There are two ways to create the topographic images: constant current mode and constant height mode. Most of our data are taken in constant current mode. In constant current mode, the STM tip moves up and down in the surface in order to keep the current constant with the help of feedback loop. A computer plots z-motion of the tip which is equivalent to the topography of the surface. In this mode, the relative variation of tip height is taken as image variable: A typical atomically resolved image taken by our STM is shown in the figure 3.4.

**ii. Density of States**

From equation 3.6, the tunneling current is given by.
\[ I = \frac{4\pi e}{h} \rho_t |M| \int_{-\infty}^{\infty} \rho_s(\epsilon)^* \{ f(\epsilon + eV) - f(\epsilon) \} d\epsilon \]

Differentiating the tunneling current with respect to the bias voltage and simplifying the equation yields.

\[ \frac{dI}{dV} = \frac{4\pi e}{h} \rho_t |M| \int_{-\infty}^{\infty} \rho_s(\epsilon)^* \frac{df(\epsilon + eV)}{dV} d\epsilon \]

\[ \frac{dI}{dV} \approx \frac{4\pi e}{h} \rho_t |M| \int_{-\infty}^{\infty} \rho_s(\epsilon)^* \delta(\epsilon + eV) d\epsilon \]

\[ \frac{dI}{dV} \propto \rho_s(eV) \]

Hence the first derivative of tunneling current with respect to the bias voltage is equivalent to the local density of states of the sample. Since tunneling measures the density of states and the density of states is directly related to \( \Delta \), information about the condensed electrons can be easily seen in the derivative of the tunnel current or the differential conductance \( dI/dV \).

![Figure 3.5: (a) Density of states predicted by theory. (b) and dI/dV spectra (DoS) taken on well studied High-T_c superconductor BSCCO obtained with low temperature STM in our laboratory.](image)
iii. Linecut

A line cut is not a completely different measurement type. It is one of the popular ways to represent the local density of states. Since there is control over x-y motion of the tip, the tip can be fixed at any desired point in the XY plane in order to measure the DoS at that location. Some materials like single crystal gold or conventional superconductors have a spatially homogenous DoS. However, other samples like high-Tc superconductors have inhomogeneous DoS. A linecut is a measurement of DoS curve at equally spaced points along a line (spaced from sub Å to a few Å apart). A typical linecut on a PLCCO sample taken in a 32 Å line is shown in fig 2.5 (a). There are 32 spectra in the linecut taken at 1 Å intervals.

iv. DoS Map

It is also another way of representing the local density of states. If a full DoS-vs-energy curve is measured at each point in the xy plane, a two dimensional DoS map at each energy can be obtained. Mapping of the DoS at a specific energy is a good way to see inhomogeneities associated with high-Tc superconductors.

Most of the maps that have been taken are 32 Å x 32 Å or 64 Å x64 Å with DoS taken at each Å spacing. Since most of the physically significant features of interest take place in less than 60 meV, most of the DoS spectra are taken in the energy range between -60meV to +60meV with the energy resolution of 0.3 meV. High-Tc superconductors have a short coherence length, \( \xi \sim 10 – 20 \) Å. Accordingly the density of states may
change significantly for over these length scales. Therefore, in order to capture spatial resolution in the density of states, at least one pixel per 5 Å spatial resolution is required. Most of our data is taken at least at one pixel per Å. A typical local density of state map in 64 Å x 64 Å region at energy $E = \Delta$, the superconducting gap is shown in figure 3.6 (b).

![Figure 3.6: The waterfall image of 32 Å linecut taken in PLCCO. Each spectra are taken in a 32 Å line with a separation of 1 Å each. (b) Density of state map of 64 Å x 64 Å image at energy $E = \Delta$, the superconducting gap.](image)

3.1.4 Significant Achievements of STM in high-$T_c$

i. STM enabled us to observe nanoscale inhomogeneity in the density of states of high $T_c$ cuprates [5].

ii. STM has made important contributions to finding the pairing mechanism of high $T_c$ cuprates which is still an unresolved problem [7, 6].

iii. STM has enabled us to observe the quasiparticle scattering and therefore obtain
momentum dependent information long with spatial information in the high Tc cuprates [8].

And many more!

**Other capabilities of STM**

i. Beside taking atomically resolved topographic images of the flat surfaces and measuring the local quasiparticle density of states STM can be used to manipulate the surface atoms [9].

ii. The real space STM data can be translated into the momentum space through Fourier Transformation [10]

iii. At present day time the spin sensitive STMs are also coming onto the scene. They will be quite effective for exploring a promising new field called spintronics [11].

### 3.1.5 STM on PLCCO

To investigate PLCCO, PtIr tips were used and it was assumed that their density of states are constant within the range of energy where data was obtained (-60 to +60 meV). Unless otherwise mentioned PLCCO sample means the Pr$_{0.88}$LaCe$_{0.12}$CuO$_4$ with T$_c$ = 24K. Samples were cleaved in ultra high vacuum and most of the data was taken at 5K unless the temperature is otherwise specified.
This is the first reproducible STM work on PLCCO and a variety of spectra were found. Some spectra have distinct coherence peaks and some don’t. Most spectra have v-shape background but some don’t. Some of the typical differential conductance spectra are shown in figure 3.7 (a) and (b). The sharp peaks of the spectra are called coherent peaks.

![Figure 3.7](image.png)

**Figure 3.7 (a)** Typical spectra taken at 5K on PLCCO with Tc =24K.

Though the spectra look different in different spots, their d-wave nature is distinct in all the spectra. Data were obtained in the form of line cuts, and maps. From all of these data it was found that the mean value of superconducting gap lies around 7 meV with spread form 3 meV to 12 meV according to rough Gaussian distribution. The most important parameter measured through these spectra is the superconducting gap energy. It is defined as the half of the energy difference between two coherent peaks as illustrated in fig 3.8. There are some spectra which do not have well defined coherent peaks. The
theory was used to help find the actual gap of the spectra which will be discussed in greater details in chapters 4 and 5.

Unlike superconductivity in BSCCO superconducting regions are not everywhere in PLCCO. There are non-superconducting regions separating the superconducting regions. These semiconducting/insulating regions could either be due to the residual Cu vacancies or could be due to the insulating phases which are byproduct of annealing.

![Figure 3.8](image)

Figure 3.8: (a) Superconducting gap is measured as half of the peak to peak energy difference. The sharp peaks followed by the gap are known as coherence peaks. (b) Histogram of superconducting gap of many maps with maximum weight at around 7 meV [ref 7]
3. 2 Other Experimental Techniques

3. 2. 1 Angle Resolved Photoemission Spectroscopy (ARPES)

Electrons in solids have three intrinsic quantities, energy, momentum and spin. Angle resolved photoemission study is an experimental technique which gives us information about the energy and momentum of the electrons in the solid. Like Scanning tunneling microscopy, ARPES is also a surface sensitive technique. The major difference is that the STM probes the real space properties but the ARPES probe the reciprocal space properties.

![Figure 3.9: Schematic diagram of ARPES experiment [12]. The emission direction of the photoelectron is specified by the polar $\theta$ and azimuthal $\varphi$ angles.](image)

ARPES is based on the photoelectric effect, which was first discovered by Hertz and
later explained by Einstein. When a photon of energy higher than the work function of an
electron in a sample hits the electron, the electron gets knocked out from the sample. By
the law of conservation of energy the electron moves out with kinetic energy $E_{\text{kinetic}}$ after
paying for work function $\phi$ and binding energy $E_B$ of the total absorbed energy $\hbar \nu$ from
photon. This electron is collected in a photo detector followed by the analyzer which
reads the kinetic energy. Once the photon energy and work function is known the binding
energy of the electron can be easily found. ARPES not only determines the energy of the
electron but its momentum as well. The momentum of the particle is angle dependent. If
the polar and azimuthal angle of the ejected electron is known its momentum can be
found with the following equations.

\[
E_{\text{kinetic}} = \hbar \nu - \phi - |E_B|
\]

\[
p_x = \sqrt{2mE_{\text{kinetic}}} \sin \theta \cos \vartheta
\]

\[
p_y = \sqrt{2mE_{\text{kinetic}}} \sin \theta \sin \vartheta
\]

\[
p_z = \sqrt{2mE_{\text{kinetic}}} \cos \theta
\]

This is how the energy and momentum of the sample is measured with ARPES. As STM
maps the density of states in real space ARPES can map the density of states in
momentum space. ARPES has played a prominent role in the study of high $T_c$ Cuprates.
Here are few of its achievements:

i. It was ARPES that first figured out the d-wave pairing of high-$T_c$
superconducting gap. The angle dependence of the gap has been mapped out by many experimental groups. [13, 14, 15, 16, 17, 18]

ii. Dramatic spectral line shape change caused by the superconducting transition [15].

iii. ARPES discovered anisotropic pseudo gap above $T_c$ [19, 20].

iv. The existence of nodal quasiparticles in the superconducting state, and “strange metal” behavior above $T_c$ [21, 22] in the so-called “normal state.”

### 3.2.2 Neutron Scattering

Neutrons are massive particles with spin. They can be utilized to probe spin systems in the sample. Thus the neutron scattering is the best way to obtain momentum space information about the magnetic properties of the material. Neutron scattering is used for two proposes. One is to locate the static magnetic ordering and another is to find the dynamic magnetic ordering in the sample.

Static ordering like ferromagnetic, anti-ferromagnetic and diamagnetic can be probed with elastic scattering of neutron. It is very similar to the x-ray spectroscopy. When monochromatic neutron rays are passed through the crystal they get scattered and the scattered rays form Bragg peaks giving information about the spins in the crystal. The dynamic spin order like spin density wave can be detected through inelastic neutron scattering. When the neutrons with certain energy are passed through the sample they gets scattered off by magnons or other spin excitations, the quanta of magnetic
oscillation. Hence the scattered neutrons either gains or lose the energy, and this gain or loss of energy gives the information of scatterer.

Neutron scattering and high-Tc cuprates

High T_c cuprates are antiferromagnetic Mott insulators. To see the magnetic structure of these materials elastic neutron scattering can play a prominent role. When the parent compounds of high T_c materials are doped, they lose the long range antiferromagnetic order which can be checked by neutron scattering.

Magnetic fluctuations are strong candidates for the pairing mechanism in high-T_c cuprates and it is an inelastic neutron experiments that has been crucial in obtaining information about spin fluctuations. Inelastic neutron scattering has been used to look for dynamic spin fluctuations in hole doped high-Tc superconductors like LSCO [23] and YBCO [24] and recently even BSCCO [25]. NCCO [26] and PLCCO [27] are the electron doped superconductors that have been studied well through neutron scattering.
References


Chapter 4

Temperature Dependence of Superconducting Gap

In superconductors, the carriers of super currents are not the normal electrons; instead they are paired electrons called cooper pairs. For convenience let’s talk about conventional superconductors, which are well understood. When two electrons of opposite spin and momentum in the Fermi surface get glued together by the attractive force of lattice vibration, a gap opens up in the Fermi surface. This gap energy is usually represented by a symbol “Δ” and is known as the superconducting gap. The superconducting gap, Δ is the energy cost to unglue the electrons of cooper pair. This gap can be seen and measured through ARPES, tunneling experiments like point contact tunneling, junction tunneling and of course through STM spectroscopy.

Since the discovery of electron doped (n-type) high Tc superconductors [1], the similarity and dissimilarity [2] of electron and hole doped (p-type) superconductors has been under dispute. For example: now it is confirmed that the superconducting order parameter of an electron doped superconductor is \( d_{x^2-y^2} \), the same as that of their hole doped counter parts [3, 4], which has long been disputed. There are many other disputed phenomena; one of them is the temperature dependence of the superconducting gap. In this chapter the temperature dependence of superconducting gap of n-type superconductor PLCCO will
be thoroughly explored.

4.1 Conventional Superconductors v/s hole doped cuprates

It is well known that electronic properties of cuprates are very different from those of the conventional superconductors. In conventional superconductors, the phenomenology of the superconducting gap closely follows BCS theory which states that the superconducting gap is weakly temperature dependent at low temperatures and falls sharply around zero at \( T_c \). Scanning Tunneling Studies of conventional superconductors reveal that:

(i) there are no single particle excitations below the superconducting gap ie the gap has s-wave symmetry

(ii) at the gap boundaries \( \pm \Delta \) there are symmetric superconducting peaks

(iii) many conventional materials are in the weak coupling limit; \( 2\Delta(0)/K_BT_c \approx 3.5 \), where \( \Delta(0) \) is the zero temperature superconducting gap averaged over entire Fermi surface

and (iv) \( \Delta(T_c) = 0 \) ie gap vanishes at transition temperature [5, 6, 7, 8].

All of these properties can be explained by the well established microscopic theory of superconductivity i.e. BCS theory.

Contrary to this, STM studies of the well known p-type high-\( T_c \) cuprate superconductors reveal that:
(i) there exist single particle excitations within the superconducting gap

(ii) these materials are in the strong coupling limit, \(2\Delta(0)/k_B T_c\) varies form 5 to 11 and

(iii) \(\Delta(T_c) \neq 0\) i.e. the gap still exists even above the transition temperature.

In the case of underdoped p-type cuprates, there exists a pseudo gap which appears at the antinodal region and may compete with the superconducting gap on the Fermi surface. Overdoped p-type cuprates have a weaker pseudo gap effect. Still, the superconducting gap doesn’t vanish at transition temperature. n-type high-\(T_c\) cuprates are not as well studied as compared to the hole doped ones. The much weaker pseudo gap effect of the electron doped n-type cuprates provides a good opportunity to investigate the superconducting gap without the influence of the “pseudo gap”. Additionally, the PLCCO sample under investigation in this thesis has \(T_c = 24\)K which lies in the optimally doped region. Thus, there is even lesser pseudo gap effect which is predominant in the underdoped region. Therefore our sample can be the ideal sample for this purpose.

By using point contact tunneling Shan et al showed that the temperature dependence of the superconducting gap of PLCCO follows the BCS prediction very well over a wide doping regime with a universal weak coupling ratio of \(2\Delta_0/k_B T_c = 3.5\). Therefore, they concluded that the electron-doped cuprates are weak-coupling BCS superconductors. Infra-red reflectivity and Raman Spectroscopy studies suggests that the superconducting pairing strength of the n-type cuprate is close to a weak coupling in optimally doped
regions.

Figure 4.1: Shan et al (ref 20) (a) temperature dependence of PLCCO superconducting spectra by point contact tunneling and (b) superconducting gap following the BCS theory.

There are still many disagreements to be resolved. Do the electron doped high $T_c$ cuprates really follow the BCS prediction regarding temperature dependence? Is the coupling ratio for n-type cuprates is weak as suggested by the BCS theory? These two questions will be answered on the basis of the finding from this STM study on PLCCO. The initial step will be the development of a background.

4. 2 **Quasiparticle Density of State and effect of Temperature**

A tunneling spectrum measures the quasiparticle density of states of the unglued electrons or quasiparticle. Theoretically the density of states can be written according to BCS theory as:
\[ \rho_s(E,T) = \text{Re} \left( \frac{|E|}{\sqrt{(E^2 - \Delta^2)}} \right) \]  

(4.1)

Tunneling measurements actually measure the local density of states which is equivalent to the differential conductance.

\[ \frac{dI}{dV} = \frac{4\pi e}{h} \rho_s |M|^2 \int_{-eV}^{eV} \text{Re} \left( \frac{|E|}{\sqrt{(E^2 - \Delta^2)}} \right) \frac{df(E + eV)}{dE} dE \]  

(4.2)

At absolute zero temperature, Fermi-Dirac distribution function will be a step function and its derivative, \( \frac{df(E + eV)}{dV} \) will be a delta function. Hence, there will be a singularity in the quasiparticle density of states at energy \( E = \Delta \). The actual meaning of this is that the energy states in the Fermi surface that were in the gap region are pushed just outside the gap and they are concentrated just after the gap. One of the typical tunneling spectra
for conventional superconductors generated by a computer program using BCS theory is shown in figure 4.2(a). The sharp peaks of the spectra are called coherence peaks and the superconducting gap is measured as the half of peak to peak energy difference. The spectrum was calculated at temperature close to absolute zero. Below the transition temperature, the superconducting gap gets wider as the temperature goes below $T_c$ and becomes maximum at the absolute zero.

As the temperature increases from absolute zero the superconducting gap should get narrowed down in order to get closed at or higher the transition temperature. But there is another effect that should be taken into account for STM spectra whose influence is just the opposite. As the temperature goes up the thermal effect on the quasiparticles begins to be effective. From equation 4.2, at finite temperatures the Fermi-Dirac distribution function will no longer be a step function. Hence its derivative will also smear out form a
delta function to gaussian. The thermal effect on Fermi-Dirac distribution function and its
derivative is shown in figure 4.3.

Obviously the broadening of \( \frac{df(E + VeV)}{dV} \) will contribute to the quasiparticle density of
states and will stretch out the spectra. This effect is called thermal broadening which is
quite visible in the coherence peaks. Thermal broadening smears the coherent peaks and
makes them more and more ill defined as the temperature rises. So on the one hand,
increasing temperature tends to broaden the superconducting spectrum which makes the
superconducting gap looks wider and on the other hand it tries to close the gap. Because
of this effect the coherent peaks are ill defined and it is hard to measure the actual
superconducting gap, which is defined by the half of the energy difference between two
coherence peaks.

Figure 4.4: (a) squeezed car: metaphor for higher temperature squeezing the superconducting gap. (b)
Stretched car: metaphor for higher temperature stretching the spectra.
4.3 Other contributions to spectral broadening

The differentiated Fermi-Dirac distribution function \( \frac{df(E + eV)}{dV} \) takes care of thermal broadening in superconducting spectra. However, mere thermal broadening is not the only effect. An extra broadening effect comes from the quasiparticle scattering.

\[
\frac{dI}{dV} = \frac{4\pi e}{h} |M|^2 \int_{-eV}^{eV} \text{Re} \left( \frac{|E - i\Gamma|}{\sqrt{(E - i\Gamma)^2 - \Delta(T)^2}} \right) \ast \frac{df(E + eV)}{dV} dE
\]

(4.3)

Figure 4.5: (a) Thermal broadening of the superconducting spectra at constant \( \Gamma = 0.001 \) meV. (b) Broadening due to quasiparticle scattering at constant temperature 1.5K.

In order to take account of quasiparticle scattering rate we have to add an imaginary term, \( i\Gamma \) to the quasiparticle energy. Extended study on quasiparticle scattering will be discussed in chapter 5. Hence the tunneling conductance will take a form:

Figure 4.5(a) sheds light how thermal effect broadens the superconducting spectra and 4.5(b) tells the story of density of state broadening caused by quasiparticle scattering.
4. 4 d-wave gap

A simple phenomenological picture used to describe the cuprates is a description as per the BCS theory with one important modification. In BCS theory the superconducting gap is a constant over the entire Fermi surface, and the paired electrons have zero relative angular momentum: i.e. they have an s-wave symmetry. In the cuprates this is not the case. In 1993 a strong anisotropy was found in $\Delta$ along the Fermi surface [9]. The variation is consistent with d-wave symmetry of the wavefunction and later experiments verified that the gap magnitude and phase does indeed change sign around the Fermi surface [10, 11]. Modifying the BCS equations to account for d-wave pairing symmetry is straightforward and was done by K. Maki [12]. It simply entails replacing the above relations with ones that retain the wavevector dependence of the gap Equation 4.3.

$$\rho_s(E, T) = \int_0^\pi d\theta \Re \left( \frac{|E - i\Gamma|}{\sqrt{(E - i\Gamma)^2 - \Delta(T)^2 \cos^2(2\theta)}} \right)$$

(4.4)

Then, by adding up all the states at each energy and taking care of thermal and quasiparticle scattering effects one can see the expected DOS for a d-wave superconductor.

$$\frac{dI(V, T)}{dV} = \alpha \int_0^\pi d\theta \Re \left( \frac{|E - i\Gamma|}{\sqrt{(E - i\Gamma)^2 - \Delta(T)^2 \cos^2(2\theta)}} \right) \frac{df(E + V)}{dV} dE$$

(4.5)

The measured spectra in this research carry the following information:
(1) The superconducting gap at the location where the spectrum was taken and is represented by $\Delta$ in the equation 4.6.

(2) The effect of temperature at which the spectra were taken which is represented by the derivative of Fermi-Dirac distribution function.

(3) The quasiparticle scattering rate which is represented by $i\Gamma$.

![Figure 4.6: (a) Superconducting gap histogram measured as half of the peak to peak energy difference in 32 Å x 32 Å map with mean value around 8 meV. (b) Actual gap histogram calculated by my program in the same map with mean value around 6.25 meV. Though the shape of the histogram remains same the mean actual gap value is decreased by 2 meV compare to the measured gap.](image)

If we measure superconducting gap as half of peak to peak we will not be measuring the actual gap because on doing so we will be ignoring the thermal broadening effect and the quasiparticle scattering effect. If we can separate the thermal effect and the scattering effect from our spectra, we will end up getting the actual quasiparticle density of states i.e. the actual superconducting gap. Figure 4.6 shows that the mean value of actual $\Delta$
calculated at 5K for 1024 spectra is smaller by 2.25 meV to mean value $\Delta$ measured from peak to peak.

The result in fig 4.6(b) was generated by writing a computer program in C++ which is provided in the Appendix A. The program generates different curves at a temperature $T$ for the different sets of $\Delta$ and $\Gamma$ and calculates the best fit with the measured spectrum using the least squares procedure. The best fit value of $\Delta$ and $\Gamma$ yields us the actual value of $\Delta$ and effective scattering rate $\Gamma$.

4.5 Temperature variation of superconducting gap in PLCCO

The STM spectra have been measured in the form of line cuts at temperature 5K, 13K, 20K and 24K. The waterfall image of typical spectra look at different temperature is given in figure 4.7.

Figure 4.7: the waterfall image of typical spectra taken at temperature 5K (black), 13K (red), 20K (green) and 24K (blue). The coherence peaks of spectra have been ill defined as the temperature rises.
From figure 4.7 it is clear that as temperature goes up the thermal effect and quasiparticle scattering comes into play and the coherent peaks becomes ill defined. In order to find the actual value of $\Delta$ the data was fitted at these temperatures and the typical fits are shown in the figure 4.8. Most of the fits are in very good agreement with the measured spectra. In order to save time and make more accurate fitting the higher energy part of the spectra above the coherence peaks was trimmed off. The least square values for most such fits fell between 0.0005 and 0.00005.

Figure 4.8: Typical spectra measured by our STM (represented by black curve) and their best fits (represented by red curve) at temperature (a) 5K, (b) 13K, (c) 20K and (d) 30K.
4.6 Results and Discussion

The actual $\Delta$ calculated by this technique was plotted against the corresponding temperature. It was found that the $\Delta$ does not vanish at transition temperature $T_c = 24K$ which is shown in figure 4.9(a) by the black curve. It was found that at low temperatures, mainly at 5K and 13K there is almost no deviation in the fitting parameters. However, the deviation increases as temperature goes higher with maximum deviation $\pm 1.5$ meV for the spectra at 24K.

![Figure 4.9: (a) variation of $\Delta$ with temperature. Our result is shown with black line where as the BCS prediction is shown with green line. (b) Spectra taken at temperature equal to the transition temperature $T_c = 24K$](image)

We find that 33% of the spectra are gapped at the transition temperature. Some of them are shown in figure 4.9(b). Gaped spectra also exist at temperatures higher than $T_c$. However, the range of error bar is too high for the fits to be optimized.
STM studies in hole doped cuprates revealed that there exist gapped spectra at the transition temperature and even at higher temperatures [13]. But in these materials there exist pseudo gap phase above $T_c$ which is tangled with the superconducting phase. Though the pseudo gap phase is disputed in n-type materials, there is no pseudo gap phase reported in the material under investigation [14 - 18]. Hence the gaped spectra at $T_c$ suggest that there should be local pockets of superconductivity at and above the transition temperature.

However the point contact tunneling studies on this material suggests that the evolution of superconducting gap follows the BCS theory. In point contact tunneling micron-sized area of the sample is in contact with the tip but STM tip can scan the atomically resolved sample surface. Literally, each point contact tunneling spectrum is equivalent to the average of thousands of STM spectra. Therefore at temperature equal to or higher than $T_c$ the gapped spectra get dissolved while averaging. Since the point contact tunneling spectrum is the average effect of wide area they found homogeneous spectra unlike inhomogenous spectra observed by our STM [19].

It is not only the temperature dependence of gap and the inhomogeneity of spectra that differ from point contact tunneling there are many other properties as well. Instead of the BCS like weak coupling ratio ($2\Delta_0 / k_B T_c = 3.5$) that bulk probes like the point contact tunneling [20, 21, 22] find, we find strong coupling limit $2\Delta_0 / k_B T_c = 5.5 - 8$, [23] which is one of the hallmarks of the high-$T_c$ cuprates.
Unlike point contact tunneling which finds a complicated anisotropic non-monotonic gap $\Delta = \Delta_0(1.43\cos(2\theta) - 0.43\cos(6\theta))$ we find that the superconducting order parameter, $\Delta$ can be fit by a d-wave form i.e. $\Delta = \Delta_0\cos(2\theta)$ [24].

The accuracy of the result depends on the sensitivity of the probe. The discrepancy is not limited to the n-type cuprates. Energy loss spectroscopy of BSCCO suggested that the evolution of superconducting gap should follow the BCS theory [figure 4.10 (a)] but STM study on the same material revealed that it does not [figure 4.10 (b)].

Figure 4.10: (a) (ref 25) energy loss spectroscopy result indicating that the temperature variation of superconducting gap at BSCCO 2212 follows the BCS model. (b) (ref 13) STM study revealing that the local superconductivity survives even beyond the transition temperature.
4. 7 Conclusion

We observe that the temperature dependence of the superconducting gap doesn’t follow BCS theory. 33% of spectra are still gapped at $T_c$. Since a pseudo gap phase is not present in these materials these gaped spectra should be superconducting spectra and hence there should be local pockets of superconductivity at or above transition temperature. Unlike point contact tunneling studies on the sample which suggest that most of the properties of PLCCO are consistent with the conventional superconductors, we find that most properties of PLCCO are consistent with their p-type counterparts.
References


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Chapter 5

Quasiparticle scattering rate (\(\Gamma\))

The electron-like excitations of a Fermi liquid or a superconductor are called quasiparticles. They carry the same spin and magnitude of a charge as an electron. Like free electrons their energy “\(E\)“ depends on their momentum \(k\), but with a renormalized mass “\(m\)” [1].

\[
E_{\mathbf{k}}' = \frac{\hbar^2 k^2}{2m}
\]

However, superconductivity is not caused by single electrons; it is caused by cooper pairs – usually described as a pair of electrons- that move through the crystal lattice without resistance. If the energy equal to the binding energy of the cooper pair (gap energy) is applied to the pair, it is broken. The broken cooper pair is called a Bogoliubov quasiparticle. It differs from the conventional quasiparticles in metal because it combines the property of negatively charged electrons and a positively charged hole.

5.1 \(\Gamma\) on density of states

According to BCS theory, the dispersion relation for Bogoliubov quasiparticles is not as simple as an electron type of quasiparticles. Instead it is given by the equation [2]:

\[
E_{\mathbf{k}} = \sqrt{\varepsilon_{\mathbf{k}}^2 - \Delta^2}
\]
Where, $E_k$ is the electron dispersion above the transition and $\varepsilon_k$ is the quasiparticle dispersion below the transition temperature. $\Delta$ is the size of the gap that opens to single particle excitations and is known as superconducting gap.

The superconducting gap is one of the hallmarks of superconductivity and in tunneling experiments it is manifested directly in the quasiparticle density of states. For conventional superconductors the quasiparticle density of states can be written as:

$$\rho_s(E,T) = \begin{cases} E \geq \Delta & \varepsilon \geq \Delta \\ 0 & \varepsilon < \Delta \end{cases}$$

According to BCS theory the superconducting gap, $\Delta$ is a constant over the entire Fermi surface, and the paired electrons have zero relative angular momentum: (i.e. have an s-wave symmetry). In the cuprates this is not the case. For hole doped as well as for electron doped cuprates there has been no doubt that the $\Delta$ has strong anisotropy along the Fermi surface [3, 4]. The variation is consistent with a d-wave symmetry of the wavefunction and later experiments verified that the phase does indeed change sign around the Fermi surface [5, 6].

Modifying the BCS equations to phenomenologically account for d-wave pairing symmetry is straightforward and was done by K. Maki [7]. It simply entails replacing the above relations with ones that retain the wavevector dependence of the gap Equation 5.4
\[
\rho_s(E, T) = \begin{cases} 
\frac{E}{\sqrt{E^2 - \Delta^2_k}} & \text{if } E \geq \Delta_0 \\
0 & \text{if } E < \Delta_0
\end{cases}
\]  
---------- (5.4)

Where, angular dependence of the superconducting gap, \( \Delta_k = \Delta_0 \cos(2\theta) \), and \( \Delta_0 \) is the maximum gap. Then, by adding up all the states at each energy one can expect the quasiparticle density of state at \( T \rightarrow 0 \) as,

\[
\rho_s(E) = \int_0^\pi d\theta \text{Re} \left( \frac{|E|}{\sqrt{(E)^2 - \Delta(T)^2 \cos^2(2\theta)}} \right)
\]  
---------- (5.5)

The quasiparticle density of state for d-wave superconductors look like the figure 5.1

Having taken account of thermal effect for finite temperature the equation 5.4 will turn to:

\[
\rho_s(T) = \int_0^\pi d\theta \text{Re} \left( \frac{|E|}{\sqrt{(E)^2 - \Delta(T)^2 \cos^2(2\theta)}} \right) \frac{df(E)}{dE}
\]  
---------- (5.6)

Here “\( f(E) \)” is a Fermi Dirac distribution function.

With the STM, the rate of change of tunnel current is measured with respect to the bias voltage which is equivalent to the local density of states. Hence, equation 4.5 can be
written as:

$$\frac{dI(V,T)}{dV} = \alpha \int \int d\theta \text{Re} \left( \frac{|E|}{\sqrt{(E)^2 - \Delta(T)^2 \cos^2(2\theta)}} \right) \frac{df(E + V)}{dV} dE$$

$$---(5.7)$$

Figure 5.1: Typical d-wave spectra at $T \rightarrow 0$.

A curve at temperature $T = 5K$ Fig 5.2(a) was generated with the equation 5.7 and we expect it to be matching with a spectrum also taken at 5K (fig. 5.2(b)). In fact they do not match. The coherence peaks are broadened more than the thermal energy could do it. This extra broadening comes from the quasiparticle scattering and it can be taken care of by adding an imaginary term $i\Gamma$ in the quasiparticle energy.

$$\frac{dI(V,T)}{dV} = \alpha \int \int d\theta \text{Re} \left( \frac{|E - i\Gamma|}{\sqrt{(E - i\Gamma)^2 - \Delta(T)^2 \cos^2(2\theta)}} \right) \frac{df(E + V)}{dV} dE$$

$$---(5.8)$$

Here, $\alpha$ is normalization constant. $\Gamma$ is a quasiparticle scattering rate or the inverse of the quasiparticle life time which manifests itself in the tunneling spectra. The quasiparticle
scattering rate is very small at low temperature. In other words, the quasiparticle lifetime is very high at low temperature.

Figure 5.2 (a) Calculated D-wave spectra at 5K, where Fermi-function is taken care of but not the quasiparticle scattering rate. (b) Measured spectra, a combined effect of superconductivity, thermal broadening and quasiparticle scattering. Comparing both the pictures the importance of quasiparticle scattering is clearly visible.

Ideally speaking, the quasiparticle lifetime is infinite at absolute zero temperature, which is projected in tunneling spectra as infinitely tall coherent peaks. As the temperature goes up the height of the coherence peaks decreases and they get broadened, which means the scattering rate of quasiparticles increases or the quasiparticle lifetime decreases. This is illustrated in diagram 5.3(a) and 5.3(b).

Hence, a tunneling spectrum at finite temperature is the combined effect of quasiparticle density of states, thermal broadening and quasiparticle scattering. From the measured tunneling spectra the actual superconducting gap, \( \Delta \) and quasiparticle scattering rate \( \Gamma \) can be extracted with the help of equation 5.8. In this chapter I will be discussing how the quasiparticle scattering rate \( \Gamma \) can be used to extract an important piece of information about the post annealing process of an electron doped high \( T_c \) cuprate superconductors.
To extract the quasiparticle scattering rate $\Gamma$ from the measured spectra, a computer program was written which is provided in Appendix A. The algorithm computes the Jacobian of the equation 5.8 and looks at the difference between the measured spectrum and the fit as a function of the small changes in the parameters. With each step, the algorithm computes this change and diminishes the difference through iterations.

The quality of the fit of the density of states to each spectrum throughout the data set can be demonstrated in a variety of methods. However, the normalized $\chi^2$, the least square fit error was chosen as a measure of the quality of the fit:

$$\chi^2 = \frac{1}{(n-v)} \sum_{i=0}^{n} \frac{(x_i - f_i)^2}{x_i}$$

Equation 5.9 is used to calculate $\chi^2$ which is normalized by the number of points "n".
minus the number of fitting parameters "ν". Here, the parameters, "x" is the measured data value and "f" is the fit value. Typical fitting spectra are shown in fig 5.4(a) and 5.4(b) is the histogram of $\chi^2$. For most of the spectra the smallest value of $\chi^2$ lies between 0.00005 and 0.0005.

Figure 5.4: (a) Red curves represents the positive biased actual data taken with STM at 5.5K for $T_c = 24$K sample and black lines are the best fit curves generated by the program. On the low temperature spectra, two coherence peaks are accompanied by low-energy depression of the quasiparticle density of states as shown in the figure 3.7. Since the research in this section of the thesis is limited around the coherent peaks, the unnecessary spectra are chopped off to save the time needed for the calculation. (b) Histogram of least square fit value for 1024 spectra of a 32 Å x 32 Å map. Each circle represents the best fit value of one spectrum. Most of the spectra have best fit values lying between 0.00005 and 0.0005.

5.2 Quasiparticle scattering through impurities

One of the crucial tests for superconducting state which arise due to a specific mechanism is how magnetic and non-magnetic impurities affect it. Though both magnetic and non-magnetic impurities are pair breakers in conventional superconductors, non-magnetic impurities have a weak effect on superconducting properties while magnetic impurities drastically affect the superconducting state [8]. Within the context of the pioneering
theoretical work of Abrikosov and Gor’kov [9] and its extensions [10, 11], a magnetic perturbation reduces the superconducting order parameter and leads to the appearance of quasiparticle excitations within the superconducting gap. There has been extensive experimental study on impurities in conventional superconductors [8, 12, 13].

However, it is just opposite in the case of high-T\textsubscript{c} cuprate superconductors. Magnetic impurities have a weaker effect on superconducting properties as compared to the non-magnetic impurities [14, 15]. Surprisingly on a macroscopic level, the magnetic and non-magnetic impurities have a smaller effect on superconductivity in cuprates with the exception of Zn-impurity, where Zn suppresses T\textsubscript{c} three times faster than Ni does [16, 17, 18, 19]. However, magnetic and non-magnetic impurities cause very different effects on their local environment.

There has been no doubt that the high-temperature synthesis process of electron doped superconductors evaporates some Cu atoms and creates a Cu deficiency (~1%) in the as-grown NCCO and PLCCO [20, 21]. Kang et. al. suggested that these vacancies behave as the Zn impurities and locally destroy superconductivity [22]. The reason for the necessity of post annealing to induce superconductivity is that there are too many Cu vacancies. Superconductivity is coherent phenomenon which arises from the harmonic behavior of free electrons. Cu deficiencies obstruct the harmony between electrons by scattering them. Post annealing fixes these vacancies and makes the CuO\textsubscript{2} plane defect free. Such defect free CuO\textsubscript{2} planes are naturally present in hole doped superconductors, therefore they don’t need post annealing.
The more the vacancies are repaired, the better superconducting the sample will be. Therefore the sample with higher $T_c$ will have less defects. In this section of the research two PLCCO samples will be explored, one with $T_c = 21$K and the other with $T_c = 24$K. The $T_c = 24$K and 21K samples were obtained by annealing the as grown single crystal in pure Ar at 970 °C and 940 °C for 24 hours respectively [23]. For convenience, the sample with $T_c = 24$K will be referenced as 24K sample and the sample with $T_c = 21$K will be referenced as 21K sample throughout the chapter.

Both samples were grown by Pencheng Dai’s group at University of Tennessee. As grown samples were synthesized by traveling solvent floating zone technique and the samples were annealed in pure Ar environment at different temperature to control the superconducting transition temperature.

5. 2. 1 Local Effect

Literally 21K samples should have more imperfections than 24K samples. This fact can be observed through different impurity related standard scientific techniques; STM is one of them. The Cu vacancies are equivalent to the Zn impurities; therefore they should manifest themselves in STM spectra in the form of some resonances inside the superconducting gap as zinc does in hole-doped superconductors. What was observed is as shown in the figure 5.5. In 21K sample there were two spots (shown with blue circle and oval in fig 5.5 (a)) where some kind impurity spectra were detected. These spectra are shown in figure 5.5 (b). But in 24K sample no such spot was found. Hence there are...
more local defects in 21K samples than 24K samples; which imply that 21K samples should have more Cu deficiencies.

![Schematic diagram of CuO2 plane with Cu sites shown in red. The spectra were taken in 64x64 spots in the 128Å x128Å region of the 21K samples and the impurity related spectra were detected in two places circled with blue line. (b) Waterfall image of spectra taken in the spot shown with blue oval. For the reference, black and orange are the superconducting spectra just before and after the vacancies. However, there are no such impurity related spectra detected in 24K sample.]

**5.2.2 Global Effect**

More impurities in a sample should cause more quasiparticle scattering and that can be seen in the superconducting spectra as a global effect in the form of broadening of the differential conductance spectra. The average of 64 typical spectra of 24K sample is shown in figure 5.6(a) and the average of the 21K spectra is shown in figure 7(b). Since both spectra were taken at the same temperature and similar conditions, the thermal
Figure 5.6: Average of 64 typical STM spectra of the sample with $T_c = 24 K$ (a) and $T_c = 21 K$ (b). The 24K spectra has very well defined sharper coherence peaks compare to those of 21 K spectrum and the superconducting gap is wider in 24K samples. Broadening should be the same in both samples. However, it was found that the spectra of 21K sample were more broadened when compared to those of 24K sample.

Figure 5.7. Histogram of superconducting gap, $\Delta$ of 32Å x 32Å map of 24K sample(a) 21K sample (b). From the histogram it is clear that the mean $\Delta$ for 24K sample is greater by 1 meV compare to that of the 21K sample.
The more broadened coherence peaks in 21K sample can be the indication of more quasiparticle scattering

5.3 Comparison of quasiparticle scattering rate in 21K sample and 24K sample

Figure 5.8 shows the histogram of quasiparticle scattering rate. The scattering rates $\Gamma$ for

Figure 5.8: 32 Å x32 Å histograms of constant scattering rate $\Gamma$: (a) and (c) 24K sample and (b) and (d). The higher scattering rate in $T_c = 21K$ samples can be clearly seen.

24 K sample 5.8 (a) and 5.8 (c) are lower compared to the scattering rates of 21K sample, 5.8 (b) and 5.8 (d). To see the bigger picture spatial maps of quasiparticle scattering rate are plotted in figure 5.9
Figure 5.9: 32 Å x32 Å maps of constant scattering rate $\Gamma$: (a) and (c) 24K sample and (b) and (d) 21K samples. The color scale increases from black (zero) to red (5). The higher scattering rate in $T_c = 21K$ samples can be clearly seen.

Because the coherence length of the high-$T_c$ superconductors is only a few nanometers (40Å for in plane and 3Å for out of plane), a high spatial resolution STM is a necessity when attempting to identify the location and geometry of scattering sites and study their atomic-scale effects on the quasi-particle density of states. Atomically resolved image of
BSCCO 2212 was shown in chapter 2 which is enough to prove the sensitivity of our STM. Hence the maps shown above are very well resolved in real space.

Maps as well as the histograms of $\Gamma$, indicates that the 21K sample should have more scattering centers than that of the 24K sample which may be attributed to the Cu deficiencies in the 21K samples. Hence from local as well as global study of STM spectroscopy it is found that there could be more Cu deficiencies in 21K samples than 24K samples and the post annealing process should be fixing the Cu deficiencies.

### 5.4 Effective Scattering rate: energy dependent approach

All of the calculations and analysis reported above were done with the energy independent quasiparticle scattering rate $\Gamma$. However, Alldredg et. al. claimed that $\Gamma$, the constant scattering rate from near unitary scatterers plays only a subsidiary role. In contrast $\Gamma = \alpha E$ term which represents an effective scattering rate that is linear in energy, plays a key role [24].

Their measurement was done at temperature $T \to 0$ on BSCCO. However, at 5K, in under doped and optimally doped PLCCO, it is found that the mere linear energy dependent of scattering rate, $\Gamma = \alpha E$, is not sufficient. Instead, the best fit takes place with the scattering rate $\Gamma = \Gamma_1 + \alpha E$. The effective scattering rate is the sum of energy dependent and the energy independent parts. The fits through this technique are more accurate compared to the one using a constant scattering rate. Some typical fits are shown in figure 5.10. Quasiparticle scattering rates for 21K sample and 24K sample were
calculated by using the effective scattering rate $\Gamma = \Gamma_1 + \alpha E$.

Figure 5.10: Best fit with PLCCO spectra at 5K using effective scattering rate $\Gamma = \Gamma_1 + \alpha E$.

We find that the energy independent term $\Gamma_1$ is clearly different for the two samples. For 21K samples the best fit is achieved with the value of $\Gamma_1$ from 2 to 3.5 meV whereas for the 24K samples the value ranges from 1 to 1.5 meV. This also indicates that the 21K sample has more defects than the 24K sample. The $\Gamma$ maps calculated through this technique for the energy $E = \Delta$ are shown in 5.11.

**Possible source of $\Gamma = \Gamma_1 + \alpha E$**

Scattering in PLCCO could be elastic or inelastic. Inelastic scattering arises from exchange of dynamic spin fluctuations or phonons, whereas the elastic scattering can arise from impurities and disorder within the conducting copper oxide planes (in-plane impurities) or due to impurities in the neighboring metal oxide planes (out-of-plane
impurities). Pairing disorder scattering by out-of-plane impurities for example, are claimed to be responsible for the inhomogeneity [25, 26] in the gap magnitude.

As established earlier, impurities in PLCCO are mainly Cu deficiencies, which behave like non-magnetic impurities. These scatterers are expected to contribute mainly to elastic scattering. In fact, our experimental data indicate that most of the scattering in PLCCO occurs in the CuO$_2$ planes by non-magnetic unitary scatterers, which are potentially the Cu deficiencies.
This conclusion is supported by the following points: (a) In hole doped cuprates the unitary scatterers in the planes give only a small and roughly constant contribution to the scattering rate [27]. This contribution is limited to energies below 10 meV. For most hole doped materials which show large gaps the coherence peaks are relatively unaffected by this low energy process. However, the coherence peaks in PLCCO lie below 10 meV and the effect of these unitary scatters should be visible in STM spectra. (b) In BSCCO, the maximum value of $\Gamma$ is around 4 meV which is about 10% of the average $\Delta$ (40 meV) [28], whereas the average $\Gamma$ for 24K PLCCO sample is about 2.5 meV which is about 35% of the average gap (7 meV). It is even higher in 21K sample about 45% of $\Delta$. (c) Moreover, Kaminski et al [29] suggested that out of $\Gamma = \Gamma_1 + \alpha E$, the energy independent part ($\Gamma_1$) is due to elastic scattering and energy dependent part is due to inelastic scattering. Not being able to fit our STM spectra without energy independent part further enhances the importance of in-plane elastic scattering in our experiments.
References:


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Chapter 6

Bosonic Modes

6.1 Introduction

According to the Pauli Exclusion Principle two fermions cannot have the same quantum numbers. However, nature is full of wonders! Two or more than two protons occupy the same nucleus in multi electron atoms. How does this happen? They are forced to stay together by a glue stronger than their repulsive force. In other words they form a strong bond with each other by exchanging particles called gluons. Today, the mechanism of gluing and ungluing protons by exchanging gluons is known and understood; if enough energy is applied to bring the protons into femto-meter range, they get glued together, and correspondingly ungluing them require the same amount of energy. Similarly, in superconductivity two electrons get glued together by a glue (bosonic mode) which is the major research topic in this chapter.

In conventional superconductors, those bosonic modes are phonons [1]. The exchange of phonon creates a bond between two electrons and glues them together. However, the source of glue that binds two electrons together in high $T_c$ cuprate superconductors is still unknown. Two contenders for superconducting glue in these materials are lattice vibrations [2, 3] (phonons) and spin-excitations [4, 5], with the additional possibility of pairing without mediators [6].
6.2 Bosonic modes and tunneling spectra

In conventional superconductors, phonon-mediated pairing was unequivocally established by many major relevant experiments including the tunneling experiments [7]. Using the strong coupling limit of Eliashberg formalism, McMillan and Rowell calculated the phonon density of states out of the electronic density of states [8, 9].

They found that the lattice vibrations that mediate electron pairing have signature at the energy greater than $\Delta$. At certain energies the second derivative of tunneling current, $d^2I/dV^2$ has minimum values. Figure 6.1(b) provides a good illustration. A is the derivative of the conductance spectra B, and C is the mode of lattice vibrations. In the superconducting state, the phonons appear in the tunneling spectra at an energy offset by
the superconducting gap, that is, \( E = \Omega + \Delta \) where \( E \) is the energy of the feature in the spectrum and \( \Omega \) is the mode energy. Since the tunneling spectra provide \( E \) and \( \Delta \) the mode energy of the phonon involved in pairing can be calculated by:

\[
\Omega = E - \Delta
\]

This theory has been quite successful in conventional superconductors and has been extended successfully for hole-doped cuprates. Recent scanning tunneling microscopy experiments on hole-doped Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) (BSCCO) revealed signature of an oxygen lattice vibrational mode whose energy is anticorrelated with the superconducting gap energy scale [10]. Here we show that high resolution scanning tunneling microscopy measurements of PLCCO (\( T_c = 24 \)K) reveal a bosonic excitation at energies of 10.5\( \pm \)2.5 meV. This energy is consistent with both spin-excitations in PLCCO measured by inelastic neutron scattering and a low-energy acoustic phonon mode [11], but differs substantially from the oxygen vibrational mode identified in BSCCO.

6.3 Signature of Bosonic modes in PLCCO spectra

In order to find the bosonic modes that pair electrons in the electron doped cuprates the study is focused on the segment of the STM spectra with energy higher than \( \Delta \) especially in the regions denoted by the arrow in fig 6.2(a). A step-like feature in the DOS (which results in a peak in the second derivative of the tunnel current \( d^2I/dV^2 \)) is normally interpreted as the signature of a bosonic excitation in the system. The derivative of
spectrum (Fig. 6.2b) reveals peaks at distinct energies marked E₁ and E₂. The result of the typical spectra shown in the figure 2a is shown in table 1. Because spectral features at multiples of Ω₁ could arise from multi-boson excitations, Ω₁,2 are found to be amenable to interpretation as multiples of the same mode Ω₁ at 10 ± 0.15 meV.

<table>
<thead>
<tr>
<th>Δ (meV)</th>
<th>E₁ (meV)</th>
<th>E₂ (meV)</th>
<th>Ω₁ = E₁ - Δ</th>
<th>Ω₂ = E₂ - Δ</th>
<th>Ω* = E₂ - E₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>17.7</td>
<td>28.7</td>
<td>10.7</td>
<td>21.7</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 6.1: Result from the typical spectra shown in fig 2

Figure 6.2 (a) A typical dI/dV spectrum taken at 5.5K by our STM with arrows indicated the region of interest. (b) The same spectrum from a (purple) as well as its derivative, d²I/dV² (red). The linear V-shaped background has been divided out for clarity and the spectra are now shown only for energies greater than the Fermi energy (EF). The peak in dI/dV (at 7.0meV) is the coherence peak, labelled as ΔR. The peaks in d²I/dV² are labelled as E₁ and E₂ respectively (ref. 26).

To determine the statistical significance of the modes high-resolution dI/dV maps over many regions of the samples were obtained and were analyzed to extract Δ and E locally. Data from one such map is shown in Fig. 6.3. The observation of multiples of Ω₁ allows
us the extraction of $\Omega_1$ in two different ways for each spectrum: $\Omega_1 = E_1 - \Delta$ and $\Omega^*_1 = E_2$

![Figure 6.3: A histogram of the occurrences of $\Delta_R$ (purple) and the energies $E_1$ and $E_2$ (red) for a map of $dI/dV$ on a 64 A° x 64 A° area of the sample. The average gap ($\Delta_{av}$) in this region is calculated to be 7.7±0.5meV, and the average peaks to be $E_{1av} = 18.5±1.5meV$ and $E_{2av} = 28 meV$ (our cut-off at 30 meV for this analysis prevents obtaining full statistics for $E_2$) (ref. 26).

- $E_1$. These are independent observables whose histograms are plotted in Fig. 6.4(A) and 6.4(B). As can be seen, the two histograms overlap strongly. It is therefore concluded that the identification of $\Omega_2$ as 2 $\Omega_1$ bears significant statistical weight, which further supports the identification of these features outside the superconducting gap as originating from bosonic excitations in PLCCO. In other word, both energies should be the harmonics of a single oscillation. Using the data from eight $dI/dV$ maps (Fig. 6.4B), an average mode energy of $\Omega_{1av} = 10.5±2.5$ meV was obtained.
From these spatially resolved spectra, the correlation between the local mode $\Omega(r)$ and the gap $\Delta(r)$ can be calculated. It was found that $\Omega(r)$ is anticorrelated with the local gap magnitude $\Delta(r)$ as visible in Fig. 6.5a. The correlation function obtained between the two is fairly short-ranged, with a normalized on-site ($r = 0$) value close to 20.4, comparable to that found in BSCCO. This anticorrelation is the first indication that this signal arises from an intrinsic excitation rather than an extrinsic inelastic excitation outside the superconducting plane.

Figure 6.4: (A) Following convention in superconducting systems, the mode energy will be symbolized by $\Omega$ ($\Omega_i = E_i - \Delta$). The mode energy is calculated in two ways for each spectrum in the map: $E_1 - \Delta$ (blue) with a mean of $10.7 \pm 1$ meV and $E_2 - E_1$ (green) with a mean of $10 \pm 1.7$ meV. These are two independent variables and the remarkable overlap between these histograms lends weight to their identification as multiples of the same mode. (B) Histogram of the mode energies $\Omega_1$ (blue) and $\Omega_2$ (pink) summed for eight maps in different areas of the sample with gaps ranging from 6.5meV to 8.5meV. The mode energies were extracted from above and below $E_F$. From these data, the average mode energy $\Omega_{\text{av}} = 10.5 \pm 2.5$meV was obtained (ref. 26).

6. 4 Contenders for pairing glue

By taking account of the actual gap and the measured gap it was found that the energy of
the bosonic mode which could mediate to pair the electrons for superconductivity in high

Figure 6.5 (a) variation of local mode energy and intensity with the local gap energy scale. a, Log intensity (two-dimensional histogram; blue to yellow shows minimum to maximum) of the occurrences of $\Omega_1$ and $\Omega_2$ plotted as a local ratio $\Omega(r)/2\Delta(r)$ against $\Delta(r)$, clearly revealing the anticorrelation between $\Omega$ and $\Delta$. Now the major question is to identify the source of this energy. There are many contenders that can possibly have this energy mode but two of them are very prominent. One is the phonon and the other a spin excitation.

**Contender # 1: Phonon**

As a well known mediator of conventional superconductors the field of lattice vibrations should be explored first. As shown in figure 6.5 it was found that $\Omega$ is anticorrelated with $\Delta$. This is strong reason to believe that if phonons mediate the pairing they should come from the CuO$_2$ plane. Thus the hunt can be focused on the CuO$_2$ plane.

The mode originates from in-plane (CuO$_2$ plane) phonons, like the B1g mode attributed to the STM feature in BSCCO. Compared with BSCCO, however, the energy scale of the mode (10.5±2.5 meV) is much lower. In the hole-doped superconductors a few phonon branches do exist at these low energies [12,13] and the important question is whether there are candidate phonons at these low energies in PLCCO. As it turns out, many of the in-plane phonons in closely related materials, including the B1g mode, have energies higher than 20 meV [14-16] and can therefore be ruled out. Acoustic phonons are viable
Figure 6.5: (a) Variation of local mode energy and intensity with the local gap energy scale. a, Log intensity (two-dimensional histogram; blue to yellow shows minimum to maximum) of the occurrences of $\Omega_1$ and $\Omega_2$ plotted as a local ratio $\Omega(r)/2\Delta(r)$ against $\Delta(r)$, clearly revealing the anticorrelation between $\Omega$ and $\Omega$. Also note that $\Omega_1(r)/2\Delta(r)$ remains below 1 for a statistically significant part of the data (whereas $\Omega_2(r)/2\Delta(r)$ remains below 2). This demonstrates the sensitivity of the mode to the energy scale $2\Delta$, which is also borne out by the intensity analysis in b and c. This plot includes data from three maps obtained in regions of the sample with different average gap values. b, Examples of $d^2I/dV^2$ spectra (from one map) for different ratios of $\Omega/2\Delta$ from 0.3 to 1.03. The intensity of the mode (defined as the height of the peak in $d^2I/dV^2$ spectra) decreases and the mode gets wider in energy as $V$ approaches $2\Delta$. Although both $V$ and $D$ can vary from spectrum to spectrum, it is the local ratio of $\Omega(r)$ to $2\Delta(r)$ that determines the intensity of the mode. This is consistent with increased damping of the mode associated with the onset of the continuum of excitations at $2\Delta(r)$. c, A plot of the mode intensity (reiterating the same behaviour as in b) now for all the measured bosonic modes in a single map. Similar intensity drops with the ratio $\Omega_i/2\Delta$ were observed for maps in different regions with average gaps ranging from 6.5 meV to 8.5 meV (ref 26).
candidates for this mode provided that the phonon dispersion results in a sharp DOS feature at this energy scale. Such phonons with a DOS peak at or close to 11 meV have indeed been found [11,17, 18] in NCCO, fig 6.6 (a). Expanding the search to in-plane phonons at nearby energies reveals an Eu oxygen mode [15] and an oxygen rotation mode [14] at energies greater than 15 meV (15 meV is the lowest energy in the dispersion). Thus the conclusion is that whereas the energy scale of the observed mode clearly rules out the B1g oxygen phonons, at least one in-plane phonon (acoustic) mode does exist at nearby energies.

Apart from these in-plane phonons, the STM mode might arise from inelastic cotunnelling processes [19] involving an excitation of a local vibrational mode in the intervening layers between the tip and the superconducting plane (‘barrier’ mode). Such ‘out-of-plane phonons associated with the apical oxygen have been postulated as an alternative explanation for the BSCCO data [20]. Although barrier modes in PLCCO might originate from Pr/La/Ce vibrational excitations in the layers adjacent to the CuO₂ planes, it is not obvious how such modes would lead to these observed correlations between \( \Omega(r) \) and \( \Delta(r) \). Indeed, based on the idea that this correlation is significant, one recent analysis of the BSCCO STM data [21] postulates two coexisting bosonic modes, only one of which is sensitive to the superconducting gap and can be considered as a signature of the neutron resonance mode in BSCCO. In conclusion, most of the in-plane phonon modes are unlikely except for one acoustic phonon mode, fig 7 (a).
**Contender # 2: Spin excitation**

PLCCO is an antiferromagnetic Mott insulator in its parent state. When the material is doped with electrons the static antiferromagnetism gets destroyed but the antiferromagnetic correlations still exist. The mode of energy of such dynamic magnetism is quantized and can be measured by inelastic neutron scattering. The particle nature of these magnetic quanta is known as magnon. These magnons are bosons and they could help two electrons to get glued together to form a cooper pair. Hence magnons are also strong contenders for superconducting glue in high $T_c$ cuprates. The measured energy mode of $10.5 \pm 2.5$ meV suggests an immediate connection to the 11-meV magnetic resonance mode discovered recently in PLCCO [22] fig 6.6(b), and NCCO [23] at $Q = (K, K, 0)$ by inelastic neutron scattering.

The neutron resonance mode, or more precisely its precursor above $T_c$, has been suggested as a possible pairing glue for the high-$T_c$ copper oxides. Theoretically, bosonic modes originating from spin-excitations can be observed by STM provided there is sufficient coupling between the charge and spin degrees of freedom [24]. Magnetoresistance measurements on underdoped non-superconducting $\text{Pr}_{1.32-x}\text{La}_{0.7}\text{Ce}_x\text{CuO}_{4-\delta}$ have provided evidence for strong spin–charge coupling in these materials [25]. It is thus possible that the magnetic resonance mode observed by neutron scattering is related to the observed bosonic mode in the STM signal in PLCCO.
Figure 6.6: Ref [11] one of the two possible modes of energy acoustic phonons shown by an inelastic x-ray scattering. The small bump around 11 meV magnified in the inset represents a phonon. Two sharp peaks around zero are the peaks due of elastic scattering (B) Wilson et. al (ref 22) found a magnetic resonance at 10 meV.

Although the low-energy phonons cannot be ruled out, this mode is fully consistent with the neutron spin resonance mode, and strongly coupled to the superconducting order parameter, making it a compelling candidate boson in the model based on the Eliashberg framework, where exchanging associated electronic (spin or charge) excitations serves as the unconventional pairing mechanism in these materials.
References


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Appendix A

C++ fitting program

//This program calculates Density of States of D-wave superconductivity at 5K

//it generates superconducting spectra from theory and match them with measured STM
//spectra to obtain actual gap

#include <cstdlib>
#include <iostream>
#include <complex>
#include <math.h>
#include <fstream>
#include <ctime>

#define R 2000
#define C 300
using namespace std;

double **s1,**s2,**s3,*s,*ss,*hh;

int Min(const double *b, const int count)          // Defined minimum function
double min = fabs(b[0]);

int temp;

for(int i =0; i < count; i++){
    if(min > fabs(b[i])){
        min = fabs(b[i]);
        temp = i;
    }
}

return temp;

double max(const double *bb, const int count)//max function to return the gap.
{
    double max = fabs(bb[0]);
    int temp;

    for(int i =0; i < count; i++){
if(max < fabs(bb[i])){

    max = fabs(bb[i]);

    temp = i;

}

return s3[0][temp];

}

double max1(const double *bbb, const int count)// max function to return the index of the gap
{

double max1 = fabs(bbb[0]);

int temp1;

for(int i = 0; i < count; i++){

    if(max1 < fabs(bbb[i]))

        max1 = fabs(bbb[i]);

        temp1 = i;

}
return max1;
}

int main(int argc, char *argv[])
{
    // ****************************Declaring Variables***************************

    complex <double> *e,*e1,*e2,**dos,*v,*f,*r,*r1;
    double *f2,**f1,**ff1,**ff2,*hh1,*x,**lamdaSq,**f3,**f4,**f5,**f6;
    int nn1,i,j,k,k1,k3,k2,*error,*error1,*count1,*count2,nofSpectra=65;
    int nn = 120, n =40, m = 25, m1=64, n1 = 12, n2 =12;
    complex <double> h1(0.3,0),h3(0.2,0),h4(0,0.2),h5(0,1.6), b(1,0),**d,*gamma;
    double start, end, ApproxTime;
    double  l =0, u = 3.14, h2, t = 5;

    //-----------------------------------------------------------------------------------------------
/m0 is the first spectra to start, it can't take a value less than 1, and m-m0 <2;

//nn = total # of energy states integrated over, n = number of Points used to match
//spectra

//m = # of angle section integrated over, m1 = # of spectra matched; n1 = gamma points,
//n2 = delta points.

//count1[1000], count2[1000], count3[1000], count4[1000];

//----------------------------------------------------------------------------------------------------------------------

start = time(NULL);       // time count starts here

s1 = new double *[R];

s2 = new double *[R];

s3 = new double *[R];

s = new double [R];

ss = new double [R];

hh = new double [R];

e = new complex <double> [R];

r = new complex <double> [R];

rl = new complex <double> [R];
e1 = new complex <double> [R];
e2 = new complex <double> [R];
v = new complex <double> [R];

f = new complex <double> [R];

gamma = new complex <double> [R];

x = new double [R];

f2 = new double [R];

hh1 = new double [R];

count1 = new int [R];

count2 = new int [R];

error = new int [R];

error1 = new int [R];

lamdaSq = new double * [R];

d = new complex <double> * [R];

dos = new complex <double> * [R];

f1 = new double * [R];

ffl = new double * [R];
ff2 = new double*[R];

f3 = new double *[R];

f4 = new double*[R];

f5 = new double*[R];

f6 = new double *[R];

for(i =0; i< R; i++)
{
    s1[i] =new double [C+1];
    s2[i] = new double [C+1];
    s3[i] = new double [C+1];
    d[i] = new complex<double> [C+1];
    dos[i]= new complex<double> [C+1];
    f1[i]= new double [C+1];
    ff1[i] = new double[C+1];
    ff2[i] = new double[C+1];
    lamdaSq[i] = new double[C+1];
f3[i] = new double[C+1];

f4[i] = new double[C+1];

f5[i] = new double[C+1];

f6[i] = new double[C+1];

} //***********Read Data file**************

ifstream in;

in.open("FileName.txt");

for (i = 0; i < n; i++)

for (j = 0; j < nofSpectra; j++)

{

    in >> s1[i][j];

}

for (i = 0; i < n; i++) // Trim the size

for (j = 0; j <= m1; j++)

{

}
s2[i][j] = s1[i][j];

}

for (j = 0; j <= m1; j++)  //Invert data for max/min

for (i = 0; i < n; i++)
{
    s3[j][i] = s2[i][j];
}

in.close();

i = 0;

for ( i =1; i<=m1; i++)
{
    s[i] = max(s3[i],n);// get gap of the spectra
    ss[i] = max1(s3[i],n);// get maximum value of a spectra
    hh[i] = ss[i]-s2[0][i];  // difference between maximum point and min point
    cout << " s[" << i << "] = " << s[i] << "   ss[" << i << "] = " << ss[i] << " hh[" << i << "] = " << hh[i] << endl;
}


cout << endl;

//*********** Initializing theoretical Parameters *******************

k3 = 0;

for (k3 = 1; k3 <= m1; k3++)  // initialize delta (d = gap)
{
    if(s[k3] >= 9 || s[k3] <= 5)
        d[k3][0] = 5;
    else
        d[k3][0] = s[k3] - 3;

    cout << " d[" << k3 << "][0] = " << real(d[k3][0]) << "  s[ " << k3 << "] = " << s[k3] << endl;
}

gamma[0] = h5;                // initialize gamma

//************************Theory starts here**************************

for (k2 = 0; k2 < n2; k2++)
\{ 
\text{d}[k3][k2+1] = d[k3][k2]+ h3; 

\text{for (k1 = 0; k1 < n1; k1++)} 
\{ 
\text{gamma}[k1+1] = gamma[k1]+ h4;  \quad //\text{gamma = scattering rate}

\text{for (k = 0; k < nn; k++)} 
\{ 
\text{v}[0] = -0.3*nn/2; 

\text{v}[k+1] = v[k]+ h1; \quad // v = bias voltage

\text{for (i = 0; i < nn; i++)} 
\{ 
\text{e}[0] = -0.3*nn/2; // e = energy

\text{e}[i+1] = e[i]+ h1;

\text{if(real(e[i])<0)} \quad // e2 takes care of negative values
\text{e2}[i] = -e[i];

\text{else}
\} 
\} 
\}
e2[i] = e[i];

e1[i] = e2[i] - gamma[k1];

for (j = 0; j < m; j++)
{
    h2 = (u - l)/m;

    x[0] = 0; // x = theta angle

    x[j+1] = x[j] + h2;

    r[i] = e1[i] * e1[i] - d[k3][k2] * d[k3][k2] * cos(2*x[j]) * cos(2*x[j]);

    if (real(r[i]) == 0)
    {
        r1[i] = r[i-1];
    }
    else r1[i] = r[i];

    if (real(v[k]) <= 0)
    {
        f[i] = (11.6/t) * (exp(11.6*(e[i] + v[k])/t)) / pow((b + exp(11.6*(e[i] + v[k])/t)), 2));

        // fermi fn derivative

        dos[n1*k2+k1][k] = dos[n1*k2+k1][k] + f[i] * sqrt((e1[i] * e1[i]) /...
r1[i]; //dos calculation

} // Densities of states calculation for negative bias

else
{

f[i] = (11.6/t)*((exp(11.6*(e[i]-v[k])/t))/pow((b+exp(11.6*(e[i]-v[k])/t)),2));

dos[n1*k2+k1][k] = dos[n1*k2+k1][k] + f[i]*sqrt((e1[i]*e1[i])/r1[i]);

} // Densities of states calculation for positive bias

} //j

} //i

} //k

//***************End of Theoretical Calculation***************

//***************Matching calculated spectra with measured ones by least sq fit***************

for( k =0; k <n; k++)
{

f1[n1*k2+k1][k] = real(dos[n1*k2+k1][k+60]);
\[ f_2[k2*n1+k1] = \max_1(f_1[k2*n1+k1],n); \quad \text{// maximum value of calculated spectra} \]

\[ hh_1[k2*n1+k1] = f_2[k2*n1+k1]-f_1[k2*n1+k1][0]; \quad \text{// height (max-min) of calculated spectra} \]

\[ \text{cout}<< " hh1["<<k2*n2+k1<<"] " <<hh1[k2*n1+k1]"<<" " ; \]

\[ \text{for( k =0; k < n; k++)} \]

\[ \{ \]

\[ f_1[k2*n1+k1][k] = (hh[k3]/hh1[k2*n1+k1])*f_1[k2*n1+k1][k]; \quad \text{//making calculated and measured height same} \]

\[ f_2[k2*n1+k1][k] = f_1[k2*n1+k1][k]-f_1[k2*n1+k1][0]-s3[k3][0]; \quad \text{//making same initial value} \]

\[ \text{lamdaSq[k3][k2*n1+k1] +} = \text{pow((s3[k3][k]-f_2[k2*n1+k1][k]),2)/((n-2)*s3[k3][k]); \quad \text{// least square equation} \]

\[ \} \]

\[ \text{cout <<"lamdaSq[" <<k2*n1+k1<<"] : " <<lamdaSq[k3][k2*n1+k1] << " gamma[" <<k1 <<"] = " <<imag(gamma[k1])<< endl ;} \]

\[ \text{cout << endl; \quad \text{// Display error and gamma.} } \]
cout << " d["<<k3<<"] = " << real(d[k3][k2]) << endl;
}

error[k3] = Min(lamdaSq[k3],n2*n1); // min value of least square

if(error[k3]>=144) //round out if there is some synthetic error
    error1[k3]=66;
else
    error1[k3] = error[k3];
    
    cout << " error["<<k3<<"] =  "<<error[k3] << endl;

    count1[k3] = (error1[k3])%n1; // this gives gamma k1
    cout << " count1["<<k3<<"] =  "<<count1[k3] << endl;

    count2[k3] = (error1[k3]-count1[k3])/n1; // this gives value of k2
    
    for( k = 0; k < n; k++)
    {
        f3[k3][k] = ff2[error1[k3]][k];
ofstream out;
out.open("matched-spectra.txt");

for(k3 =0; k3 <=m1; k3++)
    for( k = 0; k < n; k++)
    {
        f4[k3][k]=f3[k3+1][k];
        f5[k][k3] = f4[k3][k];
    }

for (k = 0; k < n; k++)
    for (k3 =0; k3 <=2*m1; k3++)
    {
        f4[k][0]=s3[0][k];
    }
if(k3%2==0)  

    f6[k][k3]= s2[k][k3/2];                           // measured value  

else  

    f6[k][k3]=f5[k][(k3-1)/2];                       // calculated value  

}  

for (k = 0; k < n; k++)  

{  

    for(k3 =0; k3 <=2*m1; k3++)  

    {  

        out <<" " << f6[k][k3];  

        cout <<" " << f6[k][k3];  

    }  

    out << endl;  

    cout << endl;  

}  

out.close();
//***************Write Error (lambda), gap(d) and gamma***************

ofstream out2;

out2.open("lamda_gamma_delta.txt");

k3 = 0;

for (k3 = 1; k3 <= m1; k3++)
{
    out2 << "   " << lamdaSq[k3][error1[k3]] << "   " << real(d[k3][count1[k3]]) << "   " << imag(gamma[count1[k3]]) << "   " << endl;
    cout << "   " << lamdaSq[k3][error1[k3]] << "   " << real(d[k3][count1[k3]]) << "   " << imag(gamma[count1[k3]]) << "   " << endl;
    cout << endl;
    cout << endl;
}

end = time(NULL);

ApproxTime = (end - start); // how long program ran
out2 << "Time Taken =" <<ApproxTime/60 <<" min "<< endl;
out2.close();
cout << "Time Taken =" <<ApproxTime/60 << " min"<<endl;
for ( i =0; i <R; i++)
   delete s1[i],s2[i],s3[i],d[i],dos[i],f1[i],ff1[i],ff2[i],lamdaSq[i],f3[i],f4[i],f5[i],f6[i];
delete s, hh, ss, s1, s2, s3, e, e1, e2, x, f, v, d, gamma, dos, f1, f2, ff1, ff2, lamdaSq,
error, error1, count1, count2, f3, f4, f5, f6, hh1;

system("PAUSE");

return EXIT_SUCCESS;
Appendix B
STM Construction
Scheme I

Vertical Magnetic manipulator

Spring as a part of vibration isolation

Vacuum chamber

Enlarged view of the highlighted region is shown in next page

STM

Magnetic vibration isolation

Table

ion pump
2D-image of STM body counter part together for home build cryogenic STM
3D Autocad Drawing: STM body counter part
STM body Sample holder and STM body counter part together