Electron Dynamics in High Temperature Superconductors Studied Using Angle and Time-Resolved Photoemission Spectroscopy

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Electron Dynamics in High Temperature Superconductors
Studied Using Angle and Time-Resolved Photoemission Spectroscopy

by

Stephen P. Parham
B.S., University of California Santa Barbara, 2008
M.S., University of Colorado, 2011

A thesis submitted to the
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Electron Dynamics in High Temperature Superconductors Studied Using Angle and
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written by Stephen P. Parham
has been approved for the Department of Physics

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Daniel Dessau

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Prof. Dmitry Reznik

Date _______________________

The final copy of this thesis has been examined by the signatories, and we find that both the
content and the form meet acceptable presentation standards of scholarly work in the above
mentioned discipline.
Parham, Stephen P. (Ph.D., Physics)

Electron Dynamics in High Temperature Superconductors Studied Using Angle and Time-Resolved Photoemission Spectroscopy

Thesis directed by Prof. Daniel Dessau

High-Temperature Superconductivity (HTSC) has inspired decades of research since its discovery in 1986 but remains an enigmatic subject to this day. At the heart of this difficulty is the highly correlated electronic behavior that limits the usefulness of modern theoretical calculations. Angle-Resolved Photoemission Spectroscopy (ARPES) has proved an invaluable tool in the study of HTSC because it can directly measure this correlated behavior through its effects on the electronic scattering rate. However, the electronic scattering rates extracted by conventional ARPES analysis techniques can be up to an order of magnitude larger than those measured by other techniques (such as optical spectroscopy). In this work we show how this discrepancy can be explained by a combination of nanoscale electronic disorder and photoelectron surface scattering. Further, with the help of numerical modeling, we can remove these extraneous scattering events and reveal the true many-body interactions in these materials. We confirm these results by performing a systematic study of the effects of magnetic Fe impurities on the electronic structure of the HTSC Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$.

The second half of this thesis is devoted to the development and use of a time-resolved ARPES (trARPES) system to study these electron dynamics directly in the time domain. This allows us to measure the nonequilibrium electron dynamics, providing complementary information to normal ARPES measurements. We find that the electron dynamics are drastically slowed by the presence of the superconducting condensate and have a complex energy and momentum structure. By modeling the electrons' behavior as following an ultrafast “pseudo-temperature” we can explain the dynamics observed with trARPES and gain new insight into the complicated electronic behavior present in these novel materials.
Dedication

For my family.
Acknowledgements

Firstly, I would like to thank my parents for nurturing my curiosity about the workings of the universe. They instilled in me a love of science and have supported me through each phase of my educational career. Without their guidance and support I would not be where I am today and for that I am forever grateful.

I would like to thank my advisor, Dan Dessau, for being an excellent mentor during my time in graduate school. He taught me how to think like an experimental physicist and has helped me understand things ranging from vacuum technology to many-body physics. His unique management style gave me the freedom to become an independent researcher while still having someone to turn to when I needed advice.

As any experimentalist knows, running a research lab is always a team effort, especially with an experiment as involved as Angle-Resolved Photoemission Spectroscopy (ARPES). Therefore, I would like to thank my fellow labmates for helping me develop and run our ARPES system. I would like to thank the older students, Ted, Nick, and Qiang, for showing my the practical aspects of running an ARPES setup, and the younger students, Justin W., Haoxiang, and Tom for forcing me to know things well enough to explain them to others. I would also like to thank the younger students, along with Justin Griffith¹, for the countless man hours spent upgrading the vacuum system, software, and light sources in order to realize our time-resolved ARPES (trARPES) system. I am grateful for each lab member’s unique contribution to my research efforts and am glad to have such competent labmates.

¹ Justin is the lab’s Senior Professional Research Assistant and is generally in charge of (among other things) minimizing the lab entropy. Justin is great.
I would like to thank my friends and classmates for reminding me that there is more to life than a physics lab. Whether it’s beer-league softball, adventurous car-camping, or just the occasional movie night, the friends I’ve made in graduate school played a major role in keeping me sane over the years and I will cherish those friendships forever.

Lastly, I would like to thank my loving wife, Carrie DeLyser, for all her support and patience over the years. She keeps me grounded and reminds me that not everyone is a physicist. It has been a long journey through graduate school and I couldn’t have done it without her.
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Chapter 1

General Introduction

In this thesis I will investigate the properties of high temperature superconductors using the powerful techniques of angle and time resolved photoemission spectroscopy. The first several chapters of the thesis will cover the necessary background in the topics of superconductivity, photoemission spectroscopy and many-body physics. In addition, since a large portion of my time in graduate school was spent developing the laser system used for time-resolved ARPES, I will devote a chapter to its design and operation. The final three chapters will discuss different investigations into the electron dynamics in the cuprate superconductors. We will cover the effects of magnetic impurities on both the electron scattering and superconducting gap through a systematic study of Fe-doped BSCCO. Next we will investigate nanoscale inhomogeneity that causes forward scattering and heterogeneous broadening of ARPES lineshapes. And finally, we investigate the electron dynamics directly in the time domain using the home-built trARPES system.
Chapter 2

Introduction to Superconductivity

The field of superconductivity is vast and has inspired more than a century of physics research. The effect was originally discovered in 1911 by Kamerlingh Onnes after he successfully liquified helium in 1908. With this new temperature regime unlocked, Onnes set about investigating the low temperature properties of metals and found that upon cooling mercury below 4.2K its resistance dropped to zero! What was initially considered an error by his lab assistant was reconfirmed and opened an area of physics that defied theoretical description for over 40 years. In retrospect this is understandable since Onnes discovered (what we now know as) a macroscopic quantum phenomenon before the infancy of quantum mechanics itself. After some digging I was able to find the data from the first reported superconductor, reproduced nicely in a Physics Today feature article [78] and shown in Fig. 2.1.

2.1 Phenomenology

In addition to the zero-resistance state for which superconductors get their name, there is another amazing feature of these systems, namely perfect diamagnetism. This effect, called the Meissner Effect [55], was discovered in 1933 and is one of the defining properties of a superconductor. The explanation was given by London [46] and the so-called “London equations” describe the electrodynamics inside a superconductor. The superfluid abhors magnetic flux in its interior and sets up screening currents at the surface that repel the applied field from the volume, as shown in Fig. 2.2. There is a characteristic penetration depth, \( \lambda \), that determines how far into the supercon-
Figure 2.1: Reproduction of the original data in the discovery of superconductivity. The axes are somewhat difficult to read, but the vertical divisions have 25$m\Omega$ spacing while the horizontal divisions are 0.1K.
ductor the magnetic field penetrates, and inside the material the field decays as \( B(x) \sim B_0 e^{-x/\lambda} \). The superconductor will always try to reduce the internal field to zero, taking on whatever screening currents necessary. At a critical field, \( H_c \), the superfluid reaches its critical current, \( I_c \), and returns to the normal state. As we will see later in this thesis there is a strong interplay between superconductivity and magnetic fields.

It was discovered that under certain applied fields not all superconductors went completely normal but instead allowed filaments of magnetic flux to permeate the superfluid. This other class of superconductors is referred to as “type-II” superconductors. Type-II superconductors permit a mixed state at intermediate fields: between \( H_{c1} \) and \( H_{c2} \) the superfluid coexists with a number of flux vortices, each containing a quantum of magnetic flux. Below \( H_{c1} \) there is no internal field, as in type-I SC, and above \( H_{c2} \) the sample goes normal state. All of the cuprate superconductors, such as those discussed in this thesis, are type-II superconductors.

2.2 BCS Theory

It was not until 1957 that Bardeen, Cooper, and Schrieffer formulated a microscopic theory of superconductivity, now known as BCS theory [7]. The core principle is that the Fermi sea is unstable against the formation of bound pairs of electrons if there is any effective attraction between those electrons, no matter how weak. Cooper showed this in 1956 for the case of individual pairs [16], now called Cooper pairs in his honor. These pairs act as bosons and can therefore condense into a state analogous to a Bose-Einstein Condensate (BEC), displaying macroscopic phase coherence and superfluid properties. BCS argues that the effective attraction between two electrons takes the form of an electron-phonon interaction that is retarded in time. A simple cartoon, shown in Fig. 2.3, illustrates the idea in two steps. First, an electron scatters off the lattice from state \( |k\rangle \) to \( |k'\rangle \), distorting the lattice. This distortion, a local net positive charge, later attracts a second electron that scatters from state \( |-k\rangle \) to \( |-k'\rangle \) and restores this lattice distortion. Note that in order to restore the lattice, the momentum transfer \( q = k - k' \) from the first scattering event must be equal and opposite to the second scattering event, i.e. \( -q = (-k) - (-k') \). This ensures that
Figure 2.2: Illustration of the Meissner Effect. For $T > T_C$ magnetic fields penetrate normally through the material. Upon cooling to $T < T_C$ the field is expelled from the superconductor by screening currents. The right picture depicts a magnet levitating over a superconductor, held below $T_C$ by a bath of liquid nitrogen.
pairs of the form \((k,-k)\) will scatter to \((k',-k')\), thus keeping their zero net momentum. At the end of each interaction the lattice remains at the same energy, but there is now an effective attraction between the electrons. In the real quantum picture the Cooper pairs are continually exchanging these virtual phonons, dancing around the Fermi surface in tandem.

### 2.3 High-Temperature Superconductivity

After the great success of BCS theory the field was considered mostly solved and was quiet for awhile. In BCS theory the maximum \( T_C \) based on electron-phonon coupling was predicted to be around 32K and all newly discovered superconductors obeyed this rule until 1986. In that year Bednorz and Müller reported a new type of superconductor, Lanthanum Barium Copper Oxide (LBCO), with a \( T_C \) of 35K. Within a year another copper oxide material was reported, Yttrium Barium Copper Oxide (YBCO), with an astonishing \( T_C \) of 90K. These new superconductors were so different, and had such increased \( T_C \), that they became known as “high-temperature” superconductors and have reinvigorated superconductivity research for the last 30 years. The progress in newly discovered superconductors is shown nicely by the plot of \( T_C \) vs time, shown in Fig. 2.4.

While breaking liquid nitrogen (77K) temperatures has enormous practical implications, these new High-\( T_C \) superconductors also proved of great interest for fundamental physics research. The incredibly high \( T_C \) defies BCS theory and suggests that the pairing boson could be different than a phonon. To date there is still no consensus on the pairing “glue” in these materials and it is one of the big questions in the field. However, much progress has been made in understanding these materials.

All the cuprate superconductors share a similar crystal structure, having CuO\(_2\) planes sandwiched between charge transfer layers. This structure is shown in Fig. 2.5. The superconductivity is thought to reside in these CuO\(_2\) planes and has quasi-2D properties with only weak coupling between planes in different unit cells. Cu has a valence of 9-3\(d\) electrons, which means each Cu contributes one hole per unit cell. The parent compound of the cuprates is typically an antiferromagnetic Mott insulator and only becomes superconducting when doped with holes. The
Figure 2.3: An illustration of the electron-phonon mechanism of superconductivity. In panel (a) an electron scatters from $k$ to $k'$, distorting the lattice at time $t_1$. At a later time $t_2$ an electron scatters from $-k$ to $-k'$, restoring the lattice. Panel (b) shows the cartoon of (a) as scattering across the Fermi surface. Panel (c) shows the electron pair propagating around the Fermi surface through successive scatter events.
Figure 2.4: Timeline of the superconducting transition temperature vs discovery year for different materials. There is a large jump in 1986 with the discovery of the High-Temperature Superconductors. Figure adapted from Ref. [31].
phase diagram of the cuprates is shown in Fig. 2.6, where we see that there is a dome of superconductivity centered around the optimal hole concentration of 16% holes per unit cell. This is known as optimal doping (OP), while hole concentrations above and below this are known as overdoped (OD) and underdoped (UD) respectively.

Another aspect of the cuprate superconductors is that their order parameter has a different symmetry than conventional superconductors. Conventional superconductors have what is known as \( s^- \) wave pairing, meaning \( \Delta \) is independent of \( k \), in both magnitude and phase. Cuprates, on the other hand, have \( d^- \) wave pairing where \( \Delta(k) \propto (\cos(k_x a) - \cos(k_y a)) \) so the order parameter changes sign (multiple times) throughout the zone and necessarily has zeros. These two contrasting situations are shown in Fig. 2.7, along with the ARPES data showing the \( d^- \) wave nature of the gap in the cuprates. ARPES can only measure the magnitude of the gap, not the phase, but clever geometries of Josephson junctions have shown that there is indeed a different phase on different lobes of the order parameter [38]. This \( d^- \) wave structure has implications on the transport properties and on the effects of impurity scattering, as discussed below.

2.4 The Anderson Theorem

The \( T_C \) of conventional superconductors proved to be surprising resilient against the addition of impurity centers [4]. Anderson explained this phenomenon in an intuitive way and the reasoning is as follows. Impurity centers disrupt the translational symmetry of the lattice and therefore \( k \) is not a good quantum number anymore. However, there still exist the same number of eigen-solutions to the Hamiltonian, although now they must be explicit functions of position, \( |u(r)\rangle \). As long as the Hamiltonian is time-reversal symmetric, the time-reversed eigen-function, \( T|u(r)\rangle \), must be degenerate with \( |u(r)\rangle \). Since there are still the same number of degenerate states with zero net momentum, we expect that \( \Delta \) and \( T_C \) will not be very sensitive to the addition of impurities.

The Anderson Theorem breaks down when the time reversed states are not degenerate, as with an applied field or magnetic impurities. These perturbations are known to more strongly suppress \( T_C \), consistent with Anderson’s Theorem. Another interpretation is that when an electron
Figure 2.5: The crystal structure of the cuprate family. Panel (A) shows four different cuprate compounds that all share the copper oxygen planes, shown in (B). The important orbitals, copper $3d_{x^2-y^2}$ and oxygen $2p_z$, are shown in (B). Panel (C) shows the crystal structure of bilayer BSCCO (Bi2212), the material heavily studied in this thesis. Dashed lines indicate the natural cleave planes between adjacent $Bi – O$ planes. Figures adapted from references [8, 58].
Figure 2.6: Generalised phase diagram of the cuprate superconductors vs temperature and hole concentration. The parent compound is an anti-ferromagnetic (AF) insulator that is quickly suppressed by the addition of holes. The superconducting dome is centered around $p = 0.16$ and is bisected into overdoped (OD) ($p > 0.16$) and underdoped (UD) ($p < 0.16$) parts. Above $T_C$ for UD samples there is a pseudogap phase that persists up to $T^*$. There are several variations of this phase diagram in the literature, sometimes dressed with other phases or with a slightly different $T^*$ line. However, the features presented here are the most general and consistent ones throughout the literature. Figure adapted from Ref. [32].
Figure 2.7: Illustration of different gap symmetries. Panel (a) shows the $s$–wave gap symmetry for the conventional superconductors. The circle represents a constant gap as a function of $k$. Panel (b) shows the $d$–wave gap of the cuprates, with the different phases marked by “+” and “−”. The nodal line, defined as $\Delta = 0$, is denoted by the orange line from $\Gamma$ to $Y$. The cuprate Fermi surface is shown in (b) as the green hole pockets, centered at $Y$. Panel (c) shows data from Shen et. al that shows the gap anisotropy in the cuprate Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (BSCCO-2212). The upper traces are measured close to the anti-node (AN) where the gap is largest while the lower traces were measured at the node, where there is no gap. Panels (b) and (c) were adapted from Ref. [68] and Ref. [73] respectively.
scatters from $k$ to $k'$ the chance of that causing pair-breaking is proportional to the difference of gaps, $\Delta_k - \Delta_{k'}$. In an $s$-wave system this difference is always zero, but for $d$-wave systems this difference can be up to $2\Delta_{Max}$, and many possible scattering events have a non-zero chance to break the Cooper pair. For this reason, the Anderson Theorem does not hold in $d$-wave systems, consistent with the reduction of $T_C$ by the nonmagnetic impurity, Zn, in BSCCO films [47].

2.5  Bogoliubov Transformation and the Superconducting Green’s Function

The Green’s Functions described in section 3.1.5 correspond to particles with many-body interactions but not in the presence of superconductivity. The following section follows closely from Bogoliubov [12] and we start with the so-called pairing Hamiltonian:

\[
H_p = \sum_{k\sigma} \xi_k c_{k\sigma}^\dagger c_{k\sigma} - \sum_{kl} V_{kl} c_{k\uparrow}^\dagger c_{-l\downarrow} c_{-l\uparrow} c_{l\downarrow} \tag{2.1}
\]

where $\xi_k = \epsilon_k - E_F$ are the single particle energies relative to the Fermi level in the absence of the pairing interaction, $c_{k\sigma}^\dagger$ ($c_{k\sigma}$) are the creation (annihilation) operators that create (destroy) a particle with momentum $k$ and spin $\sigma$, and $V_{kl}$ is the pairing interaction. The term $V_{kl} c_{k\uparrow}^\dagger c_{-l\downarrow} c_{-l\uparrow} c_{l\downarrow}$ represents scattering of a pair from ($l \downarrow, l \uparrow$) to ($-k \downarrow, k \uparrow$). In order to work with this Hamiltonian it is customary to convert the interaction term to a series of bilinear terms in the following way.

First, in the superconducting state we expect nonzero expectation values of quantities like $c_{-k\downarrow} c_{k\uparrow}$ so we can rewrite them as:

\[
c_{-k\downarrow} c_{k\uparrow} = b_k + (c_{-k\downarrow} c_{k\uparrow} - b_k) \tag{2.2}
\]

\[
b_k = \langle c_{-k\downarrow} c_{k\uparrow} \rangle \tag{2.3}
\]

where we expect the term in parentheses in Eqn. 2.2 to be small so we can neglect those terms beyond first order. Further, we define $\Delta_k$ as:

\[
\Delta_k = -\sum_l V_{kl} b_l = -\sum_l V_{kl} \langle c_{-l\downarrow} c_{l\uparrow} \rangle \tag{2.4}
\]

Substituting the definitions of $b_k$ and $\Delta_k$ into Eqn. 2.1 we arrive at:

\[
H_p = \sum_{k\sigma} \xi_k c_{k\sigma}^\dagger c_{k\sigma} - \sum_k \left( \Delta_k c_{k\uparrow}^\dagger c_{-k\downarrow} + \Delta_k^* c_{-k\downarrow} c_{k\uparrow} - \Delta_k b_k^\dagger \right) \tag{2.5}
\]
where now the Hamiltonian is bilinear in particle creation and annihilation operators. For clarity we distinguish the complex conjugate of numbers, denoted by "*", from the adjoint of an operator, denoted as "†". This Hamiltonian can be diagonalized by the famous Bogoliubov transformation [12]:

\[ c_{k\uparrow} = u_k^* \gamma_{k0} + v_k \gamma_{k1}^\dagger \]  
\[ c_{-k\downarrow} = -v_k^* \gamma_{k0} + u_k \gamma_{k1}^\dagger \]  

where the coefficients \( u_k \) and \( v_k \) satisfy \( |u_k|^2 + |v_k|^2 = 1 \). When we substitute these definitions into Eqn. 2.5 and carry out the multiplications we find that the Hamiltonian is diagonal in \( \gamma_k \)'s (no terms of kind \( \gamma_{k0} \gamma_{k1} \)) if \( u_k \) and \( v_k \) satisfy:

\[ 2\xi_k u_k v_k + \Delta_k^* v_k^2 - \Delta_k u_k^2 = 0 \]  

We can solve for a useful constraint on \( u_k \) and \( v_k \) by multiplying through by \( \Delta_k^*/u_k^2 \) and solving the quadratic formula:

\[ \frac{\Delta_k^* v_k}{u_k} = \sqrt{\xi_k^2 + |\Delta_k|^2 - \xi_k} \equiv E_k - \xi_k \]  
\[ E_k = \sqrt{\xi_k^2 + |\Delta_k|^2} \]  

where \( E_k \) is the energy of elementary excitations, \( \gamma_{k0} \) and \( \gamma_{k1} \). These excitations, called Bogoliubons, have energy \( E_k = \sqrt{\xi_k^2 + |\Delta_k|^2} \).
Figure 2.8: The effect of superconductivity on the electron dispersion and density of states. Panel (a) shows a general electron band for a material in red and the corresponding “hole” band in dashed black, defined as the reflection of the electron band across the line \( E = E_F \). In panel (b) we zoom into the Fermi level, indicated by the black box in (a), and show the superconducting dispersion in blue for a gap of \( \Delta = 10 \text{ meV} \). The four branches of the SC dispersion are labeled “e-like” or “h-like” depending on whether the eigenstate is mostly electron-like \((u_k > v_k)\) or mostly hole-like \((u_k < v_k)\). Panel (c) shows the density of states near the Fermi level for both the normal (N) and superconducting (SC) states.

and now we explicitly see that \( \Delta_k \) serves the role of an energy gap in the excitation spectrum of a superconductor. As shown by the Bogoliubov transformation, the superconducting pairing interaction leads to the mixing of particle and hole states, which in turn gives the “avoided crossing” behavior typical in quantum mechanics. This behavior is illustrated in Fig. 2.8 where we explicitly show the effect of superconductivity on the electron dispersion and density of states.

While the Bogoliubov transformation gives excellent insight into the superconducting excitation spectrum, when looking for the Green’s function of the superconducting state I prefer the derivation provided by Nambu [57] where we explicitly work in the particle-hole basis:

\[
|e\rangle = \left( \begin{array}{c} 1 \\ 0 \end{array} \right) \quad |h\rangle = \left( \begin{array}{c} 0 \\ 1 \end{array} \right)
\]  

(2.14)

Note that it is not electrons and holes within one band that are mixing, it is the electron and hole bands that are mixing. In this context, if the energies of the electron states are \( \epsilon_k \) then the energies of the hole states are \(-\epsilon_k\), as shown in Fig. 2.8(a). Then we can write the inverse Green’s function as:

\[
G^{-1} = \omega - H_p = \begin{pmatrix} \omega - \xi_k & \Delta \\ \Delta^* & \omega + \xi_k \end{pmatrix}
\]

(2.15)
where the particle-hole mixing is explicit in the off-diagonal terms $\Delta$ and $\Delta^*$. We can invert this matrix to get the electron Green’s function, $G_{11}$, but before we do let’s add the many body self-energy, $\Sigma = \Sigma' + i\Sigma''$:

$$G^{-1} = \omega - H_p - \Sigma = \begin{pmatrix} \omega - \xi_k - \Sigma & Z\Delta \\ Z\Delta^* & \omega + \xi_k - \Sigma \end{pmatrix}$$

(2.16)

where $Z = 1 - \Sigma'/\omega$ is the renormalization factor caused by the self-energy. After inversion we obtain the electron Green’s function, $G_{11}$, including both self-energy and superconducting pairing:

$$G_{11}(k,\omega) = \frac{\omega - \Sigma + \xi_k}{(\omega - \xi_k - \Sigma)(\omega + \xi_k - \Sigma) - Z^2|\Delta_k|^2} = \frac{\omega - \Sigma + \xi_k}{(\omega - \Sigma)^2 - \xi_k^2 - Z^2|\Delta_k|^2}$$

(2.17)

This is the form of the Green’s function we will use for simulating ARPES spectra in the superconducting state.
Chapter 3

Introduction to ARPES

Angle resolved photoemission spectroscopy (ARPES) is arguably the most powerful spectroscopic tool for investigating solid state systems. It provides direct access to the electronic structure of a material in momentum space, the natural basis for band solids. Unlike bulk probes like transport, which integrate over momentum, and optical reflectivity, which provides a two-particle response (electron and hole), ARPES provides a single particle response of all the occupied states in the solid, in a momentum resolved way. ARPES necessarily measures the fully renormalized band structure, which can be quite useful for strongly correlated systems where theoretical band calculations fail. In this chapter I will review the fundamentals of the photoemission process and the practical aspects of this powerful spectroscopic tool.

3.1 Photoemission Principles and Theory

Before discussing the angle-resolved portion of ARPES it is helpful to first discuss it’s earlier incarnation, angle-integrated photoemission spectroscopy, or simply PES. According to Einstein, when a photon of sufficiently high energy ($h\nu > \Phi$) is absorbed by an electron in the solid that electron can escape into vacuum. Einstein’s explanation of this effect earned him the Nobel Prize and helped prove that photons are composed of discrete packets of energy. When an electron leaves the solid its kinetic energy in vacuum is given by:

$$E_f = E_i + h\nu - \Phi$$

(3.1)
where \( E_i \) and \( E_f \) are the initial and final kinetic energies, \( h \nu \) is the photon energy, and \( \Phi \) is the work function. Since the work function of most materials is around 4-5 eV the photoemission process requires the use of ultraviolet or x-ray photons. For this reason, PES experiments have traditionally been performed at large synchrotron facilities with access to a wide variety of X-Ray wavelengths. More recently, laser sources up-converted to UV [40] or X-Ray wavelengths [54] have proven useful for PES and ARPES as well, and at much reduced operational cost.

In typical photoemission experiments the number of electrons is measured for a series of different \( E_f \) values. This signal reproduces the density of states in the material, as shown in Fig. 3.1. There is also a photoemission background, shown in blue in Fig. 3.1, that arises from photoelectron scattering on the way out of the sample. This scattering is primarily inelastic, so it increases as the photoelectron energy decreases.

### 3.1.1 1-step vs 3-step model

An intuitive way to think about the photoemission process comes from Spicer [43] wherein the process is broken down into three steps. First, an electron absorbs a photon in the sample bulk, then it travels to the surface, and finally, it overcomes the work function and escapes into vacuum. This is known as the three-step model and is shown schematically in Fig. 3.2. Also shown in Fig. 3.2 is another interpretation, known as the one-step model, which more closely follows quantum mechanics. In this model the electron transitions directly from the initial state to a traveling plane-wave final state and whose transition probability is given by Fermi’s Golden Rule [35]:

\[
    w_{fi} = \frac{2\pi}{h} |\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu) \tag{3.2}
\]

where \( |\Psi_i^N \rangle \) is the initial state of the N-particle system and \( \langle \Psi_f^N \rangle \) is the final state of the excited, (N-1)-particle system plus the traveling plane wave of the excited electron, and \( H_{int} \) is the electron-photon interaction Hamiltonian given by:

\[
    H_{int} = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} \tag{3.3}
\]
Figure 3.1: The electronic density of states as measured by photoemission spectroscopy. The occupied DOS is shown below the vacuum level (VL), with the highest occupied state at the Fermi level, $E_F$. The workfunction is shown as $\Phi = \Phi_e$. Photons of energy $h\nu$ photoemit a fraction of these electrons into vacuum where they reproduce the original DOS plus an additional photoemission background, shown in blue, arising from photoelectrons scattering on their way out of the sample.
where A is the electromagnetic vector potential, p is the electron momentum operator, c is the speed of light, and e and m are the electron’s charge and mass.

### 3.1.2 Kinematics

In the angle-integrated photoemission process we made use of conservation of energy to determine the density of states in a solid. In ARPES, we additionally make use of conservation of momentum to extract the momentum space distribution of electrons based on their photoemission angles. The momentum of the photon is typically much less than that of the electron, so the photoemission angle relative to sample normal is determined by the ratio of in plane to out of plane momentum. (The momentum of a 10eV photon is only $5\text{mÅ}^{-1}$, or about 0.3% of BSCCO’s first Brillouin Zone). In this approximation the in-plane momentum, $k_||$, is conserved while the out of plane momentum, $k_\perp$, is reduced by the fields of the work function, similar to how light is refracted at a material interface. These kinematic relationships are summarized in Eqn. 3.4. It should be noted that even when the photon’s momentum is too large to be ignored all of the photons have the same momentum so in effect it just shifts the entire ARPES band structure slightly, without distorting or broadening it. Since the exact sample normal position is typically uncertain due to mounting details, this momentum shift can be grouped with that uncertainty as just a Γ-point offset.

\[
k_|| = \sqrt{\frac{2m}{\hbar^2} (E_i + h\nu - \Phi) \sin \theta}
\]

\[
k_\perp = \sqrt{\frac{2m}{\hbar^2} (E_i + h\nu - \Phi) \cos \theta}
\]

### 3.1.3 The Photocurrent

The ARPES intensity, given in Eqn. 3.5, is the product of the dipole matrix element times the material’s spectral function times a Fermi-Dirac distribution, added with incoherent background, all convolved with the experimental resolution in both energy and momentum. This equation is
Figure 3.2: Models of the photoemission process. At left is the three-step model where the process is broken into three independent steps: absorption of a photon (1), travel to the surface (2), and escape into vacuum (3). At right is the one-step model where the electron directly transitions into the final state and is wave-matched at the sample surface. Figure adapted from Hüfner [35].
quite a beast and we will dissect it piece by piece in the following sections. The true quantities of interest are the spectral function, \( A(\vec{k}, \omega) \), which contains all the many-body interactions in the solid, and \(|i\rangle\), the initial state of the measured photoelectron. Each of these will be covered in more detail in the following sections. The other factors, in particular the background and resolution terms, are inherent to the photoemission measurement, but extrinsic from the sample’s perspective, and need be understood only so as to better extract the intrinsic quantities of interest.

\[
I(\vec{k}, \omega) = \left\{ |\langle f | \vec{A} \cdot \vec{p} | i \rangle|^2 * A(\vec{k}, \omega) * f(\omega) + BG \right\} \otimes R(\vec{k}, \omega) \tag{3.5}
\]

### 3.1.4 Matrix elements

The first term in Eq. 3.5, known simply as the “ARPES Matrix Element”, expresses the dependence on the dipole selection rule for an electron to absorb a photon. As shown by Damascelli [21], this dipole term, \( \vec{A} \cdot \vec{p} \), is the leading term in the interaction of electrons and photons and in practice is the only one ever kept. The main effect of the matrix element term is to suppress photoelectron intensity from certain parts of the Brillouin zone or from certain energies. There must be an available final state for the electron (in the solid) in order to absorb the photon, and so certain photon energies will not overlap with high energy, unoccupied, bands required for absorption. In this sense the matrix element can obscure the intrinsic signal of the spectral function. However, recent studies have also shown the power of manipulating the matrix element to learn about the symmetries of the initial state and their orbital character [76].

The most striking effect of the matrix element is when it sends intensity all the way to zero, typically for symmetry reasons. The electron final state, \( \langle f \rangle \), is a plane wave (free electron) so it is even with respect to any mirror symmetry plane. The symmetry of the initial state, \(|i\rangle\), depends on the orbital wavefunction and the symmetry of the \( \vec{A} \cdot \vec{p} \) operator is the same as \( \vec{A} \). Therefore, when \( \vec{A} \) and \(|i\rangle\) have opposite symmetry, as in Fig. 3.3a, the entire matrix element is odd and integrates to zero, giving no photoemission. This seen nicely in the surface state of the topological insulator material Bi\(_2\)Se\(_3\) where there is orbital-momentum locking and electrons moving in different directions occupy different real space orbitals. Shown in Fig 3.3(c) is the Dirac-cone surface state of
Bi$_2$Se$_3$ superposed with the different p-orbitals that comprise it. This structure was uncovered by manipulating the ARPES matrix element to turn off different portions of the cone using different photon polarizations [76], as shown in Fig. 3.3(d). This is an excellent example of manipulating the ARPES matrix element to uncover properties of the electron’s initial state $|i\rangle$.

For the material studied in this thesis, Bi2212, the electrons of interest primarily occupy the Cu 3$d_{x^2-y^2}$ orbitals, which have a symmetry shown in Fig. 3.4(a). This symmetry is odd with respect to the ΓY ((0,0) to (π,π)) line, which means we need an E-field that is also odd with respect to ΓY in order to achieve photoemission. Shown in Fig. 3.4(b) is the Fermi surface of BSCCO measured by ARPES with linear polarization. Note how one node has a large suppression of intensity, caused by this matrix element effect. The other nodes are not as perfectly suppressed because the sample is tilted to produce different cuts, so the geometry isn’t perfect for cancellation at all angles.

### 3.1.5 Green’s Functions

The second term in Eqn. 3.5, $A(k,\omega)$, is known as the electron spectral function and is of primary interest when doing modern ARPES experiments. As we will show below, the spectral function (in principle) contains all the information about the many-body interactions of the electron so understanding $A(k,\omega)$ is of great importance. To do so we must start with the electron Green’s function, from which the spectral function is derived.

The Green’s function formalism is a way of doing quantum mechanics based on propagators that is quite well suited to studying many body physics. The Green’s function in the position and time domain essentially describes how a particle propagates through a system when it is inserted at $(x_i,t_i)$ and measured at $(x_f,t_f)$. A more common way of using Green’s functions is the fourier transform of this object, $G(k,\omega)$, which describes the propagation of a particle with frequency $\omega$ and momentum $\hbar k$. We won’t go through the derivation of $G(k,\omega)$ but simply state the result for particles in a non-interacting system, shown in Eqn. 3.6:
Figure 3.3: Illustration of the ARPES matrix elements. Panels (a) and (b) show an example orbital along with the symmetry plane, defined by the photon Poynting vector and the photoelectron momentum vector ($k_f$). In both cases the example orbital is even with respect to the symmetry plane but the E-field is odd in (a) and even in (b). Panel (c) shows the orbital breakdown of the surface state in the topological insulator Bi$_2$Se$_3$, determined by ARPES matrix element analysis [76]. Panel (d) shows the nodes of ARPES intensity for s-polarized photons (right panels), indicating the orbital structure changes at the Dirac Point (DP). Light of p-polarization couples to the $p_z$ orbitals shown in (c) and has no nodes around the cone (left panels in (d)). Figure adapted from Ref. [76].
Figure 3.4: Matrix element effects on cuprates. The relevant orbital is the Cu $3d_{x^2-y^2}$ orbital, shown in (a). Panel (b) shows ARPES data taken with linear vertical polarization on Pb-doped BSCCO-2212. The sample is oriented so the matrix element suppresses photoemission intensity along the ΓY direction, shown as a loss of counts along the vertical direction.
where $\omega$ is the electron energy, $\epsilon_k$ are the band energies at $k$, and $i\delta$ is an infinitesimal imaginary part included so integrals converge properly. This noninteracting picture is the natural starting place for studying many-body physics. When including interactions, the Green’s function of Eqn. 3.6 is replaced by Eqn. 3.7:

$$G(k, \omega) = \frac{1}{\omega - \epsilon_k - \Sigma(k, \omega)}$$  \hspace{1cm} (3.7)$$

where we have included the complex quantity, $\Sigma = \Sigma' + i\Sigma''$, which is known as the quasiparticle “self-energy”. All of the complexities of many-body physics are captured in $\Sigma$, which, with a few restrictions, can be an almost arbitrary function of $k$ and $\omega$. $\Sigma$ is defined in a perturbative and self-consistent way such that $G(k, \omega)$ is still the electron propagator, but now for the full Hamiltonian including interactions. The meaning of the self-energy becomes clear when we look at the spectral function, $A(k, \omega)$, defined in Eqn. 3.8:

$$A(k, \omega) = -\frac{1}{\pi} Im G(k, \omega)$$  \hspace{1cm} (3.8)$$

$$A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''}{(\omega - \Sigma' - \epsilon_k)^2 + (\Sigma'')^2}$$  \hspace{1cm} (3.9)$$

In Eqn. 3.9 we have decomposed $\Sigma$ into its real and imaginary parts via $\Sigma = \Sigma' + i\Sigma''$ and rationalized the expression for $A(k, \omega)$. If $\Sigma'$ and $\Sigma''$ are constant with energy then, for a given $k$, this expression for $A(k, \omega)$ is that of a lorentzian with a peak at $\omega = \epsilon_k + \Sigma'$ and a full width at half maximum \textit{(FWHM)} of $\Gamma_{EDC} = 2\Sigma''$. Now we come to the physical interpretation of the self-energy; $\Sigma'$ represents the extra energy added to that k-state by the interactions and $\Sigma''$ represents the lifetime of the quasiparticle. When $\Sigma' = \Sigma'' = 0$ the spectral function consists of $\delta$-function peaks at $\omega = \epsilon_k$, representing infinitely long lived states (eigenstates) at that energy, and shown in Fig. 3.5(a). However, in physical systems $\Sigma$ is never constant as a function of energy, so the exact lineshape of the energy distribution curve \textit{(EDC)} is typically not lorentzian. For example, in a Fermi-Liquid system $\Sigma \propto \omega^2$ and the spectral function takes on the form shown in Fig. 3.5(b). However,
Figure 3.5: Example of how interactions modify the Green’s Function and corresponding spectral function. Panel (a) shows a non-interacting system with a single band crossing $E_F$. The spectral function is given by a series of $\delta$-fns at the band energy that are occupied below $E_F$ and unoccupied above it. Panel (b) shows the same system but with Fermi-Liquid (FL) interactions turned on. Each $\delta$-fn is replaced by a complicated lineshape given by Eqn. 3.9 with the proper FL self-energy. Figure adapted from Damascelli [21].

Typically $\Sigma$ varies weakly with momentum so the momentum distribution curve (MDC) lineshape is much closer to a lorentzian, which can be seen by transforming $A(k, \omega)$ using the linear bare-band approximation:

$$
\epsilon_k = v_b(k - k_F) \quad \text{(3.10)}
$$

$$
\Rightarrow A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''}{v_b^2 (k - (k_F + \frac{\omega - \Sigma'}{v_b}))^2 + (\Sigma'')^2} \quad \text{(3.11)}
$$

$$
\Rightarrow A(k, \omega) = -\frac{1}{v_b \pi} \frac{\Sigma''/v_b}{(k - k_0)^2 + (\Sigma''/v_b)^2} \quad \text{(3.12)}
$$

where $v_b$ is the bare band velocity and $k_0 = k_F + \frac{\omega - \Sigma'}{v_b}$ is the renormalized peak location. Because of the weak momentum dependence of $\Sigma$ it can be approximated as a constant over the scale of an MDC peak. Therefore, at a constant $\omega$, $A(k, \omega)$ can be considered a lorentzian with peak location $k_0$ and FWHM of $\Gamma_{MDC} = \frac{2}{v_b} \Sigma''$. These formulas are at the center of modern ARPES analysis and show how to relate raw ARPES linewidths to intrinsic self-energies.

When we include superconductivity the Green’s function gets more complicated but Eqn. 3.8 still holds and the concepts discussed above are still valid. We explicitly discuss the superconducting Green’s function in Section 2.5.
3.2 Experimental Considerations

3.2.1 Surface Sensitivity

ARPES is inherently surface sensitive due to the necessity of photoelectrons leaving the sample. The mean free path (MFP) for electrons in a solid is on the order of 1 – 10 nm so even though the photons penetrate microns or more into the sample, the only useful photoelectrons for ARPES arise from within 1 MFP of the surface. As soon as a photoelectron scatters in the sample its original energy and momentum information are lost and it is demoted to a portion of the photoelectron background. This surface sensitivity can be of concern when the goal is to investigate bulk physics. The energies used in traditional synchrotron based ARPES, 20 – 50 eV, have close to the smallest MFP based on the so-called “universal curve”, shown in Fig. 3.6. One can achieve better bulk sensitivity by using either lower or significantly higher photon energy. However, it is more difficult to get good energy resolution with higher photon energy. In this regard, laser sources around 6 – 7 eV offer two advantages; increased bulk sensitivity and increased flux per energy bandwidth. Because of this general surface sensitivity maintaining a clean surface is crucial to performing ARPES. For this reason, ARPES experiments are typically performed in ultra-high vacuum (UHV) conditions, as described below.

3.2.2 Vacuum Details

The ARPES chamber, shown in Fig. 3.7, has three distinct vacuum sections, used to incrementally move samples from atmosphere to UHV conditions. The load-lock takes samples from atmosphere to $10^{-9}$ Torr after several hours of bake out. The prep chamber is the secondary vacuum stage and is typically held at $5 \times 10^{-11}$ Torr via a large turbo and frequent bakes. The main vacuum is the final stage, where samples are stored and studied, and is kept at $< 3 \times 10^{-11}$ Torr using a combination of turbo pumps, cryo pumps, and sublimation pumps. If necessary, the entire transfer procedure can be done in under two hours if the load-lock bake is skipped. However, we have found that such a fast transfer adds small amounts of water to both the prep and main
Figure 3.6: Universal Curve for electron mean free path in a solid as a function of electron kinetic energy. Energy ranges used in ARPES are highlighted; 6 eV for laser-based ARPES and 20 – 50 eV for synchrotron light sources. Figure adapted from Seah and Dench [72].
vacuum, which then require bakes to remove effectively. Therefore, baking the water out of the load-lock each time helps the long term usability of the system.

The sample can be cooled with liquid N\textsubscript{2} or He (open-cycle) and can get to 3K if necessary. Supplemental cooling is achieved with a thermal braid to a cold-head held at 20K. With this braid we can achieve 45K without using helium. Inside the main vacuum the sample is typically surrounded by two layers of copper cryoshrouds, held at roughly \( \sim 70\text{K} \) and \( \sim 20\text{K} \) by cryogenic cold-heads. The sample is only exposed to the inner shroud (at \( \sim 20\text{K} \)), minimizing the gas load on the sample surface. Vacuum is estimated to be in the low \( 10^{-12} \) Torr inside the cryoshroud, but there is no direct measure of this. Any sensitive vacuum gauge uses a hot filament to boil electrons and this thermal load on the shields would increase their temperature enough to change the vacuum measured. Therefore, we can only infer the vacuum based on the rate of surface degradation, which is quite slow.

All the laser sources are housed in dust-free HEPA tents, shown behind the chamber in Fig 3.7. The lasers enter the chamber from the back side, and impinge on the sample at 45\(^{\circ}\) from normal emission, as shown in Fig. 3.8. The UV beam (shown in purple) comes in parallel to the ground, in the same plane as the normally emitted electrons shown in Fig. 3.8. When doing pump-probe experiments, the MIR beam (shown in red) enters through an upper laser port (ZnSe window) and hits the sample at 17\(^{\circ}\) relative to the UV beam. Also shown in Fig. 3.8 is the manipulator radiation shield (shown in gold) that serves as the final layer of thermal shielding for the sample.

### 3.2.3 Electron Analyzer

We employ a SPECS Phoibos 225 hemispherical electron analyzer to sort the electrons in both energy and momentum. The analyzer is composed of two parts; the lens that does the angular sorting and the hemisphere that does the energy sorting. The lens stack consists of 8 cylindrically symmetric electrodes with different electrostatic voltages on them to bend the electrons, analogous to how optical lenses bend light. However, the lens stack can also accelerate or decelerate the electrons so they have the appropriate energy to make it through the hemisphere. The ratio of
Figure 3.7: A picture of the Dessau Lab UHV chamber used for ARPES experiments at CU. The three stages of vacuum, discussed in the text, are highlighted by boxes. Also highlighted is the hemispherical electron analyzer.
Figure 3.8: Sample geometry for ARPES measurements at CU. The sample denoted by the black square on the green disc. Lasers enter from the backside through two different ports. The UV laser forms a $45^\circ$ angle with the normally emitted electrons, shown heading towards the lens entrance. The front half of the lens has been removed for visualization purposes, but the real lens has cylindrical symmetry. When doing trARPES, the pump laser enters from above, forming a $17^\circ$ angle with the UV beam.
the energy at the beginning of the lens (termed “Kinetic Energy” for reasons elucidated below) to that at the end of the lens (termed “Pass Energy”) is called the retarding ratio and governs the amount of aberration in the imaging system. The end of the lens stack is an effective “Fourier Plane” for the electrons, meaning that initial angles of the electrons get mapped to different spatial positions, as shown in Fig. 3.9B. At this Fourier plane is the entrance slit to the hemispherical energy analyzer portion. The hemisphere consists of an inner and outer hemispherical electrode, see Fig. 3.9C, which have the proper voltages to produce a 1/r potential between them. Thus, the electrons entering the entrance slit undergo Keplerian orbits through the analyzer and get sorted by energy. The electrons at the “Pass Energy” have the right energy to traverse a circular orbit and end up directly between the two electrodes (green trajectory in Fig. 3.9C). However, due to the retardation of the lens those electrons actually started with energy equal to the “Kinetic Energy” parameter, which explains the name; electrons leaving the sample with that “Kinetic Energy” end up at the center of the spectrum after sorting. Electrons with higher energy take an elliptical path and end up closer to the outer hemisphere while those with less energy end up closer to the inner hemisphere. This is the main principle by which the electrons are sorted. To detect the electrons there is a multi-channel plate (MCP) stack with a phosphor screen placed at the “exit plane” of the analyzer. The MCP amplifies individual events that then impact the phosphor, the light from which is then collected by an external CCD camera. The size of the MCP stack determines the available energy window for a single spectral image and our system’s 40mm diameter MCP corresponds to a window of roughly 10\% the Pass Energy.

There are several things that affect the energy resolution of a hemispherical analyzer but the main contributions come from the Pass Energy, the entrance slit size, and electronic noise. The Pass Energy and slit size are actually two components that both affect the imaging quality of the hemispherical imaging system. The entrance slit is typically between 50 – 3000 \( \mu \)m wide (our system has several different slits available) and this physical width is imaged 1-to-1 onto the exit plane. Therefore, the larger the slit, the larger an area of the MCP will be taken by electrons with identical energy. (Imagine that two electrons with identical energies enter the hemisphere from
Figure 3.9: Cartoon of the operation of the hemispherical electron analyzer. Panel (A) shows the general setup including the electron source and the components of the analyzer. Panel (B) shows the electron lens operating in “angular” mode where initial electron angles are transformed to different spatial positions at the end of the lens. Panel (C) shows the hemispherical portion of the analyzer. The analyzer entrance slit is denoted by the hole in (C). Also shown are electron trajectories including those at too low (purple) or too high (red) to make it to the detector. Panel (D) shows a schematic of the MCP including grounding and accelerating meshes, phosphor screen, and camera. Figure adapted from Ref.[68].
either side of the slit. They will take different paths and end up at different locations on the MCP despite having the same initial energy). The effect of the Pass Energy is similar to that of the slit. As stated above, the full spectrum covers roughly 10% of the Pass (because all the hemisphere voltages scale with Pass) and so a large Pass will give a big energy window and corresponding small energy spacing. Therefore, when the slit gets physically imaged onto the detector it will take up more energy at high Pass than at low Pass. These two effects are summarized by Eqn. 3.13:

\[
\frac{\Delta E_a}{E_{\text{pass}}} = \frac{w}{R_0} + \frac{\alpha^2}{4}
\] (3.13)

where \( \Delta E_a \) is the analyzer energy resolution, \( E_{\text{pass}} \) is the Pass Energy, \( w \) is the entrance slit size, \( R_0 \) is the nominal radius (225 mm), and \( \alpha \) is the acceptance angle in the dispersion direction. Typically the \( \alpha \) term is significantly smaller than the slit size term and is often ignored.

The effects of electronic noise are typically more subtle than those discussed above and its sources can be varied and extremely difficult to ferret out. If any of voltages in the hemisphere have AC components then the imaging quality of the hemisphere will also have them, resulting in energy broadening. For this reason there are large RC filters on the voltage feedthroughs, but the filters are never perfect. Since the voltages scale with Pass but the noise typically does not, electronic noise contributions are always worse at low Pass energy. In addition to imperfect voltage generation, there is also significant effect from so called “ground loops”, or imperfect grounding. The reference point for all the hemisphere voltages is typically tied to the vacuum chamber wall, which is also the reference for any vacuum pumps, electrical equipment and others. Nominally there shouldn’t be any currents flowing through ground, but ground “loops” can cause currents to flow, resulting in slight shifts to the voltage of the reference point. This is typically not an issue except when trying to achieve the ultimate resolution possible with the instrument. In addition to these noise sources, which affect the instrument voltages, there can also be noise that affects the electron energies themselves. If there are fields between the sample manipulator (the electron source) and the front of the lens, those fields can accelerate/decelerate the electrons and add noise to their actual kinetic energy. To overcome this problem it is important to limit any electronic noise to the
manipulator from any sample diagnostics, and to force any residual noise to be common mode with the lens stack via an electrical short.

### 3.2.4 Effects of Resolution

ARPES data is affected by resolution in a similar fashion to all imaging techniques; it controls the finest features resolvable. In ARPES, the resolution is decomposed into the energy resolution and momentum resolution since they come from different sources. The energy resolution is comprised of the instrumental portion, discussed above, and the photon bandwidth, which add in quadrature. For typical laser-based ARPES the photon bandwidth is small ($\lesssim 1$ meV) compared to the instrument portion. However, for trARPES the ultrafast nature of the pulses leads to large energy broadening, typically $5 - 30$ meV, so it is comparable to or greater than the instrumental component. The momentum resolution, on the other hand, comes entirely from the angular resolution of the instrument. Since the angular resolution is constant, typically $\delta \theta \sim 0.1 - 0.3^\circ$, after differentiating Eqn. 3.4(a):

$$
\delta k_{||} = \sqrt{\frac{2m}{\hbar^2} (E_i + \hbar \nu - \Phi) \cos \theta \delta \theta}
$$

we see that the momentum resolution can be improved for low photon energies and high emission angles. This increased momentum resolution is one of the reasons low energy ARPES has proven so powerful, producing significantly sharper spectra as in Fig. 3.10. Note that while the laser-based ARPES spectrum shown in Fig. 3.10 does have improved energy resolution, the majority of the improved sharpness comes from the increased momentum resolution.

### 3.2.5 Analysis of ARPES Data

In modern day ARPES experiments the raw data is a 2D map of electron counts versus energy and momentum. A characteristic spectrum is shown in Fig. 3.11 where we see a single band crossing the Fermi level. Panel (a) shows a spectrum very close to raw ARPES data. We have converted the energy axis from kinetic energy to binding energy using Eqn. 3.1 and photoemission angle to in-plane momentum, $k_{||}$, using Eqn. 3.4. The two traditional ways to analyze ARPES
Figure 3.10: Comparison of ARPES spectra taken on nodal, near optimally doped, Bi2212 with different light sources. Panel (a) shows data taken at 25K with a 6 eV laser source. Panels (b) and (c) use synchrotron-based photons at 28 eV and 52 eV respectively. All images are plotted on identical E,k axes. The red circles in all panels are the MDC-derived dispersion from the laser data in (a). Dispersions from synchrotron data are shown as blue squares and black triangles in (b) and (c), respectively. Figure adapted from Koralek, et al [40].
data involve taking linecuts of the spectrum at either constant energy or constant momentum. A linecut at constant momentum is called an Energy Distribution Curve, or EDC, while a linecut at constant energy is called a Momentum Distribution Curve, or MDC. Examples of MDC’s and EDC’s are shown in Fig. 3.11 (b) and (c) respectively. The position of the peak in an EDC denotes the \((\omega, k)\) location of the electron state, including all many-body renormalization effects. The width corresponds to the energy uncertainty of that state and is related to the scattering rate, or lifetime, of that quasiparticle. Because of the dispersion of the band structure these energy widths are also mapped into momentum widths, according to \(\Delta E \sim \left(\frac{\partial E}{\partial k}\right) \Delta k = v_F \Delta k\). There are extra contributions to both the energy and momentum widths coming from experimental resolution, surface scattering, and other extrinsic broadening mechanisms. A major part of this thesis will be to disentangle these extrinsic broadening effects to reach the intrinsic broadening due to many-body interactions.

Connection of ARPES data to many-body interactions was originally done with EDC fitting to extract directly the energy widths of individual \(k\)-states. The reason for this is a historical one because old ARPES analyzers did not have a 2D detection scheme, instead having a pinhole and a channeltron that could only measure one EDC at a time. 2D spectra analogous to Fig. 3.11 were time-consuming to generate because the sample had to be rotated for each new \(k\)-point (the spectrum of Fig. 3.11 has over 300 momentum channels). In principle EDC analysis is more direct than MDC analysis because no conversion with velocities is required. However, the inelastic photoemission background, Fermi distribution, and electron self-energy change strongly with energy, which all complicate the EDC lineshape. MDC’s, on the other hand, are relatively unaffected by these terms because all have a very weak (if any) momentum dependence on the scale of a single ARPES spectrum. Therefore, MDC’s are typically closer to the lorentzian lineshape expected from the electron Green’s function which makes peak fitting easier and more reliable.

A newer method of ARPES analysis, called the Tomographic Density of States (TDoS), was developed by my labmate and mentor, Ted Reber. The TDoS is formed by a partial momentum integration of the spectral function and represents the density of states of a particular slice through
Figure 3.11: Example of an ARPES spectrum. ARPES was performed on nodal Bi2212 at 5K using 7eV photons. Panel (a) shows the 2D ARPES spectrum where the x-axis has been converted to momentum and the y-axis has been from kinetic energy to binding energy. Panel (b) shows an example MDC cut, in this case taken at $E = E_F$. Panel (c) shows an example EDC, in this case taken at $k = k_F$. The two linecuts are shown on the ARPES spectrum as light blue lines.
the Brillouin zone. (Tomography is the process of imaging through individual slices). The advantage of the TDoS is that it integrates out any excess momentum broadening (regardless of source) and tracks how spectral weight is distributed in energy. As Ted showed [68, 69, 67], TDoS analysis can be a very sensitive probe of the superconducting gap structure and we will use this technique throughout this thesis.

In order to form the TDoS spectrum properly the ARPES data has to be treated very carefully. The data is first linearized, normalized to an Au reference, and converted to momentum space. It is important to distinguish the “coherent” spectral weight from the “incoherent” photo-emission background. For near-nodal BSCCO this is accomplished using a lorentzian MDC fitting procedure. The coherent weight is the fitted area of the lorentzian while the background is a constant offset. For spectra with multi-peak MDC’s or otherwise broad features that make lorentzian fitting unreliable, the ARPES background can be estimated by averaging several EDC’s for $k > k_F$, referred to as the “EDC0” method. In order to remove the Fermi distribution the coherent weight at any momentum is divided by the nodal coherent weight. In principle, a theoretical Fermi edge (convolved with the proper energy resolution) would work just as well. However, the nodal edge is already at exactly the same resolution and temperature as the off-nodal spectrum, so it is an ideal choice. After this division the TDoS spectrum is complete and represents the partial density of states at a particular point in momentum space.

Ted found that these TDoS curves are well described by a lifetime-broadened BCS density of states, fitting well to the so-called Dynes’ Formula [22]:

$$I_{Dynes} = Re \frac{\omega - i\Gamma}{\sqrt{(\omega - i\Gamma)^2 - \Delta^2}}$$  \hspace{1cm} (3.15)

where $\Delta$ is the superconducting gap and $\Gamma$ is the inverse lifetime, or pair-breaking rate. Dynes proposed this form in 1978 when studying the strongly coupled $s$-wave superconductor Pb$_{0.9}$Bi$_{0.1}$. It works well for the $d$-wave cuprates because the partial $k$-integration of the TDoS is along a line of constant $\Delta$, so the $s$-wave formula holds locally. As Ted showed, the pair-breaking rate is much larger in the cuprates than in conventional superconductors, and also has a strong temperature
dependence. As shown in Fig. 3.12, as Γ grows, the superconducting gap gets “filled” whereas when Δ decreases the gap “closes”. The case for cuprates is predominantly gap-filling as Γ increases more rapidly near \( T_C \) than Δ decreases [67].

### 3.3 trARPES Details

The above discussion applies to all ARPES experiments. However, there are some additional experimental considerations when performing trARPES, namely spatio-temporal overlap of two laser beams, and an additional time resolution term. Here we will discuss each of these aspects.

#### 3.3.1 Spatio-Temporal Overlap

One of the most challenging aspects of the trARPES experiment is overlapping two laser beams in both space and time. In particular, both the MIR pump and the UV probe beams are invisible to human vision, requiring special alignment cards to visualize the beam path. Fortunately the bleach in most business cards fluoresces under ultraviolet (UV), and mid-infrared (MIR) can be seen on an appropriate color changing liquid crystal. Furthermore, MIR and UV are so far apart in wavelength that no material will transmit both of them. This means using separate vacuum windows for each beam, and having some method of aligning the beams inside vacuum (where we can’t use cards). UV is simple to visualize in vacuum using a YAG scintillator, which glows green under sufficient radiation above \( \sim 5 \text{ eV} \). However, the MIR is too low energy to be seen on the scintillator, and to my knowledge there are no vacuum compatible materials that visualize MIR (liquid crystals are not vacuum compatible). Therefore we need a completely different method of aligning the MIR beam inside vacuum. My solution is to make a tiny metal target, roughly 50–100 \( \mu \text{m} \), surrounded by colloidal graphite (DAG) because the multiphoton photoemission cross-section of copper is significantly higher than carbon (see Sec. 7.2.2 for more details on multiphoton photoemission). A target this small can be made by first spraying the entire sample block with DAG and then scratching through the DAG with the corner of a razor blade. When done under an optical microscope, scratches of \( \sim 50 \mu\text{m} \) are relatively easy to obtain, though directly after morning
Figure 3.12: Example of gap-filling vs. gap-closing. For constant $\Delta$ as $\Gamma$ increases the gap “fills”, as shown in (a), increasing the weight at $E_F$ but keeping the peak in roughly the same place. Conversely, when $\Gamma$ is constant but $\Delta$ decreases, as in (b), the gap “closes” and the peak position moves toward $E_F$. 
coffee this increases to approximately 200µm. The alignment algorithm starts with the UV beam aligned (via the scintillator) and rastering near the target to maximize the photoemission counts. Then we switch to the MIR beam and manually move the final steering mirror to maximize the photoemission counts with MIR only. This ensures that both beams are hitting the same position within 50 – 100 µm. The location and performance of the Cu target is shown in Fig. 3.13.

After spatial overlap is confirmed we need to overlap the pulses in time. In the probe beam path there is a computer controlled stage which can travel 100 mm with 1µm precision (see Fig. 4.2). Each 1µm of delay stage travel adds 2µm of optical path length, which is equivalent to 6.667 fs. This level of precision is plenty since the laser pulses are ≳ 100 fs. However, the total optical path where the two lasers are separated is roughly 10 meters, so matching the paths to the micron amounts to 1 part in 10 million. The delay position where the two paths are perfectly matched is defined as $t_0$ and corresponds to both laser pulses hitting the sample at the same time. We define a “positive” delay for any probe path length longer than that for $t_0$, corresponding to probing the sample some time after the pump pulse hits. Similarly, a “negative” delay corresponds to probing the sample before the pump pulse excites the system and should reflect the equilibrium state of the system.

The best way to define $t_0$ is to use an actual trARPES signal from the sample position using a material with a relatively long response time. Here we use a combination of GaAs, highly ordered pyrolytic graphite (HOPG), and BSCCO to define $t_0$ progressively more precisely. GaAs has a uniquely long trARPES signal when pumped at energies above the bandgap (1.42 eV at 300K) because the pump can excite an electron-hole plasma that gives rise to a surface photovoltage (SPV) [88]. This SPV effect has a long temporal signature in the negative delay (probe beam hits first) region because the leaving photoelectrons can still feel the effect of the SPV even when they are in vacuum. Due to the relatively slow speed of the low energy photoelectrons, they remain close enough to the sample surface to be affected by the SPV for up to 100’s of picoseconds [88]. The total travel of the delay stage covers 666 ps so we can move in very course steps to quickly narrow down the location of $t_0$. This procedure on GaAs is shown in Fig. 3.14.
Figure 3.13: Using a Cu target for laser alignment. Panel (a) shows intensity maps versus position for both the MIR laser beam. Panel (b) shows a cartoon of the target location relative to the sample. Panel (c) shows horizontal linecuts for both UV and MIR linecuts, giving a FWHM of 100\(\mu\text{m}\) and 280\(\mu\text{m}\), respectively. Panel (d) shows similar linecuts for different MIR wavelengths, showing that the beam size does not change appreciably with wavelength.
Figure 3.14: Signatures of temporal overlap using p-type GaAs. The system is pumped with 650 nm, 1.9 eV, photons and probed near the Γ-pt. The sample is also biased by 3.6 V to increase the photoelectron energy. Panels (a) and (b) show the ARPES spectrum at delay stage positions of 45 mm and 50 mm, respectively. Panel (c) shows the EDC’s indicated by the dashed lines in (a) and (b) with arrows highlighting the peak locations. Panel (d) shows scans covering the entire delay stage travel. The horizontal axis has been converted to ps of delay, though the top axis connects back to physical delay stage position. The inset to (d) shows a zoom-in around $t_0$ to clearly observe the fast decay at positive delay.
The main disadvantage of using GaAs to find $t_0$ is that we need to use a pump photon energy that is greater than 1.42 eV while the available DFG energies are restricted to 60 – 310 meV. My solution is to double the residual signal beam (1300 nm) exiting the DFG box to produce a 650 nm pump, which is roughly 1.9 eV. The signal and idler beams normally exit the DFG vertically separated from the MIR light and pointed down (into a beam dump). However, using a computer controlled mirror in the DFG we can move the signal beam very close to the actual MIR beam path (the idler is blocked during this procedure). The signal is doubled with a 0.2 mm BBO and then rejected by a polarizer, while the doubled signal is transmitted through it. Then the doubled signal travels the same optical path as the MIR light, with the only differences arising from the added BBO/polarizer (and the index change of the ZnSe optics).

After we have narrowed the location of $t_0$ using GaAs and the 650 nm pump we switch back to 4 µm pump to fine tune the $t_0$ location on HOPG. Due to the difference in ZnSe index at 650 nm vs 4 µm, the $t_0$ location will change slightly between the two pump energies. Also, ZnSe becomes highly dispersive for wavelengths below 800 nm so the temporal cross-correlation measured on GaAs is not the truest measure of the time resolution. Fig. 3.15 shows the $t_0$ behavior on HOPG using the 4 µm pump.

The photoelectron response is a combination of multiphoton (MP) effects, near $t_0$, and transient electronic heating that lasts for several picoseconds or more. The thermal response is limited to energies around $E_F$ so for energies above this scale the temporal dynamics look more like a symmetric gaussian, as one would expect for the cross-correlation between two gaussian pulses. This is shown explicitly in Fig. 3.16 where we integrate from $\omega = (0, 300)$ meV above $E_F$ and compare it to just $\omega = (250, 300)$ meV. The higher energy window has a more symmetric lineshape. The limit of high energies and low pump powers (to limit thermal response) yields a perfectly symmetric lineshape.
Figure 3.15: Signatures of temporal overlap using HOPG and MIR pump. Panel (a) shows \( k \)-integrated counts vs. energy for three different time delays. Panel (b) shows similar traces for all delays, shown in a log-scale false color map. Panel (c) shows the integrated weight above \( E_F \) vs. delay along with a bi-exponential fit as a guide.
Figure 3.16: Spectral Weight above $E_F$ in different energy ranges for 4µm pumped HOPG. The black trace is integrated from $E_F = 0$ to +300 meV while the red trace is only from 250 to 300 meV. The traces are normalized to show the change in weight more clearly.
3.3.2 Temporal Resolution

The true time resolution of the system is set by the cross-correlation between the pump and probe lasers. This can be measured by the symmetric gaussian response on HOPG, or similar material. Shown in Fig. 3.17 is such a gaussian response, measured in the interval $\omega = (250, 300)$ meV above $E_F$. The data in Fig. 3.17 used a lower pump power than Fig. 3.16 and so the electronic heating effects do not enter the energy window, giving a nicely symmetric response. Fig. 3.17 also shows how we can control the time resolution of the experiment. The system is pumped with the 4$\mu$m pump and probed with the full energy bandwidth of the UV pulses in panel (a), roughly 20 meV, giving a time resolution of roughly $\sim 300$ fs. When probing with a reduced UV bandwidth of 3.6 meV, as in Fig. 3.17(b), the time resolution changes to $\sim 700$ fs. (See Section 4.5 for details on changing the bandwidth). Clearly, reducing the energy bandwidth of the UV probe results in worse time resolution, which is to be expected from the Heisenberg uncertainty principle. However, the change in energy bandwidth (20 to 3.6 meV) does not match the change in time resolution because the time resolution involves the cross-correlation with the pump pulse, which did not change between the two measurements.

The time resolution can also be estimated from the asymmetric response by fitting to an exponential impulse (or two) convolved with a gaussian distribution. Here the exponential(s) represent the hot carrier dynamics and the gaussian represents the temporal dynamics. When fitting to such a function the gaussian component is most sensitive to the rising edge of the data, which helps decouple the carrier dynamics from the resolution contribution. Fitting to this asymmetric lineshape yields similar numbers to the symmetric case discussed above.
Figure 3.17: Measuring the temporal resolution using the SW above $E_F$ in HOPG. Here we show the counts in an energy range $\omega = (250, 300)$ meV above $E_F$ when probed by the full UV bandwidth (a) or a reduced bandwidth (b). The 4 $\mu$m pump in unchanged between the two measurements. Fitting to a gaussian gives a FWHM of 320 fs in (a) and 700 fs in (b).
Chapter 4

Laser Development for trARPES

In this section we will discuss the basic operating principles of the laser system required to do trARPES. Contrary to conventional ARPES, where any photons (with energy greater than the work function) can be used, time-resolved ARPES necessarily requires pulsed laser sources. In addition, since the relevant time scales in solids are typically on the femtosecond to picosecond scale, one requires ultrashort pulses to adequately probe the solid. Fortunately, over the last several decades there have been vast improvements in ultrafast laser technology and it is relatively easy to produce laser pulses shorter than 100 fs (10 fs is slightly more difficult). Due to the extremely short temporal profile, these pulses have extremely high peak intensities, which make them well suited for nonlinear conversions.

Ti:Sapphire lasers can produce radiation in the 600 – 1000 nm range, with typical spectra being centered around 800 nm, or 1.55 eV photon energy. In order to do photoemission one needs photons with energy at least the material workfunction (typically 4 – 5 eV). Previous trARPES work has used the Ti:Sapphire fundamental as an optical pump [63, 18, 74]. However, we would like to pump with lower energy (≪ 1.55 eV) so that excitations are concentrated around the Fermi energy. Therefore, from 800 nm photons, we need to convert both up and down in frequency in order to make an effective trARPES instrument. In order to up convert the photons to UV wavelengths we employ a series of sum frequency generators to produce the fourth harmonic of the Ti:Sapphire energies, the details of which will be described below. Down conversion to the Mid Infrared (MIR) wavelengths requires a combination of an optical parametric amplifier (OPA) and
a difference frequency generator (DFG). The OPA is tunable, and can essentially split the 1.55 eV photons into two photons whose energy sums to 1.55; 1 and 0.55 eV, or 0.75 and 0.8 eV. Then the DFG mixes those frequencies and produces light at the difference of the two input frequencies. However, all these nonlinear processes require intense laser pulses with pulse energies higher than achievable with laser oscillators. We need to use a powerful regenerative amplifier to produce pulses strong enough to drive these nonlinear conversions. Since this complex system of nonlinear processes is necessary to do trARPES I will explain all the components in further detail below.

4.1 Regenerative Amplifiers

The pulse energies typically produced in a Ti:Sapphire laser oscillator (∼ 1 nJ) are too small to drive an OPA. The standard solution to this is use an amplifier system to increase the pulse energy at the expense of repetition rate. The two types of single stage amplifiers are regenerative amplifiers (regen) and multipass amplifiers. Here we make use of a regen amplifier because it affords higher repetition rate than the multipass option. The basic operating principle of a regen is to seed a laser cavity with a pulse so that the stimulated emission from the pulse is much stronger than that of any spontaneous emission from the gain medium. Then, due to the exponential growth of the pulse, most of the energy in the gain medium will get transferred to the pulse instead of other laser modes. In practice, one starts with a cavity that has a variable amount of loss and a way to inject and eject the seed pulses. When the cavity is configured to have high loss the gain medium can store all the energy from the pump laser because lasing is suppressed. Then, one injects the seed pulse (typically with an electro-optic (EO) or acousto-optic (AO) modulator) and the loss is set as low as possible. This allows the seed pulse to resonate in the cavity until it has removed most or all of the energy. Once the pulse has depleted the gain medium it is ejected, often with over 1000 times the original pulse energy. Finally, the gain medium has to recharge, or regenerate, before it is ready for the next pulse.
4.2 Nonlinear Optics: SHG, SFG, and other three letter acronyms

In standard electrostatics the polarization of a dielectric is directly proportional to the applied electric field. This is typically written in terms of the linear susceptibility, $\chi^{(1)}$, as:

$$\vec{P} = \epsilon_0 \chi^{(1)} \vec{E}$$ (4.1)

where $\vec{P}$ is the induced polarization, $\vec{E}$ is the applied electric field, $\epsilon_0$ is the permittivity of free space, and $\chi^{(1)}$ the linear susceptibility tensor. The fact that $\chi^{(1)}$ is a (rank 2) tensor allows for $\vec{E}$ and $\vec{P}$ to point in different directions. For nonlinear (NL) optics we are interested in higher order processes, and we can generalize Eqn. 4.1 to a power series in the field strength, $E$:

$$\vec{P} = \epsilon_0 (\chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}^2 + \chi^{(3)} \vec{E}^3 + \cdots)$$ (4.2)

where $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second and third order nonlinear susceptibilities, respectively. We will focus in particular on the $\chi^{(2)}$ processes, which will cover all the nonlinear conversions utilized in the experiment. Note the response of the second-order polarization, $\vec{P}^{(2)}$, when two different fields are applied:

$$E(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c.$$ (4.4)

$$P^{(2)}(t) = \epsilon_0 \chi^{(2)} [E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1 E_2 e^{-i(\omega_1 + \omega_2)t}$$

$$+ 2E_1 E_2^* e^{-i(\omega_1 - \omega_2)t} + c.c.] + 2\epsilon_0 \chi^{(2)} [E_1 E_1^* + E_2 E_2^*]$$ (4.5)

Here we see explicitly that each term of Eqn. 4.5 corresponds to a polarization at a frequency other than that of the driving field. The first two terms, at $2\omega_1$ and $2\omega_2$, are referred to as second harmonic generation (SHG), while the next two terms, at $(\omega_1 + \omega_2)$ and $(\omega_1 - \omega_2)$, are sum-frequency generation (SFG) and difference-frequency generation (DFG) and the final term with no frequency dependence is optical rectification (OR). It is also clear that SHG is a special case of SFG with $\omega_1 = \omega_2$. Therefore, if $\chi(2) \neq 0$ it is possible to get SHG, SFG, and DFG all from the same crystal.
However, there are several other considerations for efficient nonlinear conversions that usually limit you to one three-letter acronym per NL crystal.

Probably the most important consideration for NL processes is phase-matching in the material. Just because there is a response from the second-order polarization doesn’t mean that there will be macroscopic generation at, for example, SHG wavelengths. For example, if $\omega$ and $2\omega$ travel through the material at different speeds (or wavevectors $k = n(\omega)\omega/c$), then fields of $2\omega$ generated at different parts of the crystal will have different phase and will, in general, destructively interfere. The condition to have constructive interference, known as phase-matching, is given by $2k(\omega) - k(2\omega) = 0$, and is equivalent to matching the indices $n(\omega) = n(2\omega)$. For (all) physical materials, material dispersion dictates that, in general, $n(\omega) \neq n(2\omega)$, but nonlinear crystals are typically birefringent, meaning they have different indices of refraction for different polarizations (and propagation directions) through the crystal. For the case of uniaxial birefringent materials, there is an ordinary (o) polarization that travels the same speed regardless of propagation direction, and an extraordinary (e) polarization for which the speed is direction dependent. This is shown in Fig. 4.1 where we use notation of “index-spheres” to denote speed. For an “index-sphere”, the radius of the circle denotes the index of refraction and the angle from the vertical axis denotes the propagation direction through the material. Therefore, the (o)-ray, which is direction independent, is denoted by a circle in Fig 4.1(a), while the (e)-ray takes the form of an ellipse. For uniaxial crystals there is one “optic axis” where $n_o = n_e$ which we have aligned to the vertical coordinate in Fig 4.1. Now, we know that the index of refraction is frequency dependent, with the general case being larger indices at higher frequencies. We can use the “index-sphere” notation to easily show the phase-matching condition $n_o(\omega) = n_e(2\omega)$, as in Fig 4.1(b). The intersection of the circle at $\omega$ and the ellipse at $2\omega$ denotes the propagation direction where the two colors are phase-matched, and is denoted by the phase-matching angle $\phi_{PM}$. When propagating at $\phi = \phi_{PM}$ the wavevectors of the two colors are matched precisely, as shown in Fig 4.1(c). The case shown in Fig 4.1 is called Type I phase-matching, which is defined as producing an (e)-ray from two (o)-rays, $(o) + (o) = (e)$. There is also Type II phase-matching where $(o) + (e) = (e)$ and follows similar reasoning, but since
all the conversions we will deal with are Type I, we won’t discuss Type II. The phase-matching condition is typically very strict, which means that in a crystal with $\chi^{(2)}$ processes typically only one of the possible SHG, SFG, or DFG conversions is phase-matched at once. Modern nonlinear crystals are cut at a particular angle that is phase-matched for a certain NL process at a particular wavelength (or set of wavelengths).

The field of nonlinear optics is far richer than the introduction given here. In particular, there are extra considerations needed when using ultrafast pulses such as group velocity mismatch and group velocity dispersion. Unfortunately, there isn’t enough time to cover all the relevant topics, so I direct the interested reader to several good texts on the subject, such as Boyd [13] and Weiner [82].

4.3 Full System Layout

The full light source for used for trARPES is shown in Figure 4.2. We start with a regeneratively amplified Ti:Sapphire laser (KMLabs Wyvern-1000) and split the output between the “pump” and “probe” generation schemes. The majority of the power is used to drive the OPA/NDFG generation while a small fraction is used to generate the UV probe. The probe beam travels along a delay stage so that the relative path length between pump and probe can be changed electronically. The probe also travels through the time-compensating monochromator so we can control the time duration (and energy spectrum) of the pulse. Finally, the two beams are recombined at the sample (through two separate vacuum ports). Each of these subcomponents is discussed in the sections below.

4.4 UV Probe Generation Scheme

Figure 4.3 shows the apparatus used to generate the UV photons used as the “probe” pulses in trARPES. Here we use three stages of Type I SFG in $\beta$-barium borate (BBO) to combine each harmonic with the fundamental beam. While this is one extra nonlinear stage compared to a double-double scheme, the phase-matching in BBO for 800nm + 267nm allow us to push out to
Figure 4.1: Type I phase-matching conditions inside nonlinear crystals. Panel (a) illustrates the concept of an “index-sphere”. Here the axes represent different propagation directions through the crystal and the circle (ellipse) is the index of the ordinary (extraordinary) ray for that particular direction. The y-axis is called the optic axis and is defined by $n_o = n_e$. Here we are showing a negative birefringent material, where $n_e \leq n_o$ for all angles. Panel (b) shows how to graphically find the phase matching condition by displaying the indices for $n_o(\omega)$ and $n_e(2\omega)$. Material dispersion requires $n_o(2\omega) \geq n_o(\omega)$ but then $n_e(2\omega)$ can intersect $n_o(\omega)$ at the so-called phase-matching angle, $\phi_{PM}$. Panel (c) shows the wavevectors for both frequencies at $\phi = \phi_{PM}$ where $k(2\omega) = 2k(\omega)$.

Figure 4.2: Schematic layout of light source for trARPES. We start with a KMLabs Wyvern-1000 that produces 40 fs pulses at 790 nm (600 µJ, 20 kHz). The majority of this light drives the commercial OPA/NDFG system to generate MIR pump pulses. A small fraction of the Wyvern output is used to generate the UV probe pulses via three cascaded SFG stages. The probe pulses then travel through the delay stage and time-compensating monochromator before being recombined with the pump pulses at the sample. The UV probe enters the vacuum chamber through a CaF$_2$ window while the MIR pump enters through a separate ZnSe window.
higher UV photon energies compared to the double-double scheme [40]. The first SFG stage is simply a 0.2mm BBO crystal ($\phi = 29.2^\circ$) that converts some ($\sim 4\%$) of the fundamental (H-pol) to second harmonic (V-pol). Due to the high pulse energies of the laser amplifier we do not need to focus the beam into the nonlinear crystals. This greatly simplifies the optical setup and reduces the material dispersion added. The SHG stage is the simplest since all the 800nm photons start in one pulse. However, due to group velocity mismatch, the second harmonic pulse lags behind the fundamental upon exiting the BBO. We compensate for this lag using a calcite time plate (TP), shown in Fig. 4.3. Calcite has “negative” birefringence, meaning that the extraordinary (e) ray has a smaller index than the ordinary (o) ray. Therefore, when aligned such that the second harmonic is along the e-axis it travels faster than the fundamental beam ($n_e(400\,nm) = 1.50$ while $n_o(800\,nm) = 1.65$). By adjusting the tilt angle one can change the effective thickness of the crystal, thereby tuning the relative optical path length (OPL) by up to several hundred femtoseconds. This technique is limited to cross-polarized beams in the wavelength range where $n_e(\lambda) < n_o(2\lambda)$ but here it is ideal. Next the beams go through a dual wave plate (DWP), which is a HWP for 800nm and a full-wave plate (no retardance) for 400nm. This results in both wavelengths having the same (V) polarization, necessary for Type-I SFG. The beams go through 0.1 mm BBO ($\phi = 44.3^\circ$) and combine to produce the third harmonic, 267 nm, with H-pol. The final SFG stage is analogous to the THG portion, except that the TP is replaced by a physical delay stage because calcite strongly absorbs 267nm. We use a dichroic beam separator to reflect the 267nm while transmitting the 800nm. Since the beams are physically separate we can use a standard HWP to rotate the 800nm to H-pol. After the delay stage the 800nm and 267nm beams are recombined using another dichroic optic and pass through the final 0.1 mm BBO ($\phi = 42.8^\circ$) crystal, producing 200nm (V-pol). As shown Fig. 4.3, we can optionally add focusing lenses to improve the efficiency of the final stage if necessary. After the final BBO we use several dielectric mirrors to separate out the unwanted harmonics, resulting in a beam of only FHG photons.

Based on Eqn. 4.5, the intensity of SHG is proportional to the fundamental intensity squared. The generalization to SFG is that the SFG radiation is proportional to the product of intensities
Figure 4.3: Fourth Harmonic Generation Setup. There are three nonlinear stages where various BBO’s are used to combine 800nm photons with each harmonic. The SHG stage is a 0.2mm BBO ($\phi = 29.2$ deg) that generates V-pol SHG light. The THG stage uses a calcite time-plate (TP) to temporally overlap the orthogonally polarized pulses, followed by a dual wave-plate (DWP) to make both pulses V-pol. The THG crystal is 0.1mm BBO ($\phi = 44.3$ deg), which generates H-pol 266nm pulses. The first and third harmonic pulses are separated with a dichroic beam splitter so the first harmonic can be rotated to H-pol and delayed via a manual delay stage (DS). Finally, the pulses are recombined using an identical dichroic coating and collinearly sent through the FHG crystal, a 0.1mm BBO ($\phi = 48$ deg), generating V-pol FHG pulses.
of each incoming beam. It follows from this that the FHG intensity of our cascaded SFG setup is proportional to the fundamental to the fourth power. However, this approximation breaks down once the SFG intensity is strong enough to significantly reduce either of the pump intensities. In this so-called saturation regime the SFG intensity quickly becomes linear with pump power, following a form similar to Eqn. 4.6 [13]:

\[ I(2\omega) = I(\omega) \tanh^2 \left( E_0 \omega d_{eff} l / n_\omega c \right) \] (4.6)

\[ I(2\omega) = I(\omega) \tanh^2 \left( \sqrt{I(\omega) \gamma_1} \right) \] (4.7)

where \( \gamma_1 = \omega d_{eff} l / n_\omega c \) contains all the NL crystal information: \( d_{eff} \) is the effective nonlinear constant, \( l \) is the length, \( n_\omega \) is the index at frequency \( \omega \), and \( c \) is the speed of light. This behavior is shown in Fig. 4.4(c) where we see that for low powers, Eqn. 4.6 follows \( I(2\omega) \propto I(\omega)^2 \) while for high powers \( I(2\omega) \propto I(\omega) \). Higher order processes follow similar reasoning. For example, producing FHG via two cascaded SHG processes results in:

\[ I(4\omega) = I(2\omega) \tanh^2 \left( \sqrt{I(2\omega) \gamma_2} \right) \] (4.8)

\[ I(4\omega) = I(\omega) \tanh^2 \left( \sqrt{I(\omega) \gamma_1} \right) \tanh^2 \left( \sqrt{I(\omega) \gamma_1 \gamma_2} \right) \] (4.9)

\[ I(4\omega) \approx \gamma_1^4 \gamma_2^2 I(\omega)^4 - \frac{4}{3} \left( \gamma_1^6 \gamma_2^2 \right) I(\omega)^5 + O(I^6) \] (4.10)

where we see the lowest order term goes as \( I^4 \). While our FHG setup utilizes three SFG stages instead of two SHG stages, the math for latter case is simpler and still illustrates the power dependence. For our setup, the transition to saturation occurs at 0.5-1.0W of input power, as seen in Fig. 4.4(a).

### 4.5 Time Compensating Monochromator

Ultrafast pulses inherently come with a broad energy bandwidth, on the 20 – 30 meV scale here. When doing photoemission this energy bandwidth corresponds directly to a decreased energy resolution and in some cases can mask the physics we are interested in probing. The near-nodal superconducting gap is one such case, where the gap sizes are on the order of 5-10 meV. In this
Figure 4.4: Harmonic output power versus input 800 nm power. Panel (a) shows the FHG power measured after the setup to input power measured before the setup. The data match better to a depleted form, as discussed in the text, rather to any single power law. Panel (b) shows the UV generation for ideal alignment (green) and slightly phase-mismatched alignment (blue). The green trace reaches saturation quicker and has better efficiency overall. Panel (c) shows the general SHG conversion including depletion (Eqn. 4.6) where the output transitions from $\propto I^2$ to $\propto I$ as input power is increased.
regime the temporal dynamics (∼ 1 ps) are typically much longer than the ∼ 100 fs pulses [74] and so the super short pulses aren’t necessary. Therefore, the ability to control the bandwidth of the UV pulses while maintaining a low time-bandwidth product (TBP) is of great advantage. Here we make use of two monochromators in a time-compensating geometry [79], shown in Fig. 4.5, to control the UV energy bandwidth while maintaining short pulses. Since we are using narrow band pulses, which are 300 – 500 fs long, we employ lenses as the focusing elements because the material dispersion adds only a negligible amount of chirp. Figure 4.6 shows the result; a tunable UV source with bandwidths from 3.5 to 20 meV. In principle we can cut the bandwidth to 1.2 meV (with a 10µm slit), but those pulses would be too long (> 1.5 ps) to be useful for our studies.

4.6 MIR Pump Generation Scheme

The mid-infrared (MIR) laser used to “pump” the solid-state system is generated by a commercial, TOPAZ-C optical parametric amplifier (OPA) in conjunction with non-collinear difference frequency generation (NDFG or just DFG). As mentioned above, the OPA can convert 1.55 eV photons into two photons that sum to 1.55 eV in a tunable way. The higher of the two photon energies is called the “signal” while the lower is referred to as the “idler”. In the TOPAZ-C the signal is tunable from 1200 – 1600nm, with the idler covering a range of 1600 – 2400 nm. The signal and idler are then mixed in a GaSe crystal in the NDFG, producing wavelengths ranging from 4000 – 20000 nm. The non-collinear geometry of the DFG allows for separation of the Signal and Idler wavelengths from the DFG wavelength. The output performance of our OPA/DFG system is summarized in Fig. 4.7.
Figure 4.5: Schematic of time-compensating monochromator. The system is inversion symmetric about the slit plane so that the angular dispersion added by the first grating is removed from the second. The gratings are plane, ruled gratings with 2400 lines/mm and are blazed for 240 nm light. They diffract roughly 60% of incident light into the $m=1$ order. The lenses are CaF$_2$ to reduce dispersion and have a focal length of 100 mm. The variable slit is achieved by a magnetic, kinematic mount that allows different fixed slits to be interchanged with reproducible positioning. The slit is also on a horizontal translator for fine control of the center wavelength.
Figure 4.6: FHG spectrum at the output of the time-compensating monochromator, measured using an OceanOptics HR4000 commercial spectrometer. The full UV bandwidth is shown in red while two different reduced bandwidths are shown in blue and green, achieved with 30 and 50\,\mu m slits, respectively.
Figure 4.7: Output performance from TOPAZ-C OPA/NDFG system used to generate pump pulses for trARPES. Signal and Idler were measured before the DFG generation and DFG was measured after separation from Signal and Idler wavelengths. All were measured using a thermopile power meter.
Chapter 5

Impurity Study on FeBSCCO

Dirty superconductors are superconductors that contain significant impurities, whether they were added intentionally or not. Conventional BCS superconductors are robust against normal impurities, but ruined with the addition of just a few magnetic impurities [51] like nickel or manganese. This difference arises because the spin flip that occurs when an electron scatters off a magnetic impurity violates time reversal symmetry and thus breaks the pair, whereas simple scattering without the spin flip cannot break the pair [4][48]. The importance of pair breaking scattering is clearly evident in conventional superconductors as seen by the rapid decrease in $T_C$.

Understanding the effects of impurities on the high temperature superconducting cuprates is even more critical as the cuprates are a very disordered system with many inherent defects. One of the best ways to study the effects of these defects is to intentionally add more in a controlled manner, through the addition of impurities [3, 6]. There is still some debate whether impurities reduce $T_C$ by decreasing the superconducting volume [56] or increasing the pair-breaking scattering [11]. Therefore, cuprate impurity studies require a good way to measure the effects of impurities, such as pair breaking scattering, and due to the material’s anisotropy, to do so in a momentum resolved way. Previous studies on impurities in the cuprates have relied on bulk measurements [87, 84] or position sensitive spectroscopies [33, 59], both of which must average over momentum space and so provide less direct information about the d-wave system.

Angle Resolved Photoemission Spectroscopy (ARPES) is an excellent probe to address these challenges because it probes the band structure directly in the momentum domain. It is expected
that adding impurities broadens the band by increasing scattering and this should be directly observable with ARPES. However, as we show below, the Fe impurities are only a small subset of the scattering events and so obtaining quantitative information about the Fe impurities is difficult with direct ARPES spectra. In the present paper we show, using our tomographic density of states (TDoS) technique, that we can separate the pair-breaking from non pair-breaking scattering and extract the pair-breaking induced by Fe impurities, which is \(1.25 \text{ meV} / (\% \text{ Fe})\).

Here we present a study where we dope \(\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CaCu}_2\text{O}_8+\delta\) (Bi2212) with the magnetic impurity \([10]\), Fe. A series of single crystal samples of Bi2212 with varying concentrations of Fe were grown using the floating zone method\([28]\). Six doping levels were studied, with Fe concentration ranging from 0\% to 2.2\%. Each sample’s \(T_C\) was measured using SQUID magnetometry. We chose Fe impurities because they are known to substitute for Cu \([28]\) in the CuO\(_2\) plane. Consequently, the impurity potential is poorly screened and therefore a more significant perturbation than out-of-plane impurities. Increasing Fe suppresses \(T_C\) from 91K at 0\% Fe to 67K at 2.2\% Fe, a 26\% decrease over the full range of doping (inset to FIG. 5.3). The \(T_C\) suppression from Fe is stronger than that reported from either non-magnetic Zinc \([47]\) or magnetic Ni \([41]\) impurities, suggesting Fe has unique physics in this class of Cu-substituting impurities.

Figure 5.1 shows a compilation of the raw nodal data from various doping levels. All data were taken with 7eV photon energy and a hemispherical electron analyzer. The total experimental energy resolution was measured to be 4.5 meV using a 10K Au Fermi edge. All spectra were taken cold (T<30K) to minimize the effects of thermal scattering processes. One might worry that adding too much Fe affects the crystal structure to the point where a band is unrecognizable. As shown in panels a1-a3, at all concentrations there is very clearly still a single band present, with very similar dispersions, widths, etc. Therefore, within this Fe concentration range the Fe impurities are only a weak perturbation to the electronic structure.

One of the standard methods to analyze ARPES data is momentum distribution curve (MDC) analysis \([77]\). The MDC width is directly related to the imaginary part of the electronic self-energy, \(\Sigma''\) \([21]\). However, this self-energy includes many different types of electron scattering processes, and
Figure 5.1: Panels a1–a3 show raw nodal ARPES of Bi2212 across the measured Fe concentrations. Each spectrum was taken in ΓY orientation at the node and at low temperature. Panel b the energy dependence of the MDC widths for all the doping levels studied. Panel c shows the MDCs at $E_F$ for different dopings. Panel d shows the $\text{Im } \Sigma$ extracted from the MDC at $E_F$ for every individual sample studied.
it is hard to deconvolve the individual contributions from these different processes. In particular, the pair-breaking scattering events are a small subset of the total events, so increases in this rate may be indiscernible using the standard MDC analysis method. Indeed, as FIG. 5.1 panels b-d show, there is no clear trend in the MDC width with Fe concentration. Raw MDCs at $E_F$, in panel c, are roughly identical and the dependence of the width with binding energy, in panel b, shows no trend beyond the sample-sample variation. Lastly, panel d summarizes these findings, showing that the $\text{Im } \Sigma(\omega = 0)$, extracted from the MDC at $E_F$, has no significant trend with Fe concentration. We propose that the contributions from cleave-to-cleave variations in surface quality [77] overwhelm the intrinsic changes in MDC width from the addition of Fe impurities.

To overcome the shortcomings of MDC analysis we have developed another technique to study electron interactions, the TDoS method, which is the density of states for a single slice through momentum space [69]. (Tomography is the imaging of a volume via individual slices.) The TDoS allows us to quantitatively measure both the gap magnitude and the pair-breaking scattering rate. Briefly, to create a TDoS we isolate the coherent states of the band from the incoherent background [69]. By integrating the resulting spectrum across momentum, we obtain the coherent spectral weight. Finally, to remove effects of the Fermi distribution we divide this spectral weight by the nodal spectral weight. More details about the TDoS method can be found in Refs. [69, 67].

The TDoS are fit to a modified Dynes formula [22] that includes resolution effects. Dynes’ formula, Eq. (5.1a), is a lifetime broadened BCS density of states. This formula was originally used in tunneling experiments on s-wave superconductors, where the gap is single valued over all of momentum space. It has been used in the cuprates in bulk transport and STM studies [2, 65] but requires a careful integration over the d-wave gap. However, our chosen experimental geometry (inset to FIG. 5.2a2) allows us to treat the gap as single valued. Fitting to the adapted Dynes form, shown in Eq. (5.1b), we extract the pairing strength, $\Delta$, and the pair-breaking rate, $\Gamma_{TDoS}$, from the TDoS spectrum.
\[ \rho_{\text{Dynes}}(\omega) = \text{Re} \frac{\omega + i \Gamma_{TDoS}}{\sqrt{(\omega + i \Gamma_{TDoS})^2 - \Delta^2}} \] (5.1a)

\[ I_{TDoS}(\omega) = \frac{[\rho_{\text{Dynes}}(\omega) \times f(\omega)] \ast R(E_{\text{Res}})}{f(\omega) \ast R(E_{\text{Res}})} \] (5.1b)

Here \( f(\omega) \) is the Fermi function, \( R(E_{\text{Res}}) \) is an energy resolution term (4.5 meV FWHM Gaussian), and we leave the subscript TDoS on the \( \Gamma_{TDoS} \) to distinguish it from a \( \Gamma \) that may be determined from EDC or MDC analysis.

Earlier, we showed [69] that the TDoS method is robust against sample to sample variations in MDC widths within the same doping level. Furthermore, \( \Gamma_{TDoS} \) is up to an order of magnitude smaller than the scattering rate found via MDC analysis [69], which is consistent with \( \Gamma_{TDoS} \) representing only a subset of the total scattering processes. For example, any forward scattering events should contribute to \( \Sigma'' \) but should not significantly increase pair-breaking and so would not be part of \( \Gamma_{TDoS} \) [20]. Since the MDC is more sensitive to the total scattering rate, it is also more sensitive to surface effects, such as any damage arising from cleaving, and is therefore a less intrinsic measure of the material. As we show in FIG. 5.3, the TDoS method can extract the pair-breaking dependence on Fe concentration that is simply masked in the MDC analysis.

Figure 5.2 shows a compilation of the TDoS data for selected dopings, along with the extracted \( \Delta \) and \( \Gamma_{TDoS} \) values. Panels a1-a3 show the angular dependence of the TDoS along with the Dynes fits for three different Fe concentrations. Note how the pile-up of states increases in size and location with \( \theta \), signifying an increase in the gap size. Note also that as \( \Gamma_{TDoS} \) increases more pairs are broken and more weight is present at \( E_F \). This trend can be seen in the \( \theta = 2.5^\circ \) curves (red online) moving from panel a1 to a3. One can see good quantitative agreement between the data and the fits with perhaps slightly degraded agreement at the high angle data. We attribute the disagreement to a higher order effect that is not captured by the simple nature of the functional form (which is only a two parameter fit). Shown in panels b1-b3 are the \( \Delta \) and \( \Gamma_{TDoS} \) values for all angles at the selected Fe concentration as well as the fit to the angular dependence. \( \Delta \) rises linearly away from the node, as a d-wave gap in the near nodal regime. We extrapolate this near
nodal data to obtain the maximum gap, $\Delta_{\text{max}}$, by fitting to a d-wave form: $\Delta(\theta) = \Delta_{\text{max}}|\sin(2\theta)|$.

In contrast to $\Delta$, $\Gamma_{\text{TDoS}}$ is roughly constant across all angles, which is consistent with our previous TDoS study on BSCCO and is applicable over a wide doping range [69, 67], but differs markedly from the result using MDC or EDC analysis [77]. Due to the angular invariance, we average $\Gamma_{\text{TDoS}}$ over all angles to extract $\Gamma_0$.

Figure 5.3 shows both $\Delta_{\text{max}}$ and $\Gamma_0$ vs. Fe concentration. $\Gamma_0$ rises by about 130% over the full experimental range while $\Delta_{\text{max}}$ remains relatively unchanged. More specifically, $\Gamma_0$ shows a linear increase with Fe concentration, which we discuss in greater detail below. Despite a slight downward slope visually, the $\Delta_{\text{max}}$ data show no real trend with added Fe; the uncertainty in the slope of a weighted linear fit is several times larger than the slope's value. Therefore, we conclude that there is no significant change in the superconducting gap from the addition of Fe impurities.

A related experiment on Zn-substituted Bi2212 found, using the standard EDC method, that the antinodal gap size was insensitive to the addition of Zn impurities [47]. In addition, Ref. [47] found a qualitative increase in the number of in-gap states with the addition of Zn impurities, consistent with an increased $\Gamma_{\text{TDoS}}$, though the TDoS technique is more quantitative than EDC analysis. Both of these results from Ref. [47] are qualitatively similar to those reported here and suggest that the physics involved in both Zn and Fe impurities is similar. Note also that while $\Delta_{\text{max}}$ didn’t change, $T_C$ decreased by 26%, indicating a departure from BCS superconductivity where these quantities are directly proportional. In addition, the fact that $\Delta_{\text{max}}$ is essentially unchanged but both $T_C$ and $\Gamma_0$ change indicates that pair-breaking processes are critical in setting $T_C$ in this material.

We propose a simple model based on ballistic transport that captures the essential physics of the linear increase of $\Gamma_0$ with Fe concentration. The dimensionality of $\Gamma_0$ suggests the simplest form would be a velocity divided by a length. The natural choices are the Fermi velocity and the mean distance between Fe impurities, respectively. Here we use the measured, nodal Fermi velocity, 1.9 eV·Å, instead of the bare velocity because the impurities are a perturbation on a system that already has self-energy effects. In this simple model, we estimate the mean distance as the Cu-Cu
Figure 5.2: A selection of TDoS spectra for different Fe concentrations and the corresponding TDoS fit results. Panels a1-a3 show TDoS curves (open circles) and the individual TDoS fits (black lines) for selected angles from the node. The inset in a2 shows the k-space cuts and our definition of $\theta$. Panels b1-b3 show the $\Delta$ and $\Gamma_{TDoS}$ values exacted from the TDoS fits. The fit to $\Delta$ is a d-wave gap with the node and gap maximum as the only fitting parameters. The fit to $\Gamma_{TDoS}$ is a simple average.
Figure 5.3: $\Gamma_0$ and $\Delta_{\text{max}}$ vs. Fe impurity concentration. Panel (a) shows $\Gamma_0$, which is extracted from the angular average of $\Gamma_{TDOS}$ for a given Fe concentration. $\Gamma_0$ shows a linear dependence on Fe concentration, as shown by the dashed line. Panel (b) shows $\Delta_{\text{max}}$, which is extrapolated from the d-wave gap fit shown in figure 2. $\Delta_{\text{max}}$ shows very little dependence on Fe concentration, decreasing less than 1% according to the linear fit (dashed line). The inset shows $T_c$ vs Fe concentration, which changes from 91K to 67K, a 26% change over the full Fe range.
spacing, 3.82 Å, divided by the concentration, \( x \), of Fe scattering sites. And we add a dimensionless parameter, \( \alpha \), that represents the 2D scattering cross-section for these events. Note that in two dimensions, the scattering cross-section has dimensions of length instead of the normal dimensions of area for a 3D scattering process. Since we have divided out the length dimension using “\( a \)”, \( \alpha \) is dimensionless and has units of Cu-Cu spacing. This model would be sufficient if Fe impurities were the only things causing scattering. However, Bi2212 has a number of native defects including Cu vacancies and several types of oxygen vacancies and dislocations [24, 52, 34, 30, 89]. Each of these scattering species should contribute to the scattering rate in the same way as outlined for Fe impurities, and so we can add a sum of terms to the formula for \( \Gamma_0 \), as shown in Eq. 5.2a. This sum includes all native defects in the material, including any not listed above. However, it is beyond the scope of this thesis to determine both the concentrations and cross-sections for all these defects. And since they are not relevant to extracting properties of the Fe impurities, we group all of the native defects together in a term called \( \Gamma_0^{\text{Native}} \), shown in Eq. 5.2b. This model should hold as long as the impurities are well separated and therefore not interacting with each other.

\[
\Gamma_0 \approx \frac{v}{l_{\text{Fe-Fe}}} ; l_{\text{Fe-Fe}} = \frac{a}{x} \Rightarrow \Gamma_0^F(x) = \frac{v}{a}(\alpha x) \\
\Rightarrow \Gamma_0 = \frac{v}{a}(\alpha x + \sum_{i}^{N} \beta_i x_i) \quad (5.2a) \\
\Rightarrow \Gamma_0 = \frac{v}{a}(\alpha x) + \Gamma_0^{\text{Native}} \quad (5.2b)
\]

Figure 5.4 shows the linear fit to our data in the context of this model. The linear increase in \( \Gamma_0 \) we attribute to Fe impurity scattering while the offset is due to the combined effects of all native defects in the material. From this fit we extract \( \alpha = 0.25 \), which means the pair-breaking scattering cross-section of a single Fe impurity is approximately 25% of the Cu-Cu spacing, or 0.96 Å. This is a reasonable value of the cross-section for a single site defect, and suggests that Fe impurities are relatively weak pair-breakers. This result is also consistent with STM work on Fe-substituted
BSCCO that claims Fe is a weaker scatterer than Ni[39, 33], Zn[59], and Cu vacancies [34, 80].

To our knowledge, this is the first time the pair-breaking cross-section has been measured for any impurity in the cuprates. Furthermore, this general experimental procedure would work on any impurity, as long as there is sufficient control to increase the concentration of a known impurity while keeping all others constant.

Using the TDoS technique we have measured the effects of Fe impurities on the superconducting gap and pair-breaking scattering rate in the high $T_C$ superconductor Bi2212. The main effect of Fe impurities is to increase the pair-breaking scattering rate, while leaving the gap parameter unchanged. This indicates that magnetic impurities do not affect the pairing strength, just the pair lifetimes. This result also confirms that cuprate superconductivity is sensitive to pair-breaking scattering. The correlation between $\Gamma_0$ and $T_C$ is suggestive and motivates further studies at temperatures near $T_C$, as well as studies of other impurities, such as Zn and Ni, in hopes of discovering any universal behavior of cuprate impurities.

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1 Ref. [39] directly compares Fe to Ni impurities. Refs. [33, 59, 34] measure the individual impurities, and a calculation of the relative strengths of Ni, Zn, and Cu vacancies is provided by Ref. [80].
Figure 5.4: Segregating the effects of Fe impurities from native defects using our simple model of impurity scattering. $\Gamma_0^{\text{Native}}$ is the pair breaking rate for all the combined native defects not including any Fe impurities, while $\alpha$ is a dimensionless parameter that represents the pair-breaking scattering cross-section (in units of Cu-Cu spacing) for Fe impurities.
Chapter 6

Effects of Doping Inhomogeneity on the ARPES lineshapes of BSCCO

Anderson showed why a dirty (conventional) superconductor can exist with such high levels of disorder, with $T_C$’s up to 30K \[4\]. His model works great for s-wave gaps and non-magnetic dirt. But the game changed in 1986 with the introduction of the High-$T_C$ materials. With $T_C$’s quickly surpassing that of liquid nitrogen, these new superconductors displayed a range of unique properties including a rich phase diagram and a $d$-wave gap. This anisotropic gap has been extensively studied by ARPES, whose k-selectively is crucially important. It is perhaps puzzling that these cuprate superconductors, with record $T_C$’s, were found to be incredibly dirty on the nanoscale using STM \[45, 14\]. These measurements show a ubiquitous nanoscale gap disorder in the BSCCO family. Many have claimed \[71, 42\] that this doping disorder can explain the large scattering rates measured in ARPES compared to other probes, such as optical reflectivity \[36\] and STM methods \[62\]. ARPES is unique among current spectroscopies in its momentum selectivity and direct mapping of electronic structure. In fact, due to this (almost) direct access to the electron’s spectral function, it is possible to extract the electron’s self energy using the energy and momentum widths, as is common practice in the field \[21, 77\]. This electron self-energy is the main object of interest (aside from the order parameter) since it contains (all) the information about the many-body interactions influencing the electron. However, ARPES’s k-sensitivity is a double edged sword because it is sensitive to other momentum broadening mechanisms that are integrated out using other probes. Since ARPES is such a powerful probe for these anisotropic superconductors, it is important to fully understand the magnitude and impact of any broadening mechanisms so that their effects are not confused with
the intrinsic scattering rate. Here we explore, in a quantitative way, the extent to which nanoscale electronic disorder affects ARPES spectra and develop a procedure to remove this dirt from the spectrum.

### 6.1 Conflicting Σ’s

Fig. 6.1 illustrates the self-consistency problem with ARPES spectra. Starting with near-nodal data, shown in Fig. 6.1(a), one can extract MDC widths by doing Lorentzian fitting on each MDC. While Lorentzians are not the proper form for a gapped spectral function, they work reasonably well far away from the gap-scale. However, there is a systematic error to the fitting near the gap-scale, which is highlighted by the red dashed line in Fig. 6.1(c). This deviation is well understood and is just a byproduct of trying to fit a Nambu-Gor’kov spectral function to a Lorentzian lineshape. Since these deviations are not true scattering rates, we replace the structure by a constant value, determined from an energy outside the gap-scale. This results in the solid red trace in Fig. 6.1(c). It is standard practice [77] to convert these MDC widths into scattering rates using Eqn. 6.1:

\[ \Sigma'' = \frac{v_{bb}}{2} \Gamma_{MDC} \]  

where \( \Gamma_{MDC} \) is the FWHM, \( v_{bb} \) is the bare band velocity (2.3 eVÅ for the spectrum in Fig. 6.1(a)), and \( \Sigma'' \) is the imaginary part of the self energy.

Note that the minimum scattering extracted from MDC widths is close to 20meV but the gap is only 8.6meV. Consequently, the gap structure should be so filled in that the gap is hardly noticeable [67]. However, as we see in the data, there is a well-defined gap with thermally occupied quasiparticles residing above it. We can extract the scattering rate near the gap-scale by using the TDoS method and fitting the coherent spectral weight to the Dynes formula. The TDoS spectrum and corresponding fit are also shown in Fig. 6.1(b) and we can see that \( \Gamma_{TDoS} \) is significantly smaller than \( \Gamma_{MDC} \). Here we distinguish the true self-energy, \( \Sigma \), from that estimated by MDC widths, which we call \( \Gamma_{MDC} \). The Dynes fitting procedure is only sensitive to the scattering rate inside the
Figure 6.1: Extraction of the scattering rate from near-nodal ARPES spectra. Panel (a) shows a near-nodal ARPES spectrum for OP Bi2212 ($T_c = 91K$) at 70K, with the photoelectron background removed. The k-space location is shown by the lower left inset. Panel (b) shows the TDoS spectrum (red circles) and accompanying Dynes fit (black line) for the spectrum in (a). The extracted $\Gamma$ and $\Delta$ are shown in (b) as well. Panel (c) shows the estimated scattering rate, $\Sigma''$, from both lorentzian MDC fits and from the TDoS fit. The systematic error from fitting a lorentzian to the Nambu-Gor’kov spectral function is shown as the red dashed line on the MDC trace. We obtain the hybrid $\Sigma''$ estimate by linearly shifting the MDC trace to match the TDoS result inside the gap scale.
gap-scale so we should only expect this constant $\Gamma_{TDoS}$ to hold in that energy range. In order to achieve the dispersion kink observed in the data the energy dependence of $\Sigma''$ must still have the step increase around 70 meV that we observe in $\Gamma_{MDC}$. Therefore, as a first order approximation, we can shift $\Gamma_{MDC}$ down to match $\Gamma_{TDoS}$ at and inside the gap-scale. The resulting hybrid estimate for $\Sigma''$ is shown as the blue trace in Fig. 6.1(c). The physical interpretation is that the MDC widths are a combination of true self-energy effects and some energy-independent scattering rate or other momentum-broadening term. We will discuss these possibilities in more detail below.

6.2 Spectral Reconstruction

Now that we know the superconducting gap from TDoS analysis and have an estimate of the self-energy we can try to reconstruct this ARPES data. Recall from Chapter 2 the formula for the electron’s Green’s function including both a superconducting gap, $\Delta$, and a many-body self-energy, $\Sigma = \Sigma' + i\Sigma''$:

$$G_{11}(k, \omega) = \frac{\omega - \Sigma + \xi_k}{(\omega - \xi_k - \Sigma)(\omega + \xi_k - \Sigma) - Z^2|\Delta_k|^2} \approx \frac{\omega - \Sigma + \xi_k}{(\omega - \Sigma)^2 - \xi_k^2 - Z^2|\Delta_k|^2}$$ (6.2)

and the spectral function is still the imaginary part of the Green’s function, as in Eqn. 3.8. For the purpose of reconstructing the ARPES data in Fig. 6.1(a) we will treat $\xi_k$ as a linear bare band of the form $\xi_k = v_{bb}(k - k_F)$ with $v_{bb} = 2.3$ eVÅ since that is a reasonable approximation for near-nodal spectra in the vicinity of $E_F$. We can obtain $\Sigma'$ by a Kramers-Kronig transform of $\Sigma''$ and then we have all the components necessary to simulate the spectral function. In order to emulate ARPES data we then multiply the spectral function by the appropriate Fermi distribution (here 70K) and convolve the spectrum with the proper energy and momentum resolutions, typically 5 meV and 3 mÅ$^{-1}$ respectively. We simulated the ARPES spectrum for each of the estimated $\Sigma''$ traces shown in Fig. 6.1(c), which are reproduced in Fig 6.2(a).

However, when we try to reconstruct the ARPES spectrum using these $\Sigma''$ values (Fig. 6.1c) the simulation fails poorly, as shown in Fig. 6.2(c). This simulation has the same gap size as the data
Figure 6.2: Attempted reconstruction of ARPES data using self-energies extracted from MDC analysis. The traces in (a) are reproduced from Fig. 6.1 and renamed $\Gamma_1$ (from direct MDC analysis) and $\Gamma_0$ (same $\omega$ dependence but matching the TDoS value at $E_F$). Panel (b) shows the real part of the self-energy, $\Sigma'$, which is extracted via Kramers-Kronig transformation of the traces in (a). Panels (c) and (d) are reconstructed ARPES spectra using $\Delta = 8.6$ meV and the self energies shown in (a), as discussed in the text. Panel (e) shows the ARPES data for easy comparison.
(8.6 meV) but the scattering rate at $E_F$, termed $\Gamma_1$, is $\sim 20$ meV. Consequently, the gap structure is obscured due to the filling in of the gap. This simulation is clearly inconsistent with observations and this forces us to reconsider the assumption that $\Sigma \propto \Gamma_M$. In principle, any source of momentum broadening would have this effect on the spectrum. However, one logical source is that from the doping inhomogeneity measured with STM. It has been suggested several times [71, 42] that the nanoscale disorder seen with STM could cause ARPES spectra to be excessively broad. In order to test that idea we propose a Local Fermi Surface (LFS) model where each doping patch has a band structure with different filling, but with their Fermi levels tied together, resulting in a different $k_F$ for each patch. Since the doping domains are on the order of the coherence length, 20-30 Å, and photoemission is done with spot sizes on the order of 50µm or more, one is forced to sample all the domains simultaneously, resulting in a heterogeneously broadened spectrum. Even the advent of nano-ARPES, which uses extremely small spot sizes on the order of 10nm, isn’t enough to avoid this effect [5]. In the simplest interpretation, the LFS model claims that the measured ARPES spectrum is a classical superposition of the signals from each separate doping domain, weighted by their abundance. There are some very important limitations of this model, which will be discussed below. However, being a straightforward model, it is a natural place to start reconciling ARPES with STM.

6.3 Nanoscale Inhomogeneity

One possible reconciliation of the problems in the previous section comes from the observation of nanoscale electronic disorder found in the cuprates, particularly the BSCCO family [45, 14, 42, 85]. Scanning Tunneling Microscopy (STM) can measure the local density of states (LDOS) with atomic scale resolution and these measurements have reported disorder in the LDOS spectra that vary on the scale of the superconducting coherence length, 20 – 30Å. This disorder manifests in both LDOS intensities and changes in gap size as a function of position. Further, this disorder appears at all doping levels, which suggests some type of universal origin [2]. A study by Wise et. al claims that these nanoscale patches with different gap size are actually patches of different doping
level, with the gap size following the typical phase diagram [85]. Based on these observations, it has been suggested [71] that ARPES measurements are actually sampling several doping regions at once and that this could account for the anomalously large broadening of ARPES spectra. In addition, there is recent work using neutron quadrupole resonance [60] showing that this nanoscale inhomogeneity manifests in phonon linewidth broadening as well.

As an aside, it has been shown that this gap disorder is correlated to apical oxygen disorder [52, 90], suggesting some connection to the charge transfer layers away from the copper oxygen planes. Such out-of-plane disorder can cause forward scattering for electrons in the Cu-O planes since the impurity potential is typically screened somewhat by the conduction electrons. This forward scattering is another possible interpretation of the effect of nanoscale disorder on the electronic scattering rate, and is thoroughly discussed in Refs. [71, 20].

Fig. 6.3 shows an example of the nanoscale disorder measured by STM. Each STM image (panels (a),(b),(d)) is a square of roughly 600 Å on a side and is colored by the local gap size [42]. These show the ubiquitous nature of this gap disorder, even for samples of different gap size. When scaled to the mean gap, $\overline{\Delta}$, all the dopings show the same disorder distribution as seen in Fig. 6.3(c). This universal distribution has a full width of roughly $\sim 0.4\overline{\Delta}$ and is quite close to a normal distribution. We will use a similar distribution when trying to simulate ARPES spectra. Fig. 6.3(d)-(f) shows how impurities affect this electronic disorder. Note how the regions around Ni impurities (red dots in Fig. 6.3(d)) tend to have lower gap value, quantitatively shown in Fig. 6.3(e). In fact, the authors reported they could not find any Ni impurities with a local gap larger than 50 meV. Because we explicitly discuss Fe impurities in this thesis I have also included gap histograms for optimally doped Bi2212 with 0% and 0.5% Fe substitution showing that the addition of impurities shifts the gap distribution towards smaller values. However, recall from Chapter 5 that $\Delta_{Max}$, as measured by ARPES, was insensitive to the addition of Fe impurities. This is a good example of how the gap measured by STM is not necessarily the superconducting gap because STM is sensitive to charge ordering gaps that could be present at the antinodes, regardless of superconductivity [42]. Some have suggested that the superconducting gap is in fact much more
homogeneous than the reported antinodal gap disorder [42], which has implications for ARPES spectra that are discussed below.

STM measures things in real space but with a technique called quasiparticle interference (QPI) this real space information can be transformed to momentum-transfer space, or $q$-space. QPI involves a spatial Fourier transform of raw STM data and more details can be found in Refs. [29, 53, 81]. The resulting QPI pattern has peaks in locations corresponding to scattering from one part of the band structure to another, as shown by the cartoon in Fig. 6.4(a) and QPI data in Fig. 6.4(b). Therefore, by tracking the dispersion of the QPI peaks in energy one can map out the $k$-space band structure of the solid. Wise et. al used a clever modification of the QPI technique to show that the gap disorder in the cuprates actually corresponds to nanoscale patches of different doping levels [85]. Prior to performing the Fourier transform the authors masked the raw data according to the gap size, generating one QPI pattern for the small gap regions ($\Delta = 10$ to 30 meV with $\langle \Delta \rangle = 26$ meV) and a separate QPI pattern for the large gap regions ($\Delta = 30$ to 60 meV with $\langle \Delta \rangle = 37$ meV). The resulting Fermi surface positions are shown in Fig. 6.4(c) where it is clear that the larger gap regions correspond to Fermi surfaces with smaller hole pockets, i.e. more underdoped. The work by Wise et. al was the first to show that the nanoscale electronic disorder is also doping inhomogeneity within a single sample and they posit that each patch, 20 – 30Å across, has its own local Fermi surface [85]. It is this model, which we call the Local Fermi Surface (LFS) model, that we will use to try to reconcile the spectral reconstruction issues presented in Sec. 6.2.

6.4 Spectral Reconstruction including Doping Inhomogeneity

While the work of Wise et. al effectively showed the doping inhomogeneity (DI) in the cuprates, we cannot directly apply their results to simulating ARPES spectra because they grouped their whole sample into only two regions; small gap and large gap. To predict the doping level of each individual gap size we need a continuous mapping from $\Delta$ to $p$. This is done by comparing the average gap of a set of samples to their doping level, defined by counting oxygen atoms with an STM, with the results shown as red dots in Fig. 6.5(a). We interpolate these data to a third
Figure 6.3: Characteristic “Gap Maps” from STM. Panels (a) and (b) show characteristic gap maps for underdoped $T_C = 79K$ (a) and as grown $T_C = 91K$ (b) doping levels, and they share a common color scale between them. Panel (c) shows a compilation of gap maps for a wide range of dopings. When scaled to the mean gap value, $\overline{\Delta}$, all dopings collapse to a universal disorder distribution with a full width of $\sim 0.4\overline{\Delta}$. The effects of impurities are shown in panels (d)-(f). Shown in (d) is a gap map with Ni impurities highlighted in red. Panel (e) shows the gap histograms for the full map (grey) and just on Ni sites (red). Panel (f) shows a comparison of an OP 91K sample and one of the same doping level but with 0.5% Fe impurities. Panels (a)-(e) are adapted from the work of Davis and collaborators [42, 2] while panel (f) is adapted from Ref. [86].
Figure 6.4: Fermi surface reconstructions from STM quasiparticle interference (QPI) measurements. QPI cartoon and data shown in panels (a) and (b). Panel (c) shows Fermi surface positions for QPI maps masked for small gaps in black and large gaps in red. Figure adapted from Ref. [85].
order polynomial to define a continuous mapping from $\Delta$ to $p$. Next we need to convert this doping level to a band structure, which will serve as the $\xi_k$ values in the spectral function. We use a tight binding band structure with coefficients determined by a combination of measured $k_F$ values and LDA calculated $\Gamma$ and $Y$ point energies [50]. Different doping levels correspond to different chemical potentials and we obtain the mapping, shown as dashed line in Fig. 6.5(b), via state counting. Once both the $\Delta \rightarrow p$ and $p \rightarrow \mu$ maps are set we can convert the gap histogram from STM to a $\mu$-histogram for simulating ARPES data.

We simulate the effects of DI on ARPES by treating the ARPES signal as a classical superposition of signals for each of the different doping domains. However, since all the domains are in electrical contact they must have the same $E_F$ and therefore different domains have different $k_F$’s. All the domains are treated as having the same self-energy, $\Gamma_0(\omega)$, referred to as the homogeneous self-energy. These individual signals are shown in Fig. 6.6(b) and are identical to the reconstruction of Fig. 6.2(d) up to a shift in $k_F$. We then add these individual signals, weighted by the histogram in Fig. 6.6(a2), to obtain the final “measurable” ARPES spectrum. The original data is shown in Fig. 6.6(d) for easy comparison. Unlike Figs. 6.2(c) and 6.2(d), the reconstruction in Fig. 6.6(c) matches the data quite well qualitatively, including both the well-defined gap structure and approximately the right MDC widths. These simulations suggest that for gapped spectra, the data is inconsistent with a $\Sigma''$ extracted from MDC widths alone. Additionally, since the MDC widths evolve smoothly from node to off-node it is reasonable to assume that the nodal spectrum is also composed of a smaller self energy with additional momentum broadening, rather than one extracted from raw MDC widths. Furthermore, the k-broadening estimated by STM disorder is of the right order to describe ARPES linewidths, helping to bring these two powerful probes into agreement.

From this analysis it appears that the measured ARPES signal in the cuprates is consistent with having a small homogeneous self-energy and an extra “heterogeneous broadening” due to doping inhomogeneity.

We can get a quantitative understanding of the success of the LFS model by comparing particular linecuts from the data and simulations, shown in Fig. 6.7. The DI broadening affects
Figure 6.5: Converting from Gap Histograms measured via STM to chemical potential distribution used in ARPES simulations. First we use sample averaged gap values measured by STM at several dopings (red dots in a) to interpolate a mapping from $\Delta$ to $p$. We limit the interpolation to a third order polynomial to capture the slow variation of $\Delta$ with $p$. However, as seen in (a), the mapping is fairly linear over the relevant range. Second we perform a similar mapping from doping level to chemical potential, as shown in (b). The mapping from $p$ to $\mu$ is determined using state counting on a tight binding model for the bare band, where the tight binding parameters come from a combination of measured $k_F$ values and LDA calculated $\Gamma$ and $Y$ point energies. There is some uncertainty in this mapping, which leads to an uncertainty in the width of the $\mu$-distribution.
Figure 6.6: Reconstruction of ARPES data including the doping inhomogeneity observed by STM. Panel (a1) shows a gap map that leads to the doping histogram in (a2). Each doping level has its own Fermi surface, with three characteristic ones shown in (a3) that match the colored bars in (a2). Panel (b) shows the simulated ARPES spectra for individual doping levels, all from the same k-slice shown in (a3). Each spectrum in (b) has the same self-energy, $\Gamma_0(\omega)$ from Fig. 6.2, but has a different $k_F$ defined by the doping level. These spectra are then combined in a weighted superposition (weighting defined by the histogram in (a2)) to produce the spectrum in (c). Panel (d) shows the original data for comparison.
both the MDC’s and EDC’s, seen by comparing the blue and red traces in Fig. 6.7(a) and (c), but the real data is broader by both metrics. It is well known in the ARPES community that there is sample to sample variation in the MDC widths [69], with people typically reporting the best (i.e. sharpest) samples they measure. However, STM measurements across many BSCCO samples and dopings all report very similar inhomogeneity histograms, suggesting that the disorder is sample independent. The ARPES MDC linewidth is in principle sensitive to all the scattering the photoelectron sees. This includes gas molecules at the surface, and any crystal defects or domain walls due to cracking (from cleaving). Therefore, it should not be surprising to find an ARPES spectrum broader than that predicted by DI broadening alone but this broadening should represent a lower bound on the sharpest measurable spectrum. Also, as seen in Fig. 6.7(b), the heterogeneous broadening does not result in a constant increase of MDC with energy. It is more accurate to view the heterogeneous broadening as convolved with the homogeneous portion, such that when the homogeneous broadening is dominant the heterogeneous component becomes negligible. Note that while the EDC’s and MDC’s were broadened significantly by DI, the TDoS spectrum is remarkably robust to this disorder, seen in Fig. 6.7(d). The simulated TDoS spectra are almost identical to each other (so much that only one trace is visible in (d)) and very similar to the data. We attribute the robustness of the TDoS to the fact that in making the TDoS we integrate out all this excess momentum broadening. While DI is fundamentally a chemical potential broadening, in the near-node it manifests as excess momentum broadening, which affects EDC’s and MDC’s but not TDoS. This robustness shows the importance of the TDoS method as it applies to cutting through the heterogeneous broadening to measure the intrinsic, homogeneous self-energy.

6.5 Momentum Dependence

One natural question is how this heterogeneous broadening affects different parts of the Fermi surface. Based on the band curvature, see Fig. 6.6(a3), one would assume that the antinodal region should have larger momentum broadening than the near nodal region. However, we have found that in the SC state the large renormalization present at the antinode dominates over the heterogeneous
Figure 6.7: Comparison of different linecuts for the data, single-$\mu$, and many-$\mu$ simulations. Panel (a) shows the $E_F$ MDC’s while (b) shows the energy dependence of the MDC widths. Panel (c) shows the $k_F$ EDC’s and panel (d) shows the TDoS spectra. In (d), the simulations have almost identical TDoS spectra so only a single trace is visible.
broadening. In the normal state, even though the renormalization is much weaker, the lifetime broadening from the higher temperature is now dominant. So in both regimes the heterogeneous broadening is dwarfed by the intrinsic broadening.

In Fig. 6.8 we show ARPES data and reconstructed spectra for several cuts around the zone, shown in inset. This data is taken from an OP doped ($T_C=91$K) Bi2212 sample, cleaved in UHV conditions, and studied with 9 eV photons for improved resolution [40, 64]. In the data we subtract the extrinsic photoemission background but otherwise the data is raw. The bilayer splitting present in Bi2212 [15] is evident in the data in panels (a2) and (a3), though the photoemission matrix element at 9eV mostly selects the anti-bonding band. The spectra are reconstructed, see panels (b1)–(b4), based on a single band with experimentally determined self energies and the heterogeneous broadening previously discussed from STM. The simulation closely matches the data in all regions of the Brillouin zone, lending credence to our model. For the off-nodal spectra we chose 70K to show the thermally occupied quasiparticles more easily while keeping a gap structure similar to low temperatures [67]. At the node we show a 10K spectrum that has very similar broadening to the 70K reconstruction, but a sharper Fermi edge. This illustrates that the excess broadening is not a result of resolution effects. At low temperatures the heterogeneous broadening dominates over the (small) homogeneous broadening caused by self-energy effects. In order to quantify the DI broadening around the zone we look at the $k_F$ EDC widths. Since the DI is modeled as an energy broadening, through a smearing of chemical potential, it is natural to look at the energy widths of the band. As the gap size changes throughout the zone this metric shows how the SC gap suppresses the heterogeneous broadening but also pushes SW towards energies with larger intrinsic scattering, $\Sigma''$. EDC analysis has an advantage over MDC analysis here because the EDC width does not depend on the orientation of the ARPES k-slice and the effects of DI are more pronounced on the EDC width. However, if we use MDC widths as a metric we extract qualitatively the same behavior. In FIG. 6.9a we compile the $k_F$ EDC widths for samples taken with several photon energies, in order to combine high resolution measurements with increased zone access. The data are shifted linearly down to approximately account for the various energy
Figure 6.8: Momentum dependence of both data and reconstruction. The model of combined heterogeneous and homogeneous broadening works all around the Brillouin zone, in places where either one is dominant.
resolutions and match the trend produced by the reconstruction simulations (which was computed using no instrumental broadening). There is a consistent trend of decreasing widths as one moves away from the nodal direction because the heterogeneous broadening is suppressed by the increasing superconducting gap. However, this trend is reversed once the intrinsic broadening overtakes the heterogeneous portion because the superconducting gap is not protected against these scattering channels. Fig. 6.9b depicts the Fermi surface broken down into the regions where each broadening type is dominant: the near-nodal and midzone regions where DI is dominant, and the anti-nodal region where intrinsic self energy is dominant.

In Fig. 6.10 we show how we can isolate and remove the heterogeneous broadening to reveal just the intrinsic broadening due to many-body effects; effectively removing the dirt in high TC cuprates. Panel (a1) shows high resolution ARPES data of Bi2212 at 70K, taken in the near nodal region, $\theta_{FS} = 15^\circ$, with the extrinsic photoemission background removed. Panel (a2) shows the fully reconstructed spectrum, where the homogeneous broadening is tuned to match the experimental TDoS result, the heterogeneous broadening is tuned to match the qualitative momentum broadening, and including an instrumental resolution function. The simulation does not include the bonding-band present in the data, which explains the extra weight to the right of main peak in the data. In panel (a3) the spectrum is recomputed using only the homogeneous broadening, revealing the true many-body spectral function in the material. For reference we also show the spectrum with only superconductivity present, no many body effects, in panel (a4). Here it is clear that the kink feature truly results from the real part of the self energy, as it is Kramers-Kronig transformed from the intrinsic scattering rate, $\Sigma''$. Panels (b1)-(b4) show the analogous spectra for a cut in the anti-nodal region, at $\theta_{FS} = 35^\circ$. In this region, as discussed above, the heterogeneous broadening has negligible effect on the spectrum, which can be seen comparing (b2) and (b3).

6.6 Limitations of Local Fermi Surface Model

In the limit of a linear bareband the shape of the doping distribution gets mapped directly from energy to momentum. Therefore, near the nodal direction the MDC lineshapes should mimic
Figure 6.9: Momentum breakdown of heterogeneous broadening effects. Panel (a) shows $k_F$ EDC widths, measured as FWHM to be model independent. Data from several photon energies is compiled to combine good resolution data with full BZ access. The two guides to the eye, determined by reconstruction simulations, show the relative proportion of heterogeneous to homogeneous broadening throughout the zone. Panel (b) shows the two regions of the BZ: the near nodal region where heterogeneous broadening dominates (at low T) and the anti-nodal region (beyond FS=30deg) where it becomes negligible.
Figure 6.10: Removing the dirt from the cuprates. Panel (a1) shows ARPES data in the near nodal region, $\theta_{FS} = 15^\circ$. Panel (a2) is a simulated spectrum, reconstructed with proper heterogeneous and homogeneous broadening components, as determined by methods discussed in the text. Panel (a3) is the simulated spectrum without the heterogeneous broadening, while in panel (a4) both heterogeneous and homogeneous broadening are removed. In (a4) we include a small, constant Sigma (3meV) to the simulation to keep the band visible. Panels (b1)-(b4) are the same set but at $\theta_{FS} = 35^\circ$, where the homogeneous broadening dominates. This is shown in panels (b2) and (b3) where there is negligible change by removing DI.
the character of the doping distribution, in this case, Gaussian. However, most high resolution ARPES results [64, 69] report near-lorentzian lineshapes near the node. This data conflicts with the results of the DI calculation and since we trust the data more fundamentally, there must be some flaw in the interpretation of how DI affects ARPES spectra. We propose several explanations to explain the discrepancy between data and model. First, we are starting with a doping distribution derived from STM results, which originally come from a gap map. There is some debate in the field as to whether STM is measuring the SC gap or, since the STM matrix elements are stronger at the antinode, is dominated by the antinodal pseudogap [42]. This can complicate the conversion between gap and doping level. However, as Hudson-Wise effectively showed, one can still obtain a doping distribution from STM gap maps [85]. The second explanation attacks one of the assumptions of our model. We proposed that the ARPES spectrum is a weighted sum of different Fermi surfaces originating from the doping patches. However, each patch is of the order \( \xi \sim 20 - 30 \text{Å} \), which gives a k-point spacing of roughly \( \Delta k = \pi / \xi \sim 0.1 - 0.16 \text{Å}^{-1} \). Since the Brillouin zone size is only +/- 0.82 Å\(^{-1} \), there would be only a handful of allowed k-points, not nearly enough to make a smooth, continuous band structure seen in experiment. Therefore, the model of classical superposed Fermi surfaces (FS) breaks down when each patch is too small to have its own FS. When one considers that the electron’s mean free path (500-1000 Å) traverses several dozen patches it becomes more natural to treat the electron as starting with a well-defined FS and scattering off patches occasionally. This picture leads to a lorentzian MDC lineshape when the scattering is treated quantum mechanically. Scalapino et al present a theoretical treatment along these lines and they explore the forward scattering caused by out-of-plane disorder [71, 20]. So while the LFS model predicts gaussian ARPES lineshapes, it is easy to see how one can recover a lorentzian lineshape using a more sophisticated quantum model.

Even with the limitations of the LFS model, one can take solace in the fact that we still get the right order of magnitude for the broadening. In the particular sample shown in Fig. 6.1, the broadening is larger than the contribution from just DI, which is easily explained by surface contaminants and extrinsic scattering effects. However, DI should be a lower bound to broadening
since there is little to no sample variation in DI [2]. It is therefore important to check these results against the sharpest samples reported. To our knowledge, Zhou et. al [44] has reported the sharpest BSCCO spectrum, with a nodal MDC width at $E_F$ of only 7 mÅ$^{-1}$. This is smaller than the $\sim 12$ mÅ$^{-1}$ predicted by our model, but within a factor of two. There are several steps required to convert between an STM gap map and the effective broadening measured with ARPES, as discussed in Section 6.4. It is possible that within those steps there is an invalid assumption that overestimates either the spread of dopings or the final effect of said spread. Given these uncertainties, a factor of 2 is a reasonable discrepancy.

6.7 Conclusion

It has long been puzzling that techniques such as STM and optical conductivity measure the scattering rate near $E_F$ to be roughly an order of magnitude smaller than those measured by high resolution ARPES. Many have suggested that ARPES lineshapes are broadened by DI and this explains the discrepancy. Here we test that claim quantitatively and by taking into account the effects of DI we can rationalize the excess broadening present in ARPES. Because ARPES is momentum resolved, it is sensitive to momentum broadening mechanisms which are averaged out using k-integrated probes. However, to properly match the scattering rates measured with ARPES to other probes, it is important to understand and remove the excess k-broadening. Starting from STM measured gap maps, we have shown that a simple model of classically superposed Fermi Surfaces gives the right magnitude of broadening and can qualitatively capture the data. However, there are limitations with the LFS model that suggests a more sophisticated quantum model is required. Our approach is further justified by the new TDoS analysis of ARPES data. With TDoS we integrate out the excess momentum broadening and just look at how spectral weight is shifted in energy. The scattering rates extracted with TDoS also match other probes, suggesting the outlier is MDC-extracted scattering rates. However, the TDoS is only sensitive to $\Sigma''$ inside the gap scale, so we cannot easily extract the energy dependence of $\Sigma''$. Accounting for DI gives new strength to the MDC technique because we can faithfully extract the energy dependence of $\Sigma''$ once we remove
the DI contribution to the width. This work shows that starting from STM data one can account for, quantitatively, the excess momentum broadening present in ARPES data and it brings ARPES measurements in line with other cuprate probes. However, perhaps a greater insight from this work is how to effectively remove the heterogeneous broadening from ARPES spectra. By combining the scattering rate's energy dependence, extracted from MDC analysis, with the $\Gamma_0$ value, extracted from TDoS analysis, one can get a complete picture of the homogenous scattering in BSCCO and effectively remove the dirt from high-$T_C$ superconductivity.
Chapter 7

Ultrafast Response of BSCCO

7.1 Introduction

The motivations behind trARPES are to directly measure the single particle decays in the time-domain so as to undercover the decay mechanisms responsible, with the ultimate goal of understanding the mechanism of High-\(T_C\) superconductivity. Over the last several years there have been several exciting advances in the understanding of cuprate physics utilizing trARPES techniques. Specifically, Perfetti [63] showed multiple timescales of electron response and the work of Smallwood [74] showed rich momentum and fluence dependence to the electron dynamics. However, there have been conflicting reports [18] regarding both the momentum and fluence dependence of the electron and gap dynamics and so their true dependence remains an open question. Furthermore, all of these studies have suffered from relatively poor energy resolution (\(\Delta E \gtrsim 22\) meV) and so they do not have the resolution to resolve the gap dynamics well. As we will see below, there is a strong energy dependence to the electron dynamics near the gap scale so having adequate energy resolution is of crucial importance in uncovering the true dynamics in these systems.

7.1.1 Previous trARPES Studies on BSCCO

In this section we will discuss previous trARPES work on the cuprate superconductors with specific emphasis on the multiple time-scales observed by Perfetti et. al [63] and the momentum dependence observed by Cortés et. al [18] and Smallwood et. al [74]. These findings helped orient my own research and speak to both the consensus and current debate in the field.
Perfetti et. al performed the first trARPES measurements on BSCCO and discovered a rich temporal landscape in this material. In this work, the authors pumped the sample with 50 fs, 1.5 eV infrared pulses and probed it with 80 fs, 6 eV pulses. The pump fluence was also quite large, 100µJ/cm², leading to a large electronic perturbation. They characterized this perturbation by its effects on the electronic temperature, determined by fitted Fermi widths to nodal ARPES cuts as in Fig. 7.1(a). In the upper panel of Fig. 7.1(a) we see that within the first 100 fs the electron distribution does not follow the Fermi-Dirac distribution, indicating a departure of the electron population from thermal equilibrium. However, after this brief, initial period the electron population closely follows a Fermi-Dirac distribution (Fig. 7.1(a)), which we interpret as the electron population effectively thermalizing. Note that the electrons have thermalized with each other but not with the lattice. As argued in Fig. 7.1(b2), the electrons thermalize with the lattice through a small subset (∼20%) of “hot” phonons on a timescale of roughly 2 ps. These “hot” phonons then anharmonically decay to the rest of the phonon branches, effectively bringing the lattice into thermal equilibrium with the electrons. At this point the sample surface is in thermal equilibrium and the decay is controlled by the macroscopic dissipation of heat away from the probed region, which happens on the nanosecond scale [63]. The authors explain these timescales within the so called 3-Temperature Model, where the electrons, (hot) phonons, and lattice (non-hot phonons) each have their own temperature, and the dynamics are controlled by the lifetimes $\tau_\alpha$ and $\tau_\beta$. They claim that the initial slow down from $\tau_\alpha \rightarrow \tau_\beta$ (110 fs to 2 ps) (see Fig. 7.1(c1)) is due to electron-phonon coupling and has nothing to do with superconductivity, as evidenced by the same timescales appearing in Fig. 7.1(c2) when the sample is studied at 300K. We will see later that there is an additional slow-down that happens when the sample enters the superconducting state. The important things to remember from Perfetti’s pioneering work is that the electron population thermalizes with itself on the 100 fs timescale and that the subsequent 2 ps decay is due to the electrons coupling to a small fraction of the phonons.

Cortés et. al explored the momentum and fluence dependence of the trARPES response in Bi2212 [18] and concluded that the decay time of excited quasiparticles above $E_F$ is momentum
Figure 7.1: Summarized trARPES results from the work of Perfetti et al. on nodal BSCCO-2212. Panel (a) shows the integrated ARPES intensity at various delays, showing the increase and decay of electronic temperature with time. The upper panel of (a) shows a non-thermalized electron distribution at $t_0$ but the distribution has thermalized by 150 fs later. Panel (b1) compares the rise in temperature to the square-root of the excess energy (see Ref. [63] for more details). Panel (b2) shows a cartoon of the 3-Temperature model discussed in the text. The temperature versus time is shown in panel (c1), with (c2) showing more detail near $t_0$. Panel (c2) also compares data sets for sample temperatures of 30K (black) and 300K (red), each scaled from minimum to maximum temperature attained. The colored arrows are guides to the proper temperature axis. Figure adapted from Ref. [63].
independent. Their results are summarized in Fig. 7.2. Instead of the Fermi edge widths employed by Perfetti, Cortés and collaborators used the change of ARPES intensity above $E_F$ as their metric, referred to as $\Delta I$ and shown in Fig. 7.2(a)-(b). This metric has an advantage when studying momentum dependence because, unlike fitting to Fermi distributions, the changing gap size does not fundamentally affect the analysis. However, as we will show below, the $\Delta I$ metric has its own subtleties that must be considered. Cortés then fit each $\Delta I$ curve to a single exponential (from the maximum $\Delta I$ to $t = 20$ ps) and plotted the extracted lifetimes as a function of momentum and fluence in Fig. 7.2(c), showing a roughly constant $\tau \sim 2 - 3$ ps. The authors claim that this constant lifetime indicates that quasiparticles are decaying directly across the gap (see Fig. 7.2(d) inset) and implies that Bi-2212 is in the strong boson bottleneck regime of the Rothwarf-Taylor model [70].

The momentum independent decays reported by Cortés et. al are in stark contrast to more recent reports by Smallwood et. al who show explicit momentum and fluence dependent decays with trARPES on Bi2212 [74]. When they plot $\Delta I$ normalized to its peak value, as in Fig. 7.3(2a)-(2c), there is a clear fluence dependence to the initial slope of the decay. In addition, the authors report that the decay rate increases as one moves away from the node, shown in Fig. 7.3(2c). Note that when plotted as $\Delta I_{\text{Norm}}$, exponential decays of a single lifetime would collapse to the same curve, unlike the data. To characterize these non-exponential dynamics the authors define the initial decay rate, $\gamma_0$, as the initial slope of the decay and plot it in Fig. 7.3(2d). They also interpret these findings within the Rothwarf-Taylor model of quasiparticle recombination. When there are more quasiparticles present, by either optical or thermal excitation, then any individual quasiparticle has more decay channels and therefore decays more quickly. This straightforward explanation for the monotonic fluence dependence observed by Smallwood et. al led them to conclude that the intrinsic decay rates should be the zero-fluence extrapolations shown by the lines in Fig. 7.3(2d). The nodal decay rate extrapolates to approximately $11 - 12$ ps, which is a big discrepancy with the $\sim 2$ ps reported by Perfetti and Cortés [63, 18]. Furthermore, after these extrapolations there is still a momentum dependent decay rate, which the authors attribute to a momentum-dependent
Figure 7.2: Summarized trARPES results from the work of Cortés et al. on BSCCO-2212. The authors measure the fractional change of ARPES intensity above $E_F$, referred to as $\Delta I/I$, as a function of momentum (panel (a)) and pump fluence (panel (b)). They fit each trace to a single exponential decay and plot the decay times and amplitudes in panels (c) and (d), respectively. The inset in (d) shows the authors’ interpretation of the decay process. Figure adapted from Ref. [18].
quasiparticle recombination rate within the Rothwarf-Taylor model.

There has been great progress in the field of trARPES on BSCCO, but clearly there are conflicting results and still unanswered questions. What is the true momentum and fluence dependence of the electron dynamics and what does this mean for the decay processes involved in cuprate superconductivity? In the following chapter we will explore these questions with our home-built trARPES setup and reconcile some of the discrepancies reported above.

7.2 Experimental Details

7.2.1 Space Charge Effects and Correction

One of the necessary parts to photoemission spectroscopy is that photoelectrons must leave the sample and travel through vacuum to the detector. These electrons will interact with one another via coulomb repulsion and, when the photoelectron densities are large enough, can have noticeable or even disruptive effects on the measured spectrum. This mutual coulomb repulsion is commonly referred to as “space charge” since it happens in the vacuum space. Space charge is most extreme for ultrashort light pulses and small spot sizes, i.e. the regime of time-resolved ARPES. When an ultrashort light pulse ejects electrons from a sample, they can be thought of as a disk of charge leaving the surface. The highest energy electrons are accelerated to higher kinetic energies while the lowest energy ones are decelerated, and there can also be some distortion of the photoemission angles for electrons near the edges of the disk. In addition to changing the kinetic energy, space charge broadens the energy distribution and so too much space charge will ruin any high resolution experiment. The effect of space charge has been studied in great detail using high intensity laser sources over a wide parameter space. For the shortest pulses ($t < 30\text{fs}$) the space charge broadening follows a square root dependence on photons/pulse [61]. This contrasts with a more linear dependence for picosecond scale pulses [26]. We have determined experimentally that for our parameters ($\Delta t \sim 700\text{ fs}$) the space charge effect follows a linear trend with photons/pulse, as shown in Fig. 7.4(c).
Figure 7.3: Summarized trARPES results from the work of Smallwood et al. on BSCCO-2212. The upper panels show raw ARPES data at different delays (1A and 1B) as well as the difference between them in (1C). In (1C) an increase of intensity after pumping is denoted in blue while a decrease is shown in red. Panel (1D) shows several EDC cuts comparing the two delays, and (1E) shows the total change in spectral weight integrated in momentum, as a function of energy. At each time delay traces similar to (1E) are integrated for $\omega > E_F$ to produce the $\Delta I$ data shown in the lower panels (2A)-(2C). These lower panels show the momentum and fluence dependence of the decay of $\Delta I$ (normalized to the maximum value). The authors fit the initial slope (for $\Delta I_{Norm} \geq 0.5$) to extract the initial decay rate, $\gamma_0$, plotted in (2D). The lines in panel (2D) are linear extrapolations to zero fluence, as discussed in the text. Figure adapted from Ref. [74].
We can partially remove the effects of space charge by correcting for the linear energy shift. However, to remove the excess broadening involves a deconvolution (which has its own issues) and is generally not worth the effort. Therefore, we keep the count rate low enough that the broadening is minimal and only the energy shift is present. We can determine the magnitude of this shift by comparing the deep energy ($-150 \text{ meV} < \omega < -100 \text{ meV}$) to the linear trend in Fig. 7.4(c). Then we shift the entire spectrum by that amount to remove the effect, as shown in Fig. 7.4(d). Note how all the spectra line up at $E_F$ but the higher power traces are clearly broader than the low power ones. By combining this correction algorithm with laser stabilization techniques we can effectively eliminate the space charge shift from our data.

### 7.2.2 Photoemission from MIR pump

As discussed previously, in order to perform photoemission one requires photons with energy higher than the material’s work function. However, this is not strictly true when laser intensities are high enough that a single electron can absorb two or more photons before leaving the solid. The case of two-photon excitations has been well studied to the point of being its own spectroscopic tool, 2 photon photoemission or 2PPE [19, 83, 9]. The general process of photoemission with multiple photons is referred to as Above Threshold Photoemission (ATP) and the theory is based on the similar phenomenon of Above Threshold Ionization (ATI) in atomic gases [23, 25]. When using photon energies well below the work function it is also possible to produce photoelectrons using sufficiently high laser intensities [1]. When performing trARPES these photoelectrons constitute a background signal and it is important to understand them in order to remove them properly.

In work performed by Aeschlimann et. al, the authors characterize the ATP behavior on metallic surfaces using different harmonics of their IR laser [1]. Shown in Fig. 7.5 is the photoelectron response from single crystal Cu at different laser wavelengths. When the photon energy is large (but smaller than $\Phi$) there are characteristic shelves in the photoelectron intensity, which correspond to electrons absorbing additional photons above the threshold. However, as the photon energy is lowered, instead of getting closer spaced shelves, there is a qualitative change to an expo-
Figure 7.4: Space Charge effects and correction. Panel (a) shows raw ARPES SW for nodal Bi–2212 at different UV probe intensities, which are normalized at deep energy in panel (b). Panel (c) shows the leading edge position vs. count rate, determined by fitting to a Fermi distribution. Panel (d) shows data with the space charge shift removed, as discussed in the text.
nentially decreasing intensity with increased kinetic energy. The authors describe this behavior as the solid state analog of tunneling ionization (TI) in atomic gases [1]. Essentially, the laser field is so strong at the surface that it distorts the work-function’s field and allows electrons to periodically tunnel out of the sample. The electrons can escape the sample with very little excess energy and then behave as free particles in the laser field [17, 1]. Therefore the final kinetic energy of the electron is related to the time of tunneling relative to the phase and strength of the laser’s electric field. The relevant parameter for determining the system’s response to a laser field is known as the Keldysh parameter, $\gamma$, and is given by:

$$
\gamma = \frac{\omega}{E} \cdot \frac{\sqrt{2m I_p}}{e}
$$

(7.1)

where $\omega$ is the laser frequency, $E$ is the electric field strength, $I_p$ is the ionization potential of the atom, $m$ is the electron mass, and $e$ is the electron charge [1]. The right factor depends on the material ($I_p$) while the left factor depends only on the laser parameters. For low laser intensities and high photon energies ($\gamma \gg 1$) the system responds in a multi-photon fashion and the behavior is typically called Above Threshold Photoemission (ATP). In the opposite limit ($\gamma \ll 1$) the response is analogous to tunneling ionization (TI) behavior. For convenience I will group both ATP and TI together under the term Multi-Photon (MP) processes. For all the experiments discussed in this thesis the MP counts are strongly in the TI regime, as evidenced by the photoyield versus kinetic energy plot in Fig. 7.6, taken using the highest pump photon energy (4 $\mu$m = 310 meV) and still clearly showing an exponential decay.

Above Threshold Ionization experiments and theories were originally used to describe behavior of atomic gases and Ref. [1] was the first to perform such experiments on solids. They point out that the required laser intensities for ATI are on the order of $10^{14}$ W/cm$^2$ but to produce analogous behavior from a metallic surface only requires roughly $10^8$ W/cm$^2$ [1], and the yield is highly sensitive to “hot spots” on the surface. The discrepancy can be traced to the field enhancement effects of surface plasmons [1, 66]. On a smooth surface it is impossible to optically excite plasmons because one cannot conserve energy and momentum for the photon and plasmon at the same time.
Figure 7.5: Photoelectron response from Cu(110) surface using different photon energies. Panels (a)-(c) show the photoyield using photon energies $h\nu_3$-$h\nu_1$, shown schematically in (d). $h\nu_1$ is the laser fundamental wavelength, 770nm (1.6 eV), while $h\nu_2$ and $h\nu_3$ are the second (3.2 eV) and third (4.8 eV) harmonics, respectively. The peak laser intensities for $h\nu_3$, $h\nu_2$, and $h\nu_1$ are $10^4 W/cm^2$, $10^7 W/cm^2$, and $10^9 W/cm^2$ respectively. Figure adapted from ref.[1].
Figure 7.6: Multi-Photon (MP) response of OP-Bi2212 to 4 micron radiation. The power and sample position were chosen to have noticeable MP near 2 eV kinetic energy, the place where we perform trARPES. Panel (a) shows the raw ARPES spectrum swept over a kinetic energy range of 0-3 eV. The red box in (a) is the integration window that produces the counts vs. KE, shown as open circles in (b). Panel (b) also includes an exponential fit, shown in red, that matches the data quite well. This is conclusive evidence that at 4 microns (and by extension, all longer wavelengths) we are firmly in the tunneling ionization (TI) regime of MP processes.
[1]. However, on the surface of a ruled grating this changes because the grating wavevector can compensate for the momentum discrepancy. A patch of rough surface on a metal can be decomposed into its Fourier components and so surface roughness allows light to couple to many different surface plasmons [66], which in turn causes a large field enhancement promoting ATP and TI.

While the experiments discussed above were done on a Cu(110) surface, we see the same behavior on BSCCO surfaces cleaved in vacuum. For “bad” samples with lots of flakes or surface defects it can be impossible to find a usable spot for trARPES. Figure 7.7 shows one such bad sample where there are only a few useable spots over the entire surface, found by rastering across the sample with both UV and IR lasers. This is in contrast to a “good” sample, shown in Fig. 7.8, where there are only a few bad spots and they are confined to the sample edges. Given the above discussion about roughness it makes sense that the edges are worse since the smooth surface is broken even with a perfect cleave. When we increase the power on the good sample the edge effects become more clear and we begin to see defects near the sample center that were invisible with lower IR power. However, with a nice surface it is easy to avoid the defects once they are mapped out with such a raster scan.

7.3 Results

7.3.1 Increase of Electronic Temperature Due to Optical Pump

Figure 7.9 shows an example of the effects of optical pumping on the ARPES spectrum of a cuprate superconductor. The spectrum is taken at the superconducting node so there is no gap, but there are several key features to point out in the spectrum. First, there is more weight above $E_F$ which is a consequence of the increased electronic temperature due to pumping. By integrating the spectrum in momentum, as shown in Fig. 7.9(d), one can extract the electronic temperature quantitatively by fitting to a Fermi distribution. The technique will be used extensively in the following sections. This can only be done reliably at the node since the superconducting gap modifies the density of states and the k-integrated weight is proportional to the product of DOS
Figure 7.7: Spatial raster map across a “bad” sample (OP Bi2212) face using both UV and MIR lasers. Each individual spectrum has axes of energy and momentum and the spectra are ordered according to their position on the sample face. In panel (a) each spectrum is color scaled to their individual maxima, while in (b) all spectra have the same color scale limits.

Figure 7.8: Spatial raster map across sample face using both UV and MIR lasers. Each individual spectrum has axes of energy and momentum and the spectra are ordered according to their position on the sample face. The color scales of all the spectra in (a) are identical. In panel (a) there was 10 mW of 4µm radiation incident on the sample. Most of the sample does not produce any significant MP counts, except the lower left side and the upper-most row. Panel (b) is an analogous image but with 33 mW incident IR light. Here it is clear that the sample edges produce significantly more MP counts than the center of the sample. The red boxed spectrum in (b) shows a bad spot near the center where a surface defect adds an unacceptable background to the measured band structure. However, 0.4 mm away in the blue boxed spectrum there are no MP counts at all.
times Fermi distribution. The second feature of the pumped spectrum is a loss of weight inside the kink scale. This is most clearly seen when we plot the spectral difference, defined as the transient spectrum minus the equilibrium spectrum, as in Fig. 7.9(c), and the lost spectral weight is represented in red. Note that outside the kink scale there is significantly less effect from pumping. This has previously been interpreted as the evaporation of the superconducting condensate, showing that the nodal quasiparticles are sensitive to the superconducting state despite having no gap [27].

The final object of interest, shown in Fig. 7.9(e), is the spectral weight difference ($\Delta SW$) between the pumped and equilibrium spectra. For the nodal case the $\Delta SW$ curve is simply the difference of Fermi functions, which has a zero crossing at $E_F$ and whose width is determined by the two temperatures involved. As we will see below, the shape is qualitatively different when looking at a gapped spectrum.

As shown above, the pump pulse causes a change in the electronic temperature, dubbed $T_{el}$. We can extract $T_{el}$ by fitting the SW to a Fermi distribution whose width is determined by $T_{el}$ and the energy resolution. As noted by Ref. [49], a Fermi distribution convolved with a gaussian resolution is well approximated (typically better than 1%) by a broader Fermi distribution with a width:

$$kT_{eff} = \sqrt{(kT_{el})^2 + \frac{\pi}{64\ln 2} E_{Res}^2}$$

(7.2)

where $T_{eff}$ is the effective temperature of the distribution, $T_{el}$ is the original temperature, $k$ is Boltzmann’s constant, and $E_{Res}$ is the FWHM of the gaussian resolution term. All the data presented here are taken with $E_{Res} \lesssim 10$ meV, which, for example, takes a $T_{el} = 20$K to $T_{eff} = 36$K. Since $T_{el}$ and $E_{Res}$ add in quadrature, for temperatures $\gg 20$K the resolution contribution becomes small (when $T_{el} = 100$K, $T_{eff} = 105$K). Conversely, when $kT_{el} \lesssim \sqrt{64\ln 2/\pi} E_{Res} \approx 3.76 E_{Res}$ then the resolution dominates and the fractional uncertainty of $T_{el}$ grows. This regime is where the higher resolution of our setup really becomes powerful. With $E_{Res} \sim 10$ meV the minimum $T_{eff} \sim 31$K while previous studies [74] (with $E_{Res} \geq 22$ meV) are limited to a minimum $T_{eff} \geq 70$K or higher. Therefore, our improved resolution widens the dynamic range of measurable $T_{el}$ and allows a more
Figure 7.9: The effects of optical excitation on a cuprate superconductor. Panel (a) and (b) show the ARPES spectrum before and after optical excitation. The spectrum is taken at the node in OP-Bi2212, at an equilibrium temperature of 20K. Panel (c) shows the difference spectrum, defined in the text. Panel (d) shows the k-integrated intensity for both delay points, while (e) shows their difference.
accurate description of the thermal decay.

After optical excitation, $T_{el}$ subsequently decays on the picosecond timescale, as shown in Fig. 7.10. We can define the hottest temperature the system reaches as $T_{\text{max}}$. When $T_{\text{max}} > T_C$ the system leaves the superconducting state upon pumping and enters either the normal state or the pseudogap state, depending on doping level. Regardless, outside the SC state the temporal dynamics are markedly faster than in the SC state, and we show later that the decay constant changes from roughly 2 ps to 12 ps at the transition. This effect is at least partly due to the decreased phase space for scattering in the superconducting state, a consequence of the gapped Fermi surface. The pump fluence required to raise the sample temperature above $T_C$ is typically referred to as the critical fluence, $F_C$, and from Fig. 7.10 we can identify $F_C$ as roughly 40µJ/cm$^2$ for 4µm pump.

When looking at the temperature decays in Fig. 7.10 it is not clear that all fluences show the same temporal dynamics. To illuminate this we plot all traces on an axis where zero is defined as the time for crossing $T_C$, shown in Fig. 7.11. This prescription collapses the data onto a single curve, at least for data that starts at the same equilibrium temperature. For sub-critical fluences where there is no $T_C$ crossing we shift the time axis positive until achieving best agreement with higher fluence traces. This procedure is justified by the relatively large time window where the traces overlap, around 5 – 6 ps. Plotting these decays on a semi-log plot reveals a temporal dichotomy: a fast component above $T_C$ and a slower component below $T_C$. This is accentuated by the linear eye guides in Fig. 7.11. Eventually the electron system comes to thermal equilibrium with the lattice and the decay constant gets even slower, seen here at $> 15$ ps past $T_C$. The interplay of the electron and lattice temperatures has been studied in previous trARPES experiments [63], and is interpreted in the so called 3–Temperature model. The lattice response is much slower than the electrons’ (due to small fraction of modes coupling), but eventually they equilibrate and the decay is governed by the macroscopic dissipation of heat away from the probed region [63].

To extract quantitative numbers for the lifetime in the superconducting state we fit each data
Figure 7.10: Electronic temperature vs. delay for various fluences of 4µm pump. The sample's $T_C$, 90K, is denoted by the dashed line. The highest fluence data was taken at a higher sample temperature (40K instead of 20K) because we ran out of helium cryogen.

Figure 7.11: Same temperature decays, but plotted against delay from $T_C$ crossing. Highest fluence trace was replaced by a lower stats trace that started at 20K instead of 45K. Panel (b) is the same data on a semi-log plot. The black lines are guides to the eye.
set to a decaying exponential plus a constant offset. The fitting function is given by:

\[ T(t) = y_0 + Ae^{-t/\tau} \]  

(7.3)

where \( T(t) \) is the electronic temperature versus time, \( y_0 \) is horizontal asymptote, \( A \) is the amplitude, and \( \tau \) is the decay constant. The asymptote term represents the final electronic temperature reached, \( T_{\text{Final}} \), and can be slightly higher than the initial temperature, in accordance with the above discussion on lattice coupling. The sum of \( y_0 \) and \( A \) is the initial temperature of the fit, and is equal to \( T_C \) for all traces except the lowest fluence where we don’t reach \( T_C \). The fit results are shown in Fig. 7.12, where we initially fit with all three parameters unconstrained. As seen in Fig. 7.12(a), the fits look slightly different and the extracted lifetimes have very large uncertainties. The curvature seen on log scale is a consequence of the finite value of the asymptote, \( T_{\text{Final}} \). It is clear from Fig. 7.12(c) that the amplitude and offset are too coupled, and their large uncertainties are reflected in the extracted lifetimes. Further, it appears that the offset value is tied to the data range of the fit, as it increases for the higher fluence traces where the system has a higher temperature on its last data point. Therefore, in order to extract reliable lifetimes we will need to constrain this fitting in some reasonable way.

Based on the appearance of the temperature decays the most reasonable fitting constraint is to force \( T_{\text{Final}} \) to be the same value for all fits. We chose \( T_{\text{Final}} = 25K \) because 25K is the extracted \( T_{\text{Final}} \) from the unconstrained fit on the lowest fluence data set. Figure 7.13 shows the fits and extracted values when we constrain \( T_{\text{Final}} \). First, note how the fits overlay more nicely in Fig. 7.13(a), a fact reflected in the roughly fluence independent decay constants shown in Fig 7.13(b). There has been disagreement in the field about whether this decay is fluence dependent [74] or independent [18] and our new data supports the latter. The fluence dependent findings reported in Ref. [74] will be discussed in more detail in Section 7.3.2 below. Doing a weighted average of the lifetimes from the constrained fitting we report a fluence independent thermal decay constant of \( \tau = 11.6 \pm 0.3 \) ps while in the superconducting state. This result matches the low fluence limit reported in Ref. [74] though we can obtain it for any fluence and not
Figure 7.12: Fitting to extract lifetimes in the superconducting state using an unconstrained exponential decay. Panel (a) shows the offset Temperature data along with the individual exponential fits, shown as black lines. Panel (b) shows the extracted decay constants while (c) shows the amplitude and offset values. All error bars are the statistical uncertainties returned by the fitting algorithm.
employing an extrapolation.

7.3.2 Chemical Potential Shift

There is a chemical potential shift caused by the pump. The chemical potential, $\mu$, increases to higher energy on the meV scale within roughly a ps after pumping. This is measured by the same Fermi fitting that extracts $T_{el}$, as shown in Fig. 7.14(a), where $\mu$ is the 50% crossing of the SW. The chemical potential increases as quickly as $T_{el}$ (rise-time controlled by the temporal resolution) but decays significantly faster than the thermal dynamics, returning to zero within $5 - 10$ ps. Fig. 7.14(b) shows $\mu$ vs. delay for various fluences. Here we can define the maximum change of chemical potential, $\Delta\mu_{Max}$, as the peak in each trace of Fig. 7.14(b). Clearly $\Delta\mu_{Max}$ changes with fluence but at this point the origin of this effect is still unclear. The magnitude of $\Delta\mu_{Max}$ may seem small, however even a few meV of $\Delta\mu$ can have large impact on the SW above $E_F$. To see this we can appeal to the definition of SW above $E_F$, shown in Eqn. 7.4. Here we integrate from the nominal value of $E_F = \mu = 0$ but include $\mu$ explicitly in the integrand to show the effect when $\mu \neq 0$. The integrand of Eqn. 7.4 is largest at $E_F$, so changes near $E_F$ will strongly affect the total value of the integral. For example, at 80K, $kT$ is roughly 7 meV but a $\Delta\mu$ of 3 meV changes the weight above $E_F$ by 35%, shown clearly in Fig. 7.15. Therefore, any analysis that relies on intensity changes above $E_F$ [74, 91] must also account for the chemical potential shift, though this has not been done in the past.

$$SW_{\omega > E_F} = \int_0^\infty \frac{d\omega}{e^{(\omega-\mu)/kT} + 1} = kT \ln(1 + e^{\mu/kT})$$ (7.4)

As seen in Eqn. 7.4, when $\mu = E_F = 0$ the intensity above $E_F$ is proportional to the electronic temperature. It follows that changes in this intensity are proportional to changes in electronic temperature. However, this argument breaks down when $\mu \neq E_F$, as shown above. Previous studies have used the $\Delta SW$ object to infer changes of electronic temperature and concluded that there are non-thermal and fluence dependent effects due to optical pumping [91, 74]. However, even though those experiments were in the fluence regime that causes a $\Delta\mu$ [75] its effects were not
Figure 7.13: Constrained exponential fitting in the superconducting state. Panel (a) shows the offset temperature data along with exponential fits where $T_{\text{Final}}$ is held at 25K. Panel (b) shows the extracted decay constants when $T_{\text{Final}}$ is held at 25K including their weighted average in a black dashed line. The weighted average of decay constants gives a fluence independent lifetime of $\tau = 11.6 \pm 0.3 \text{ ps}$. 
Figure 7.14: $\Delta \mu$ vs. delay for different pump fluences. Also shows two example Fermi edges from which the $\mu$’s were extracted.

Figure 7.15: The effect of a 3 meV chemical potential shift on the Fermi distribution. Area above $E_F$ is shaded to accentuate the differences. For the 80K case shown, the 3 meV shift results in a 35% increase in area above $E_F$. For reference, kT at 80K is 6.9 meV.
discussed. When we use the metric of electronic temperature, as measured by the Fermi distribution width, we see that all fluences show the same decay time in the superconducting state, as shown in Fig. 7.11.

7.3.2.1 Modeling the Effects of Chemical Potential Shift

We have performed numerical simulations to model the effects of time-dependent chemical potential shifts on the ARPES spectra. For the input to the simulation we use an electronic temperature that decays from 90K to 20K with a time constant of $\tau_T = 11.6$ ps and a chemical potential that decays from a few meV to zero with a time constant of $\tau_\mu = 3$ ps. These inputs are shown in Fig. 7.16(a) and (b). At each time step we calculate a Fermi distribution with the temperature and chemical potential given by these inputs. Then we subtract the initial distribution ($T_{el} = 20$K and $\mu = 0$ meV) in order to emulate the spectral weight differences typically plotted in trARPES experiments. In order to highlight the effects of the chemical potential shift we exclude the energy and temporal resolution that are present in the actual experiment. The results of the simulation are shown in Fig. 7.16(c) and (d) where we plot the $\Delta SW$ above $E_F$ for different values of the maximum chemical potential shift, $\Delta \mu_{Max}$. The black trace in (c) shows the $\Delta \mu_{Max} = 0$ case where we see just the effects of the electronic temperature decaying at 11.6 ps. All the other traces show additional weight near $t_0$ but collapse to the black curve after the chemical potential shift has decayed to zero. Note how $\Delta SW$ curves in (c) resemble a bi-exponential decay, which one might expect from inputting two distinct time constants. However, there is a serious distinction between having a bi-exponential thermal decay and having a single thermal decay coupled with a chemical potential shift. In the former case, when the traces are properly normalized they would collapse to show the same bi-exponential regardless of initial peak height. However, as seen in Fig. 7.16(d), when the traces are normalized to maximum height they do not collapse, but rather show a “faster” response for larger $\Delta \mu_{Max}$ values. Coupled with the fact that higher pump fluences result in larger $\Delta \mu_{Max}$ values, this simulation shows normalized $\Delta SW$ curves can show an apparent fluence dependence even when $\tau_\mu$ and $\tau_T$ are held constant. Here we note that the chemical potential
shift results is a fluence dependence very similar to that reported by Smallwood et al [74], which the authors ascribed to bi-molecular recombination dynamics within the Rothwarf-Taylor model [70]. This model results in non-exponential dynamics because the quasiparticle decay is related to the number of other quasiparticles present, so a larger quasiparticle population decays at a faster initial rate than a smaller population. As we just showed, it is possible to achieve similar behavior using fixed lifetimes but changing only the magnitude of a chemical potential shift. At this point it is unclear whether this means the Rothwarf-Taylor model does not apply to optically pumped cuprates or whether it is simply a different mathematical description of the same phenomenon.

Based on the origin of the extra weight above \(E_F\) due to \(\Delta \mu\) there should be a corresponding loss of weight below \(E_F\). This is indeed the case and is shown clearly in Fig. 7.17(c) and (d). Panel (c) is a subset of the data from Fig. 7.16 for the specific case of \(\Delta \mu_{Max} = 0\) and 3 meV. Panel (d) shows the corresponding traces for the energy window below \(E_F\). The \(\Delta \mu_{Max} = 0\) case is symmetric about \(E_F\) while \(\Delta \mu_{Max} \neq 0\) transfers weight from below to above \(E_F\). Below \(E_F\) the thermal and chemical potential dynamics pull weight in opposite directions and since they have different time constants their competition manifests as a rounding of the \(\Delta \mu_{Max} = 3\) meV trace, seen in Fig. 7.17(d). Panels (a) and (b) show the spectral weight difference maps from which the traces in (c) and (d) are generated. For the \(\Delta \mu_{Max} = 0\) case, shown in (b), the response is symmetric about \(E_F\). The deviation from this symmetry is highlighted in (a) by the yellow color, which represents differences beyond the maximum change in (b). In real trARPES data it is more difficult to measure the dynamics below \(E_F\) because the changes in intensity are resting on a large, finite background instead of the nominally zero background level above \(E_F\). However, we do expect to see these effects in the hole dynamics based on the above \(E_F\) behavior.

### 7.3.3 Dependence on Starting Temperature

In the last section we showed that the decay rate of \(T_{el}\) in the superconducting state is independent of fluence. In this section we explore how the decay rate depends on the starting sample temperature, \(T_{start}\). We find that the general behavior is that as \(T_{start}\) increases, the
Figure 7.16: Mu Shift Simulation showing the effect on the SW above $E_F$. Each curve has a thermal decay of 11.6 ps and a mu decay of 3 ps, but the maximum mu shift changes from 0 to 5 meV. When the curves are normalized to peak height they produce an apparent fluence dependent time dynamics. However, in all simulations the two lifetimes were the same.
Figure 7.17: $\Delta \mu$ simulation showing the weight transfer from holes to electrons. Panels (a) and (b) show $\Delta$SW maps for the cases $\Delta \mu_{\text{Max}}$ of 3 and 0 meV, respectively. The yellow color in (a) denotes the region where the $\Delta \mu_{\text{Max}} = 3$ meV case exceeds the maximum change of the $\Delta \mu_{\text{Max}} = 0$ meV case. Panels (c) and (d) show the $\Delta$SW traces for the two $\Delta \mu_{\text{Max}}$ scenarios, energy integrated both above and below $E_F$, respectively.
Figure 7.18: Comparison of thermal decay times for two different starting sample temperatures, $T_{\text{start}}$. Panel (a) shows $T_{\text{el}}$ vs. delay for a 4µm pump with a fluence of 35µJ/cm$^2$ and $T_{\text{start}} = 20K$. The red and yellow solid lines are exponential fits over different domains, as discussed in the text. Panel (b) shows the thermal response for the same pumping parameters but with $T_{\text{start}} = 46K$.

decay rate increases as well, as shown in Fig. 7.18. Since we are interested in the response of the superconducting state we are limited to $T_{\text{start}} < T_C$.

In this section I have fit the thermal response over a longer decay window than Sec.7.3.1. As shown in Fig. 7.18(a), fitting an exponential that has a non-zero asymptote affects the reported lifetime. Fitting over a small domain and holding $T_{\text{final}} \sim T_{\text{start}}$ (yellow trace in Fig. 7.18(a)) yields a lifetime similar to that of the last section, around 11.2 ps. However, fitting the same data over a longer domain yields a lifetime $\sim 7.2$ ps (red trace) even though the two fits match well over the common domain. This discrepancy can be traced to the dependence of the lifetime on the final asymptote for a constant initial slope. As shown in Eqn. 7.6, the same initial slope, $dT/dt$, can yield different lifetimes depending on the asymptote, $T_{\text{final}}$. Therefore, when we fit over larger time domains (and don’t hold $T_{\text{final}}$) we expect the reported lifetime to be smaller than the 11.2 ps reported by fitting the initial slope and holding $T_{\text{final}} \sim T_{\text{start}}$, as in Sec.7.3.1.

\[
T(t) = (T_C - T_{\text{Final}})e^{-t/\tau} + T_{\text{Final}}
\]

(7.5)

\[
dT/dt|_0 = (-1/\tau)(T_C - T_{\text{Final}})
\]

(7.6)

Using exponential fitting over this extended decay range, we compare two different starting
sample temperatures in Fig. 7.18. Both data sets used a subcritical fluence of 35\(\mu\)J/cm\(^2\) and stayed in the superconducting state throughout the measurement. Fitting to an exponential decay reveals a lifetime of roughly 7.2 ps for a starting temperature of 20K but a shorter lifetime of 5.7 ps when the sample starts at 46K. This increased decay rate can be understood in the context of the Rothwarf-Taylor Model of bimolecular recombination. With a higher starting temperature there are more thermally generated quasiparticles present and therefore more possible decay channels to relax the excited electrons.

We see similar temperature dependence using a fluence of 80 \(\mu\)J/cm\(^2\), enough to drive the system into the normal state. As shown in Fig 7.19, when we fit only the portion of the thermal response below \(T_C\) we see increased decay rate as the sample temperature is increased from 20K to 46K.

It is perhaps surprising that by investigating nodal states, where there is no gap, we can learn things about the superconducting state. However, I think this speaks to how the quantum system is really going through a phase transition, which affects all the electrons in the zone. There is also precedent for measuring changes to the superconducting phase by studying the nodal quasiparticles [27, 91]. Furthermore, because of the high level of electron-electron interactions in the cuprates, the electron system can very effectively thermalize with itself, which justifies the concept of defining a non-equilibrium temperature. In the next section we will see how we can use this “pseudo-temperature” to quantitatively describe the electron dynamics in the gapped part of the Fermi surface.

### 7.3.4 Momentum Dependence of Decay Dynamics

In the previous section we looked at the nodal quasiparticles, where the lack of a superconducting gap allowed us to quantify the amount of electronic heating through fitting the non-equilibrium Fermi distribution. When we look off-node the superconducting gap affects the density of states, making similar analysis impossible. Furthermore, it has been shown that the gap structure has a strong temperature dependence, where the states in the gap get “filled” as temperature
Figure 7.19: Comparison of decay times using a pump fluence of 80 $\mu$J/cm$^2$, enough to drive the system above $T_C$. For both starting temperatures we fit the decay once $T_{el} < T_C$ to an exponential decay. For $T_{start} = 20$K the fit returns a lifetime of $\tau = 6.1$ ps whereas for $T_{start} = 46$K the fit returns $\tau = 4.8$ ps.
increases, causing a corresponding drop in the coherence peak [69]. Therefore we cannot just track the EDC peak locations either. However, we will show in this section that the off-nodal dynamics follow the electronic temperature measured at the node and can be understood by comparing to equilibrium data at those temperatures.

First we look at the qualitative features of the off-nodal data after application of the optical pump. Shown in Fig. 7.20(a) is a near nodal spectrum at various time delays after pumping. The $-1$ ps spectrum is photoemitted before the pump pulse hits the sample so it represents the equilibrium state of the system. This spectrum, taken at the Fermi surface location indicated by the inset to Fig. 7.20(b), shows a roughly 12 meV gap and the corresponding bent-back dispersion characteristic of superconductivity. After optical excitation there is a large increase in occupation above the gap edge and sample looks similar to the excited nodal spectrum in Fig. 7.9(b). This excited state subsequently decays, decreasing the weight both inside the gap and above $E_F$. Interestingly, the rate at which the weight decays inside the gap is different than that of weight above $E_F$. To see this clearly we plot the spectral transients, defined as the spectrum at “t” minus that at equilibrium, in Fig. 7.9(b). Blue color indicates an increase in counts, red a decrease, and all panels are on the same scale. The differential decay is most clear comparing the transients at 3 and 4 ps, where the in-gap weight changes much more than the weight above $E_F$. The differences in the temporal dynamics will be studied in more quantitative detail in the following sections. By 10 ps, the coherent pile-up within the 70 meV kink scale has mostly recovered and there is only a small population of excited bogoliubov quasiparticles remaining.

In order to quantify the temporal electron dynamics we first need to define the $\Delta$SW Map from which we will be taking linecuts. The procedure for generating the $\Delta$SW Map is shown schematically in Fig. 7.21. In panel (a) we plot several SW curves at different delays. The SW is defined as the k-integrated intensity at a given energy, minus the photoemission background signal. We form $\Delta$SW curves in an analogous fashion to the transient spectra of Fig. 7.20; namely $\Delta$SW(t)=SW(t)-SW(-2ps). A characteristic $\Delta$SW curve is shown in Fig. 7.21(b) where we can clearly see the increase of weight in and above the gap scale at the expense of weight in the kink
Figure 7.20: Gapped Spectrum at various pump-probe delays. The (a) panels show the measured ARPES spectra at the delays indicated in each panel. The (b) panels are the differences between the equilibrium spectrum and the one at that delay. The equilibrium temperature is 20K and the Fermi surface location is shown by the inset in (b). The pump has a wavelength of 4\(\mu\)m and a fluence of 80\(\mu\)J/cm\(^2\).
scale. Note that in the presence of a gap, the ΔSW zero-crossing is pushed down to \( \omega \sim \Delta \) rather than being at \( E_F \) like in the nodal case shown in Fig. 7.9(e). We can make a ΔSW curve for each delay measured and combine them into a 2D image, the ΔSW Map, as shown in Fig. 7.21(c). The vertical dotted line in (c) shows where the ΔSW trace from (b) fits into the map in (c). The faster in-gap dynamics are clearly visible in (c), as evidenced by their change from blue to white before the states above \( E_F \) change from blue to white. Finally, we can take temporal linecuts from the map in (c) in order to measure the decay constants. Typically the statistics are too low to reliably extract a decay constant at a given energy, so we integrate in energy over carefully chosen intervals to improve the fitting results. Here we have chosen three characteristic energy windows; one from \( E_F \) to +30 meV, one from \(-\Delta\) to 0, and one from \(-\Delta\) to the kink scale. These windows are shown as horizontal dashed lines in (c) and their integrated weights form the linecuts in (d). For the window above \( E_F \) we stop at \( \omega = +30 \) meV because above this energy the only counts are from LAPE (near \( t_0 \)) or MCP dark current and only serve to obfuscate the signal. We can see in (d) that the above \( E_F \) quasiparticles decay at 2.9 ps while those inside the gap scale decay at the faster rate of 1.6 ps. This is the first observation, to my knowledge, of different decay rates inside and outside the superconducting gap. We attribute this increased sensitivity to the improved energy resolution of our system compared to previous works [63, 18, 74].

In order to understand the differential temporal dynamics we will make use of the previous result of Perfetti et al., who showed that electrons thermalize within 150 fs after optical excitation [63]. Since our time resolution is roughly 700 fs, a price paid for the improved energy resolution, we can consider the electron system as effectively thermalized for all the delays measured. Note that the electron system can be thermalized with itself while still being out of equilibrium with the underlying lattice, which is the case in the first several picoseconds after excitation [63]. Since the electrons are thermalized it is reasonable to compare the transient time-resolved data to high-resolution equilibrium ARPES measurements, such as those previously measured by our group [69, 67].

One of the main results of our group’s previous work is that the superconducting gap structure
Figure 7.21: Generation of the $\Delta$SW Map used to extract the temporal electron dynamics. Panel (a) shows SW curves at several time delays. Panel (b) shows a single SW difference curve, defined by the subtraction of the equilibrium SW from the SW at time $t$. Panel (c) shows the $\Delta$SW Map generated from a series of traces similar to (b). Finally, panel (d) shows the temporal linecuts extracted from the $\Delta$SW Map by integrating over selected energy windows, discussed in the text.
in BSCCO is governed by interplay of the pairing strength, $\Delta$, and the pair-breaking rate, $\Gamma$ [69]. The gap structure is then given by the Dynes’ formula where $\Delta$ controls the position of the coherence peak and $\Gamma$ controls the weight inside the gap. The temperature dependence of $\Delta$ follows a roughly BCS-like behavior, albeit one that closes at a temperature higher than $T_c$. For temperatures $T < T_c$ the gap is always greater than $\sim 60\%$ of its low temperature value. On the other hand, the pair-breaking rate has a very strong temperature dependence in the vicinity of $T_c$. The exact temperature dependence of $\Gamma$ changes with doping but qualitatively there is always a strong upturn near $T_c$ [68]. When $\Gamma$ is large relative to $\Delta$ the gap is mostly “filled”, which comes with a corresponding decrease in the coherence peak. Therefore, when we combine the rapid temperature dependence of $\Gamma$ with a time-dependent temperature we expect the weight inside the gap to decay faster than the thermal response.

To model these off-nodal dynamics we will rely on the temperature response measured at the node and the $\Delta(T)$ and $\Gamma(T)$ obtained by high-resolution equilibrium ARPES measurements [67]. The $\Delta(T)$ and $\Gamma(T)$ curves are reproduced in Fig. 7.22(b) for convenience. At each time delay measured we can assign an electronic temperature based on the nodal data, shown in Fig. 7.22(a). Next, we can use the $\Delta(T)$ and $\Gamma(T)$ curves to define $\Delta$ and $\Gamma$ at that given time delay and compute the $SW$ as the product of a Dynes lineshape and the appropriate Fermi distribution, shown in Eqn. 7.7:

$$SW(t) \equiv \text{Re} \frac{e^{-i\Gamma(t)}}{\sqrt{(\omega - i\Gamma(t))^2 - \Delta(t)^2}} \cdot \frac{1}{e^{(\omega - \mu)/kT(t)} + 1}$$

where $\Gamma(t) \equiv \Gamma(T(t))$ and $T(t)$ is the electronic temperature vs. time. $\Delta(t)$ is defined similarly. The SW curves given by Eqn. 7.7 are then stacked into a SW map. Some representative SW curves are shown in Fig. 7.22(c) including a $40K$ curve from before the excitation. Note the difference between the $70K$ and $90K$ curves in (c); while they have roughly the same weight above the gap scale, the $70K$ has significantly less weight at $E_F$, which comes from the smaller $\Gamma$ at $70K$. In order to properly take into account the experimental time and energy resolution we must account for them before converting the SW map to the $\Delta SW$ map. Therefore, we take the SW map generated
by the above procedure and convolve it in energy by a 10 meV gaussian and in time by a 0.7 ps

gaussian before the subtracting the equilibrium SW to obtain the ΔSW map. Finally, we arrive at

a ΔSW map analogous to the experimental data, as shown in Fig. 7.22(d).

At this point we are ready to compare the data to the simulation. First, note the qualitative

agreement between the model and the data, shown together in Fig. 7.23. We see the extra weight

above $E_F$, shown in blue, and the loss of weight from below the gap scale, shown in red. Also, the

zero-crossing (white stripe) occurs at roughly the gap scale, here 12 meV, just as in the data. Finally,

the simulation reproduces the faster response of the in-gap electrons, seen as the return to white

color by roughly 5 ps for energies within the gap-scale. We can perform quantitative comparisons

between data and simulation by taking identical linecuts from the ΔSW maps and fitting them
to exponential decays, shown in Fig. 7.23(c)-(d). Here we have chosen three energy windows over

which to integrate: one from $-70$ to $-12$ meV representing the weight lost in the kink scale, one
from $-12$ meV to $E_F$ representing the in-gap weight, and one from $E_F$ to $+30$ meV representing
the excited quasiparticle weight. Because the linecuts have different integration windows we have
plotted them normalized to their peak value. Each trace is fit to a single exponential decay over a
range from the peak value to $+7$ ps, which covers $> 2\tau$ in all cases. The extracted $\tau$’s are shown

next to the traces and we can see that the in-gap and above $E_F$ quasiparticle traces have good
agreement between data and model. The kink-scale decay from the data has a longer recovery than
the simulation, but this could be from the reduced signal to noise in the kink region. Therefore, both
qualitatively and quantitatively the thermal model describes the data well and we can understand
the faster in-gap dynamics within this framework.

One logical extension of this thermal model is to other parts of the Brillouin zone where
the superconducting gap has different values. In Fig. 7.24 we show ΔSW maps for two extra cuts
in momentum space with successively larger gap values. These maps are generated in the same
fashion as above and their temporal linecuts are shown in Fig. 7.24(b1)-(b3). Here we see a rich
momentum dependence to the decay dynamics. First, as we move away from the node, the decays
above $E_F$ get progressively faster. For the smallest gap size ($\Delta = 12$ meV) the in-gap decay is
Figure 7.22: Model for describing off-nodal electron dynamics based on an electronic temperature that changes on the ultrafast timescale. The thermal decay is shown in (a). The temperature dependence of the gap, $\Delta$, and pair-breaking rate, $\Gamma$, are shown in (b). SW curves at characteristic timescales are shown in (c), and the simulated $\Delta$SW map is shown in (d).
Figure 7.23: Comparison of thermal model to trARPES data. Panel (a) shows the $\Delta SW$ Map for 13$\mu$m pumped, off-nodal BSCCO. Panel (b) shows the equivalent map generated from the thermal model. (c) and (d) show selected linecuts, discussed in the text, and their corresponding exponential fits.
significantly faster than that above $E_F$, as discussed above. However, as we move away from the
node this in-gap decay gets slower, in contrast to that above $E_F$, and eventually there is a crossover
between the two. This is shown clearly in the progression of linecuts in Fig. 7.24(b1)-(b3). This
crossover behavior may seem confusing at first, but it arises naturally in the context of our thermal
response model, as discussed below.

We have performed simulations representing different parts of the zone by changing the equi-
librium gap value, $\Delta_{eq}$, while keeping $\Gamma$ and the thermal response the same. The $\Delta SW$ maps are
shown in Fig. 7.25(a1)-(a4) for various different gap sizes. Note how drastically different the re-
response is for $\Delta = 20$ meV than for the nodal, $\Delta = 0$ case. The extracted linecuts (produced in the
manner discussed above) are shown in Fig. 7.25(b1) and (b2) for above $E_F$ and in-gap, respectively.
For the different gap sizes, the in-gap region is always defined as $(-\Delta, E_F)$ and integrated accord-
ingly. As seen in Fig. 7.25(b1), the decay above $E_F$ gets faster with larger gap size, consistent with
the data. There have been previous reports of momentum-dependent quasiparticle dynamics [74].
There the authors attribute this behavior to k-dependent quasiparticle recombination dynamics
within their own extension of the Rothwarf-Taylor model [74]. Our data and model produce simi-
lar behavior but all the electrons in the zone are responding to the same thermal impulse and it is
just the different gap edges that cause different time dynamics. This thermal model also captures
the physics of the decay rate crossover seen in the data, appearing at roughly $\Delta_{eq} = 17$ meV in
Fig. 7.25(c). This crossover can be explained by a Fermi windowing effect. Imagine, for the sake of
argument, that $\Gamma$ and $\Delta$ don’t change upon optical pumping and the only change is the increase of
$T_{el}$. Then the weight measured above $E_F$ is simply the portion of the Fermi distribution above the
gap-scale. This Fermi tail decays at the thermal decay rate and once $\Delta \gtrsim kT_{el}$ there won’t be any
significant occupation of the states above the gap. Thus, for the same thermal decay, a larger gap
implies a shorter time window where $kT_{el} \gtrsim \Delta$ and therefore faster decay rates. The occupation
of states below $E_F$ is less sensitive to $T_{el}$ so this windowing effect doesn’t affect the in-gap decay
rates as much. These are controlled, rather, by the strong temperature dependence of $\Gamma(T)$ and
the decay represents the un-filling of the gap as the system cools. Therefore, the electron dynamics
Figure 7.24: Momentum dependence of $\Delta$SW maps. Panels (a1)-(a3) show $\Delta$SW maps for three different cuts, with k-space locations shown by the inset in (a2). Panel (a1) is the same data from Fig. 7.21, reproduced for ease of comparison. Panels (a2) and (a3) have gap sizes of $\Delta = 15$ meV and $\Delta = 22$ meV, respectively. All maps use the color scale denoted in the lower left; blue for increase and red for decrease. Panels (b1)-(b3) show the temporal linecuts corresponding to each $\Delta$SW map. The integration windows used to generate the linecuts in (b) are shown by dashed, black lines in (a). The window above $E_F$ is always from $\omega = (0, 30)$ meV while the in-gap window is always from $\omega = (-\Delta, 0)$ meV. Panels (b1)-(b3) also show single exponential fits in black dashed lines, with extracted $\tau$’s indicated in the panels.
throughout the zone can be understood as following from a single control parameter, the electronic
temperature, and we can measure this with unprecedented accuracy compared to previous works.

7.4 Conclusion

We have performed trARPES experiments on optimally doped Bi2212 \((T_C = 90\text{K})\) using
a novel pump wavelength and a significantly improved energy resolution over all previous works
\([63, 18, 74]\). With this higher resolution we can track the electronic heating in the system by
studying the Fermi widths of the nodal states. This is an improvement over tracking \(\Delta SW\) because
it clearly disentangles the heating from the chemical potential shifts due to photodoping. By
tracking \(T_{el}\) at different pump fluences we find that above the critical fluence, the system goes
normal-state and decays rapidly until it hits \(T_C\), where it slows drastically. Once returning to
the superconducting state the dynamics are governed by a single decay, which depends only on
equilibrium sample temperature, not optical fluence. As the sample temperature is raised, the
decay rate increases and this is evidence that thermally generated quasiparticles are facilitating the
decay. The improved energy resolution is once again useful when we look at the off-nodal states
where, for the first time, we can resolve different dynamics inside and outside the gap-scale. We
can understand these different dynamical scales by connecting to both the thermal decay, measured
at the node, and high-resolution temperature dependent ARPES data. Within our time resolution
the electron system is always thermalized, so the data can be fit and modeled well by considering
each spectrum to have a \(T_{el}(t)\) that matches the nodal thermal decay. Furthermore, within the
context of this ultrafast thermal model, we can understand the momentum dependent quasiparticle
decay rates that have been previously reported \([74]\).

Despite our increased understanding from these trARPES experiments, there remains much
more to do. A systematic doping dependence should be done as all the data in this thesis was done
on optimal doped Bi-2212. Also, in the future we would like to use lower energy pump wavelengths
to study excitations closer to the gap-scale as there have been reports in YBCO that 95 meV
photons can perturb the superconducting state differently than 310 meV photons \([37]\).
Figure 7.25: Simulating the momentum dependent dynamics by changing $\Delta_{eq}$. Panels (a1-a4) show simulated $\Delta SW$ maps for four different $\Delta_{eq}$ values. Panels (b1) and (b2) show extracted linecuts from above $E_F$ and in-gap, respectively, along with exponential fits shown in dashed lines. Panel (c) shows the extracted decay constants from the fits in (b) as a function of equilibrium gap value. Simulated values are shown as solid lines and data are shown as red circles and blue triangles.
Bibliography


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