Use of tunneling spectroscopy in high-temperature superconductivity

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1 Introduction

Superconductivity is one of the most interesting phenomena that has been observed in material in recent history. Despite being discovered in 1911, it was nearly 50 years before a universal theory was published describing the observation. The Bardeen, Cooper, and Schrieffer (BCS) Theory became the universally accepted basis for superconductivity. Among the many experimental techniques to test BCS theory, quasiparticle tunneling introduced by Giaever [1] was the most promising. He theorized that the derivative of the current-voltage
spectra—the tunneling/differential conductance—has a voltage dependence that reflects the BCS quasiparticle density of states (DOS). Probing DOS is a key method when investigating superconductivity signatures in electronic spectra. Giaever’s theory was given a firm basis by Bardeen in 1961. [4]

Twenty years later, tunneling microscopy saw a major advancement with the development of the scanning tunneling microscope (STM) by Binnig and Rohrer. This exciting advancement allowed the possibility to conduct scanning tunneling spectroscopy (STS) with a spacial resolution down to the atomic scale. Around the same time a new species of high temperature superconductors were discovered. The two events set into motion a variety of new activity in the superconductivity field. The goal of the paper is to explain the theory of tunneling microscopy and the role it had in superconductivity research. It will also cover important research that can only be done using STM/ST including: gap spectroscopy, the pseudogap, and temperature dependence.

2 Scanning Tunneling Microscopy and Spectroscopy

The invention of scanning tunneling microscopy by Binnig and Rohrer[3] was a major advancement beyond superconductivity research. It provided experimental physicist the ability to image and probe conductive surfaces with atomic spacial resolution. Scanning tunneling spectroscopy measures the tunneling current of electrons tunneling from a metallic tip to a conductive sample through an insulating barrier, in most cases a vacuum. The tunneling microscope scans by controlling the tip-sample spacing through piezoelectric ceramics. Piezoceramic technology produces picometer control of the STM tip leading to atomic resolution to scan topographically and probe local density of states (LDOS). The precision of STM is a key factor that opens insight into the fundamental properties of superconductivity.

This section will briefly cover the theory of STM/STS and the experimental aspects of a tunneling experiment.

2.1 Experimental Aspects of STM

As mentioned previously, scanning tunneling microscopy uses quantum tunneling of electrons through thin vacuum potential barrier. (see fig 2.1a) While quantum tunneling was known since the invention of quantum mechanics, Giaever was the first to use it to study the superconducting gap in superconductor/insulator/normal metal (SIN) junctions.[1] However in Giaever’s case there was no spatial resolution. This changed when the scanning tunneling microscope was developed in 1981 by Binnig and Rohrer.[3] Their idea was to mount an conical metallic tip to a 3-dimensional piezoelectric drive. (see fig 2.1b) Applying a sawtooth voltage to the x-drive and a ramp voltage to y-drive causes the piezos to expand and contract forcing the tip to raster across the x-y plane, while the z-drive height is controlled by a feedback loop. Applying a voltage across the tip-sample junction creates a measurable tunneling current leading to a resolution down to the sub-angstrom scale. [2] This resolution is possible from the exponential dependence of the tunneling current $I$ and potential barrier space $d$:
Figure 2.1: Principle of STM (a) The quantum mechanical process of tunnel between tip-to-sample. The vacuum at the junction is treated as the potential barrier with width \( d \) and a height \( \Phi \) (work function). The electron wave function \( \Psi_1 \) decays exponential into the barrier and overlaps with the bulk wave function \( \Psi_2 \), allowing tunneling. Electrons can either tunnel from tip-to-sample or vice versa depending on bias voltage parameters. (b) Schematic of a standard STM. STMs operate ideally with a single atom termination at the tip. From [31]

\[
I \sim e^{-2\kappa d}, \quad \kappa = \sqrt{\frac{2m\Phi}{\hbar^2}} \approx 0.5\sqrt{\Phi(eV)} \AA^{-1}
\]  

(2.1)

A standard metallic sample (\( \Phi \sim 5eV \)) will see a current drop of about 1 order of magnitude per 1 angstrom increase in \( d \). For reference, the following parameters are typical for tunneling experiments: tip-sample distance \( d \) (5 - 10 Å), tunneling current \( I \) (0.01 - 10 nA), and bias voltage \( V \) (0.01 - 2 V).

2.2 STM Modes

As we know, STM offers the ability to measure topographic and spectroscopic data at a local scale. For topographic measurements, the surface is mapped using the tip-sample distance dependence and tunneling current. For spectroscopic measurements, the LDOS is measured using the tunneling conductance. Both modes will be discussed in this section beginning with Topography.

**Topography**

There are two types of methods that measure topography. The first method is called "Constant-Current Imaging". The tunneling current is kept constant in constant current mode. Using a feedback-adjustments, the tip-sample distance is continuously being adjusted so that current remains constant. (see fig 2.2a) The recording of tip height as a function of its 2-dimensional position gives a 3-dimensional image of the surface.
The second method is called "Constant-Height Imaging". In constant-height the tip-sample distance is held fixed and variations in tunneling current are recorded at the tip positions. (see fig 2.2b) Both methods have flaws that need to be accounted for before scanning. For example, in constant-height imaging can achieve fast scanning but the scan area must be relatively flat with corrugations less than a few angstroms. [31]

**Local Spectroscopy and Spectroscopic Imaging**

A more sophisticated operation of STM is the measuring of local electronic density of states. The operation of scanning tunneling spectroscopy (STS) allows measurements of the density of states (DOS) by measuring the tunneling current as bias voltage is modulated with a fixed tip. The theory of tunneling conductance is non-trivial, but the result is worth considering. The following is the equation for tunneling conductance.

\[
\sigma(V) = \frac{dI_s}{dV} = \frac{2\pi e^2}{\hbar}|T|^2N_t(0)N_s(eV) \tag{2.2}
\]

Eq 2.2 has some important features to consider. First is the quantity \(T\), which is known has the tunneling matrix element. This element is often hard to evaluate, but essentially depends on the geometry of the tunneling junction. Next is the measured DOS: \(N(\omega)\), with \(t\) and \(s\) denoting 'tip' and 'sample'. Eq 2.2 shows the following result: that bias dependence of tunneling conductance allows direct measurements of the DOS provided that \(T\) is known. It is important to note that this result is not always acceptable, but as shown by Giaever [1] it is an acceptable answer to understand qausiparticle DOS.

Tunneling conductance, often called \(dI/dV\) spectra, can be probed by taking derivatives of the \(I(V)\) curves measured, or by lock-in amplification technique. In lock-in amplification, an AC modulation is imposed to the bias voltage and the resulting current modulation is measured.

A popular spectroscopic technique often used in tunneling experiments is current-imaging tunneling spectroscopy (CITS). In CITS, an array is composed over a set sample area. A tip scans across the sample area with set scan parameters, measuring topographic data. At each array point the scan parameters and tip are frozen to measure spectroscopic data before resuming the topographic scan. The result is a topographic image with simultaneous
spectroscopic data. An important feature of CITS is the ability to create simultaneous spectroscopic maps at different energies in a single topographic scan.

The next section will explore the theory of electron tunneling and how to interpret superconductor tunneling experiments.

3 Electron Tunneling and Interpretation

The theory of electron tunneling began around the same time that quantum mechanics was created. Most tunneling experiments done on superconductors uses the Hamiltonian formalism. This section is dedicated to exploring the Hamiltonian tunneling formalism and the incredibly important tunneling matrix element. It will also explore common theoretical interpretations of tunneling experiments of high temperature superconductors (HTS).

3.1 Theory of Electron Tunneling

Electron tunneling is considered to be a transport phenomena. Particles hop across some vacuum or insulating barrier making the process a nonequilibrium event. However in STM experiments, the current amplitude is low enough that time between two tunneling events is longer than the quasiparticle relaxation time [31]. Thus it is safe to take an equilibrium stance and to assume that there are no correlations from the barrier and that a tunneling event is a single electron hopping. These assumptions lead to the tunneling Hamiltonian formalism.

Hamiltonian Formalism

The Hamiltonian formalism according to Bardeen and Cohen [4] [5], begins with two materials forming a tunneling junction. (see fig. 3.1a) Each material are considered to be independent system. The exchange of particles between the barrier is described by the Hamiltonian:
\[ H_T = \sum_{\lambda\rho} T_{\lambda\rho} c^\dagger_\rho c_\lambda + h.c. \] (3.1)

The indices \( \lambda \) and \( \rho \) represent states on the left and right sides of the junction in fig. 3.1a. The creation operator \( c^\dagger_\rho \) creates a particle in state \( \phi_\rho \) and the annihilation operator \( c_\lambda \) eliminates a particle in state \( \phi_\lambda \). \( T_{\lambda\rho} \) is the tunneling matrix element mentioned in section 2.2.

For a small bias across the junction, the tunneling current is given as the rate of change of particle number on the right side.[5] By using this statement, eq. 3.1 and some work, the single particle tunneling current becomes:

\[
I_s = \frac{2\pi e}{\hbar} \int d\omega [f(\omega - eV) - f(\omega)] \times \sum_{\lambda\rho} |T_{\lambda\rho}|^2 A_\lambda(\omega = eV)A_\rho(\omega)
\] (3.2)

The function \( A(\omega) \) are the single particle spectral functions for the left and right material. \( f(\omega) \) is the Fermi function. The Fermi factors in eq. 3.2 select the energy interval where the occupied states of the left side material and the empty sides of right side can align. The remaining terms drive the tunneling of electron within that interval. Tersoff and Hamann [6] related the DOS:

\[
I_s = \frac{2\pi e}{\hbar} \int d\omega [f(\omega - eV) - f(\omega)] \times N_{\text{tip}}(\omega - eV)N_{\text{sample}}(x, \omega)
\] (3.3)

Tunneling Matrix element \( T \)

As shown earlier, the tunneling matrix element is found in almost all related tunneling phenomena. Instead of investigating the direct definition and evaluation of \( T \), it will be better to state a few simple facts to remember going forward. The tunneling matrix depends upon two entities: the geometry of the tunneling junction, and the electronic states on both side of the barrier.

For planar junctions, \( T \) has a large dependence on barrier thickness \( d \) which suggests the tunneling current is dominated by states with large out-of-plane velocity components in \( z \).

For STM junctions, often a cut Pt/Ir wire, the tunneling matrix is harder to calculate. Tersoff and Hamann proposed a solution by representing the tip apex as a spherical potential well. The result showed that the tunneling matrix is proportional to the sample wave function [6].

Each junction type has certain sensitivities to sample surfaces and need to be accounted for accordingly depending on the experiment.

3.2 Interpretation of HTS Tunneling Experiments

STM results require consistent interpretation in two parts. The first concerns a question of the electronic nature of the material being measured. The second is the question of tip-surface interactions themselves. The answer to the first question has been answered by
Figure 3.2: Crystal structure for two different cuprates. (a) A Tetragonal unit cell of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ with $a = b = 5.4\,\text{Å}$ defined along $[1\,1\,0]$ and $[\overline{1}\,1\,0]$. (b) An Orthorhombic unit cell of YBa$_2$Cu$_3$O$_{6+\delta}$ with $a_0 = 3.82\,\text{Å}$ along $[1\,0\,0]$ and $b_0 = 3.89\,\text{Å}$ along $[0\,1\,0]$. From numerous studies. This section will focus on the second question, the coupling of tip to surface interactions.

**BiO surface**

Many STM experiments on Bi2212 (Bi$_2$Sr$_2$CaCu$_2$O$_8$) have been successfully interpreted LDOS using eqs. 2.2 / 3.3. At first it was assumed that LDOS was measured from the CuO$_2$ bilayer. However the equations suggest a LDOS measured around $10\,\text{Å}$ above plane. As seen in fig 3.2a, The CuO$_2$ layer lies $4.5\,\text{Å}$ under the weakly bonded BiO sheet. The crystal geometry raises the question of the role BiO plays in the tunneling process. It will become apparent in a later section that the BiO layer certainly does play a major part. Interestingly, band calculations indicate that the BiO layer is metallic [7], which contradicts the previous idea that it’s insulation. BiO’s metallic nature can be attributed to a pair of conduction hybrids (Bi(6p)-O(2p)) that disperse below the Fermi energy around the ($\pi,0$) point in the Brillouin zone. Therefore the spectral functions for a BiO band should show a narrow peak near $E_F$. ARPES measurements do not report seeing this peak, suggesting that the band is indeed above $E_F$. [8]

**Momentum dependence of matrix element**

As mentioned in the previous section, it was theorized that the matrix element could be proportional to the sample wave function at a position $x$. This would change the tunneling conductance in to the form:
\[
\sigma(V) \propto \int d\omega [-f'(\omega - eV)] \sum_k |M_k|^2 A(k, \omega)
\] (3.4)

where the function \( M_k \) weighs the various contributions of the sample wave function to the tip in k-space and \( A(k, \omega) \) is the sample spectral function. In the case of HTS's the \( k_z \) is neglected since the entire \( k_z \) does not contribute to the bias dependence of the tunneling conductance.

Measurements on zinc impurities on doped Bi2212 revealed sharp peaks in LDOS at the impurity sites. [9] These results contrast with BCS theory that state a vanishing LDOS at impurity sites. [10] The reason for the contrasting results is still be discussed. Often, the anisotropic nature of \( M_k \) is called upon for interpreting the differences in results. An interesting result from Misra [17] saw STS spectra on Bi2212 that exhibited a U shape on the CuO\(_2\) layer, and a d-wave V shape on the BiO layer, which the author attributed to different matrix elements.

4 Crystal Structures of Bi based Materials

The superconducting gap (\( \Delta \)) can be seen in both types of superconductors: standard isotropic superconductors and in HTS. For isotropic BCS types, the superconducting gap is independent of position in real space and momentum in k-space (called s-wave gap symmetry). In essence, this means that STS of s-wave superconductors is independent of tunneling direction and surface position, leading to unambiguous experimental results. Interpretation is not as easy for layered HTS. HTS cuprates are often compositions of different superconducting cuprate layers alternating between nonmetallic layers. (see fig 3.2a) The alternate layer stacking along the [001] direction causes non-trivial interpretation of tunneling spectra in the same direction. Additionally, the d-wave symmetry of the gap (see fig 3.2c) means that spectra may also depend on momentum states. The interpretation is that tunneling spectra on HTS depends on the exposed cleaved surface, the orientation, and the tunneling matrix element.

This section explores common HTS surfaces and tip-to-sample surface characterizations. These items play important roles in STM experiments.

4.1 Bi Cuprates

Bi2212 is the most extensively studied HTS material since it is easily cleaved to an atomically flat surface. Cleaved surfaces typically occur between adjacent BiO layers (see fig 3.2a). BiO was the first surface of any HTS to produce atomic-scale resolution. Steadily improvement of resolution eventually revealed the tetragonal unit cell and the incommensurate supermodulation along [1\( \bar{1} \) 0]. BiO and CuO\(_2\) surfaces have been observed by STM and both surface will be discussed.

BiO
Figure 4.1: STM images of Bi based HTS, BiO plane. (a) Bi$_2$Sr$_2$CuO$_6$: 13.1 $\times$ 13.1 nm$^2$, 4.6K. [16] (b) Bi$_2$Sr$_2$CaCu$_2$O$_8$: 15 $\times$ 15 nm$^2$, 4.2K [13] (c) Lead-doped Bi$_2$Sr$_2$CaCu$_2$O$_8$: 4.3K. [15] (d) Zinc-doped Bi$_2$Sr$_2$CaCu$_2$O$_8$: 15 $\times$ 15 nm$^2$, 4.3K [13]

Topographical features common to BiO surfaces are similar in all Bi-based HTS cuprates. The features are a nearly commensurate supermodulation along $[\bar{T}10]$ and accompanying dark-atom rows along the supermodulation. Supermodulations (see fig 4.1a and 4.1b) develop from bulk effects and not from surface effects.[11] However the origin of the supermodulation are still uncertain. The current reasoning for supermodulation is a structural mismatch of underlying bulk layers in Bi2212. The dark-atom rows could be attributed to additional oxygen atoms from a specific rotation of the BiO trimer in the BiO plane. [12] Interestingly, supermodulation can be suppressed through lead-doping as seen in fig 4.1c. STM topography show single lattice sites but BiO layers contains two atomic species. This difference needs to be addressed. Research finds that BiO layers have no dependence on bias polarity leading to speculation that BiO layers are insulating and only contribute a single atomic species to topography. But constrasting research of Zn-substituted single crystals indicates that STM imaging is through Bi lattice points. [13] Additionally, it was shown that tunneling into the BiO layer probes the underlying CuO$_2$ layer leading to the idea that the CuO$_2$ superconducting gap can be measured from the above BiO layer.

**CuO$_2$**

The most groundbreaking study of the CuO$_2$ surface was done by Misra in 2002 on thin films. [17] They were able to clearly image the tetragonal lattice of both BiO and CuO$_2$ layers on the (001) surface and found an interesting difference. (see fig 4.2) Both layers contained a notable supermodulation in topography but the modulation in the CuO$_2$ layer was much smaller than in BiO. Tunneling spectra of the BiO layer remained consistent with d-wave
gap observations but CuO\textsubscript{2} terminated layers showed an unexpected superconducting gap that was wider with an unusual U-shape energy dependence and a suppressed conductance near the Fermi energy. (see fig 4.2c/d)

Electronic structures in BiO layers are likely to remain consistent whether in bulk or surface since the cleaving between adjacent layers is unlikely to disrupt any contributing bonds. Cleaving at CuO\textsubscript{2} layers is far more disruptive and could likely lead to changes in the tunneling spectra. However Misra ruled out any surface reconstruction and proposed that the taken U-shaped spectra should be consistent with d-wave superconductivity in CuO\textsubscript{2} provided that the tunneling matrix is of an anisotropic form \[ |M_k|^2 \propto (\cos(k_x a_0) - \cos(k_y b_0)). \]

Misra’s choice of \( M_k \) allowed them to produce a gap amplitude close to their measured values. Misra’s analysis implied that the CuO\textsubscript{2} layer is indeed superconducting. Misra’s model provided a crucial result but it should be mentioned that the model only partially reproduces the experiment. It did not account for higher peak structures nor did it explain the difference in \( M_k \) between BiO and CuO\textsubscript{2} layers.

4.2 Tip-to-sample Tunneling Spectra

Tip-to-sample distance \( d \) dependence in STS plays a crucial role in assessing the STM tunneling junction. If tunneling only occurs in surface states, spectra would show independence of \( d \). However, if the surface is contaminated or if bulk states contribute to the tunneling spectra then one might see \( d \) dependence. Early STM experiments on HTS cuprates often saw large \( d \) dependencies, and were only able to see superconducting gaps at low-resistance junctions (\( R_t \approx M\Omega \)), i.e. when tip distance was very small.[18] Moving the tip further away caused superconductivity features to vanish and STS evolved into semiconductor line forms. Advances in single-crystal synthesis and STM instrumentation lead to better junction management and enabled \( d \) independent STS studies. [19]
Ideal tunnel junctions are characterized by $d$ independent imaging and by sharp DOS structures. On Bi2212, there were two distinct STS features that indicate an ideal junction. (i) The background DOS is flat at energies (eV < 500meV). (see ref in [19]). (ii) Conductance peaks at gap edges are sharp when the aforementioned background DOS are flat at 500meV. A smeared conductance peak and a parabolic background DOS indicate a subpar tunneling junction. All things considered, a surface may appear non-uniform from a spectroscopic stand point with $dI/dV$ curves varying between weak parabolic gap structures to sharp structures, all of which depending on the local tunneling junction.

5 Gap Spectroscopy

Tunneling microscopy has lead to a plethora of successful electronic studies in superconductivity. STM has become an industry staple for probing the superconducting quasiparticle density of states and is unparalleled in its ability to measure landmark features in the electronic spectra for superconducting material. This section will look at the iconic feature, the superconducting gap, in Bi compounds and the spatial homogeneity found in the tunneling spectra.

To begin, fig 5.1 shows a series of SIN tunneling spectra. Niobium (fig 5.1a) shows all features of a classic low-T BCS superconductor: (i) a developed gap ($\Delta$) centered around $E_F$ with a U-shaped conductance curve starting with zero conductivity at the Fermi energy. (ii) A symmetric singularity at each side of the gap edge. For convenience, sometimes the superconducting gap is sometimes defined half the energy between the two conductance peaks ($\Delta_\rho$). Another useful term used for HTS is the reduced gap, defined as $2\Delta_\rho/k_BT_c$. The following sections will show how HTS tunneling spectra deviates from the BCS superconducting tunneling spectra.

5.1 Bi Compounds

The conductance spectrum on single crystal Bi2212 and Bi2223 is shown in fig 5.1b and c.[19] [20]. The most notable feature of Bi2212 are the large conductance peaks at the gap edge that contrast well to show the clear gap centered at $E_F$. Breaking from convention however is a linearly increasing energy dependence around $E_F$. For HTS, the reduced gap measured from the tunneling spectra is far below the values expected for weakling coupling s-wave (3.5) or d-wave (4.3) BCS superconductors.

The most noticeable features in conductance spectra of Bi2212 is the V-shaped energy dependence around the Fermi energy and the large peaks at the gap edges. The V-shaped dependence is indicative of nodes in the gap. This is consistent with d-wave symmetry (see fig 3.2c) but it does not account for the large conductance peaks at the gap edges. Hoogenboom in 2003 successfully simulated both features simultaneously by also taking into account the band structure, including the Van Hove singularity. [22] The large spectral weight in the conductance peaks can be enhanced by assume an anisotropic tunneling matrix element that would favor tunneling in antinodal states over nodal states. [23] However, this method also produces spectra more akin to s-wave superconductors that are inconsistent with experiments. [22]
Figure 5.1: SIN tunneling conductance curves for single crystal superconductors. (a) Niobium (Nb) at 333 mK (circles) and a BCS gap fit $\Delta = 1.0$ meV (solid line). [14] (b) Doped Bi2212 ($T_c = 92$K) at 4.8K (solid line) and a s-wave BCS gap fit with $\Delta = 27.5$meV and low-energy V-shaped d-wave BCS conductance (dashed line). [19] (c) Y123 at 4.2K. [32] (d) Overdoped Bi2201 ($T_c = 10$K) at 2.5K (solid line) and 82K (dashed line). [21] (e) Optimally doped Sr$_{0.9}$La$_{0.1}$CuO$_2$ at 4.2K [24] (f) Underdoped Bi2223 ($T_c = 111$K) at 4.2K [20]
Three layer Bi2223 (Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_{10+\delta}$) has similar tunneling spectra to Bi2212 except the waveform has shifted into higher energies. (see fig 5.1f) Even more interestingly, single layer Bi2201 (Bi$_2$Sr$_2$Cu$_2$O$_6$) is drastically different than either Bi based HTS’s. (see fig 5.1d) with a zero-bias conductance and a much larger reduced gap. (2$\Delta_p/k_BT_c \approx 28$) [21] The appreciable difference between Bi2201 and Bi2212 may come from the 2-dimensional nature of Bi2201. Superconductivity in Bi2201 happens in the CuO$_2$ single layer and was previously discussed in section 4.1. It is likely that large fluctuations are reducing the critical temperature $T_c$ and increasing the gap.

The gap amplitude of HTS cuprates was found to increase with $n$ number of CuO$_2$ layers per unit cell, with current research maxing out at $n = 3$. The increasing gap for Bi cuprates is shown in Figs 5.1b, 5.1d, 5.1f with $n = 1, 2, 3$ respectively. Similarly, $T_{c\text{max}}$ increases with $n$ up to $n = 3$. The dependence of the gap and $T_{c\text{max}}$ on CuO$_2$ plane number will be important to understanding the underlying mechanisms of HTS’s.

## 5.2 Spatial gap homogeneity

A topic of interest in superconductivity research is the question of spatial homogeneity of the superconducting gap. Such interest is spurred by models where electronic phase separation is at the core of high temperature transition temperature. Bi2212 studies show two types of spatial inhomogeneities concerning LDOS: (i) spatial inhomogeneity of the superconducting gap amplitude and (ii) spatial inhomogeneity of the low energy DOS near the Fermi energy. This section will discuss the former case as observed in Bi2212.

Inhomogeneous gaps have been reported since the early 2000’s.[13] Using CITS, real space maps have been taken to illustrate the nanoscale islands with varying gap amplitudes. (see fig 5.2a and b) The question has always been to what extent is this an intrinsic phenomenon to HTS? Is this related to the core mechanisms for HTS? One potential answer explores the electronic phase separation since the boundaries between domains were on order with the superconductivity coherence length.[25] [26] However more recently it was shown that homogeneous tunneling spectra could be obtained with proper annealing. [22] The research concluded that any inhomogeneity was the result of oxygen distribution in the sample and not related to the core mechanisms of HTS’s. In fact, a study conducted by McElroy captured a direct correlation between gap amplitude and oxygen impurity distribution. [28] The result of the experiment provides a good agreement with the spectra spread taken on doped Bi2212. (see fig 5.2c) [29] This provides a convincing argument that spatial inhomogeneities in the gap are an extrinsic property relating to the concentration of defects in the sample.

## 6 Pseudogap

A newly found state was found to exist in HTS’s. The unconventional normal state is characterized by the opening of a gap in the electronic excitation spectrum at a temperature $T^*$ above $T_c$, called the pseudogap (PG). The PG phenomenon once again sparked intense debates over its legitimacy to explain the mechanisms of HT superconductivity. There are two main theoretical explanations for the emergence of the PG: (i) The pseudogap is the outcome of some static or fluctuating order and hypothesized to be magnetic in origin. The
Figure 5.2: CITS spectra for spatial gap inhomogeneity. $56 \times 56$ nm$^2$ spatial gap distributions in (a) underdoped / (b) as-grown Bi2212. [27] (c) $dI/dV$ spectra spread on inhomogeneous Bi2212 [29] (d) Scatter plot of gap amplitude versus LDOS in doped Bi2212 [13]
unknown order is thought to either be unrelated to and/or competing with the superconducting order—related to doping. (ii) The pseudogap is the precursor to the superconducting gap, meaning that the PG is the related to Cooper pair fluctuations above the critical temperature. Tunneling spectroscopy at present favors the latter. This section will review important STS results relating to the pseudogap, the LDOS temperature dependence, and any scaling relationships between the pseudogap and the superconducting gap.

6.1 Temperature dependence of LDOS for Bi2212/2201

Unconventional normal-state behavior above $T_c$ was already known since the 1980s but it took more than a decade for technology to develop to the point where sample/surface quality improved and allowed PG spectra to be measured. [33]

The most prevalent challenge when measuring $T$ dependent LDOS is thermal shifts. Measuring LDOS requires that the STM tip be held fixed. The challenge is to keep the tip-sample junction from fluctuating during temperature shifts. Tip shifts will often cause variations in $I(V)$ measurements and possibly spacial shifts. Spatial shifts obscure $T$-dependent signatures from thermal shift making it hard to draw conclusions. That being said, the first successful $T$-dependent STM study was done on Bi2212 [33] and Bi2201 [21]

Bi2212

The first experiment that revealed a PG was conducted by Renner using STM junctions. [33] The culminating result showed the superconducting gap not closing abruptly at $T_c$, 15
Figure 6.2: Two $T$ dependent models fit with d-wave superconductivity to data taken from fig6.1. (dashed line) (a) a $T$-dependent BCS d-wave model. (b) a $T$-independent model. From [33]

definitively showing that HTS’s do not follow the conventional behavior that BCS theory predicts. In BCS Theory, both cooper pairing and phase coherence ends abruptly at $T_c$. This behavior is illustrated through the reduced gap for an s-wave superconductor: $2\Delta/k_BT_c = 3.5$, which indicates that thermal fluctuations are large enough to overcome the pairing energy $2\Delta$. However for underdoped Bi2212, the reduced gap values were reported to be as high as 20 which hints that the $T$ dependence of the superconducting gap may be different in HTS’s than what was reported by BCS theory.

Figure 6.1 illustrates the temperature dependence of the quasiparticle density of states in niobium [14], and underdoped Bi2212. [33] The remarkable feature in Bi2212 is the clear pseudogap present at $T_c = 83$, with nearly the same amplitude as the superconducting gap. Additionally, both gaps appear to be robust against increasing $T$ by filling up rather than closing. In contrast, Nb DOS shows a well defined superconducting gap that closes as $T$ increases to $T_c$. Thermal smearing is only considered when observing Nb due to its small gap ($\Delta_\rho = 1.5$meV) which prevents measurements of DOS up past the critical temperature. Thermal smearing in Bi2212 is less of an issue for the same reason. The gap for Bi2212 is an order of magnitude higher making $\Delta_\rho \gg k_BT_c$ and thermal smearing less invasive during imaging.

Renner further investigates the temperature dependence by fitting the data in fig 6.1 using two different models: (i) Assumes a BCS d-wave $T$ dependence and simulates a closing gap. (see fig 6.2a) and (ii) Assumes a $T$-independent gap. (see fig 6.2b) Quick comparison shows the latter option reproduces data better than the former. Comparison to taken data also reveals features commonly found in Bi2212 material.

The first feature shows a reducing coherence peak at the gap edge for increasing tem-
temperatures up to $T_c$. (see fig 6.2b) A possible explanation for this occurrence is in the doping level of Bi2212. It is commonly known that underdoped samples are more prone to inhomogeneous oxygen distributions. Therefore, it could be that thermal drift coupling with an inhomogeneous oxygen distribution causes the tip to probe regions with varying doping levels. However, this is unlikely for fig 6.2b considering the gap magnitude is not changing with temperature.

The second feature occurs when crossing $T_c$. Upon crossing the critical temperature, the superconducting gap continuously changes into the pseudogap. Further inspection of fig (6.1b) shows that the PG form does not vary much with increasing temperature, and gap edge broadening can be ignored due to thermal smearing. Hence, the pseudogap is filling up, resulting in a zero-bias conductance before vanishing completely at $T^*$.

**Bi2201**

There were certain challenges that kept Bi2201 from being actively studied when compared to Bi2212. The single CuO$_2$ layer cuprate has a much lower $T_c$ and is harder to grow with a reasonable crystal homogeneity. Despite challenges, research still needed to be done to understand the extent that Bi2212 behavior applied to other Bi based materials.

The first work was done by Kugler, which revealed as superconducting gap at $\Delta_{\rho} \approx 12$ meV. This is noteworthy considering the that for a $T_c = 10$ K, the gap magnitude is unusually large. For comparison, according to BCS theory the gap should be $\Delta_{BCS} = 2.14k_BT_c = 1.8$ meV. That is nearly an entire order smaller than measured. For similar reasons, the reduced gap is also high, $2\Delta_{\rho}/k_BT_c = 28$. Based on evidence from Bi2212, the expectation is that a PG state would extend over a large temperature range above $T_c$.

Data collect by Kugler (see fig 6.3) shows the temperature dependent DOS on a slightly overdoped Bi2201. While spectra is less sharp than Bi2212 the pseudogap is still resolved with a magnitude comparable to the superconducting gap. [20] Additionally, by inspection the gap magnitude is approximately $T$ independent and follows a similar DOS evolution that was found in Bi2212. (see fig 6.1b)

The temperature range that the PG state exists is much larger than the superconducting range. The difference between $T_c$ and $T_*$ and similarly between $\Delta_{BCS}$ and $\Delta_{\rho}$ is about a factor of seven. In that sense, $T_*$ scales with $\Delta_{\rho}$. Based on the discussed results, Kugler constructed as doping phase diagram that illustrates the PG phase state exists directly over and around the superconducting state. (see fig 6.3c) For undoped Bi2201, $T_c \approx 13$ K. For Lanthanum doped Bi2201, the reported $T_c$ increased to about 26 K but the gap magnitude remained comparable to undoped Bi2212, suggesting that La doping does not effect the cooper pairing energy but does effect the wavefunction phase coherence. These results indicate that the relationship between $\Delta_{\rho}$ and $T_c$ is less robust than previously thought.

### 6.2 Scaling Pseudogap to Superconducting gap

Another important comparison that can be made is the relationship between superconducting gap and pseudogap magnitudes, including $T_c$ and $T^*$. This relationship can help identify the origin of the PG state. The material that will be covered in this section will be limited to
Figure 6.3: Pseudogap measurements on Bi2201. (a) $T$-dependent DOS in overdoped Bi2201. (b) Heatmap of (a). Grayscale represents the DOS. (c) Doping phase diagram showing $T^*$, $T_c$, and $\Delta_\rho$ for various doping levels. From [21]
Bi2212 and Bi2201. Bi2212 will act as the "control" material and be compared with Bi2201 which as a similar crystal structure but drastically different $T_c$ and $\Delta_\rho$. (see fig 6.4a).

Figure 6.4a provides gap and pseudogap spectra for Bi2212 and Bi2201 for overdoped and underdoped samples. By inspection, it can be seen that the superconducting gap magnitude increases with underdoping. The pseudogap behavior remains consistent between both compounds. Fig 6.4b illustrates the relative amplitude between gaps is comparable, showing no effect from doping. [21] The amplitude consistency is extraordinary when considering that the gap magnitude varies by $\sim 400\%$

The scaling relationship between $\Delta_\rho$ and $T^*$ was first observed by Oda [30] and eventually lead to the connection with mean-field BCS theory. Figure 6.4c shows a collage of various material following the d-wave relation $2\Delta_\rho/k_B T^* = 4.3$. By inspection, most materials listed follow the scaling law to a certain degree and is strong evidence the current fit is robust. By closer inspection of the d-wave relation shows that $T^*$ is playing the role of $T_c$ which supports the theory that $T^*$ is the mean-field BCS temperature and is characteristic of the interaction energy leading to superconductivity. [21]

7 Conclusion

Tunneling microscopy is a powerful tool that allows users to spatial scan atomic topography and probe the local density of states of conductive material. The success of STM is the exponential dependence of tip-sample distance allowing unparalleled resolution. STS allows users to probe the electronic spectra and identify unique landmarks. When applied to high temperature superconductors, STM and STS experiments revealed important information about the crystal structure and temperature dependencies. STS has lead to important measures of the superconducting gap and of the spatial gap inhomogeneities. It revealed an unconventional normal state, the pseudogap, which lead to a more refined understanding of HTS's. It is clear from this paper that STM and STS research have made and continue to make essential progress in the field of high temperature superconductors.
Figure 6.4: Scaling relationships between HTS's. (a) Comparison chart for OD/UD Bi2212 and Bi2201. (b) Same data, rescaled with energy $\Delta_\rho$. (c) $T^*/T_c$ versus $2\Delta_\rho/k_B T_c$ for well studied cuprates. Dashed line is the mean-field d-wave relation with $T^*$ replacing $T_c$. From [21]
References


