CHARACTERIZATION OF COLLECTIVE PHENOMENA IN CUPRATE SUPERCONDUCTORS BY MOMENTUM-RESOLVED ELECTRON ENERGY LOSS SPECTROSCOPY

BY

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DISSEarrow_ATION

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Abstract

There exists a wide variety of strongly correlated electronic materials, including high temperature superconductors, exotic topological insulators, and charge density wave materials, that exhibit emergent behavior that cannot be understood through current theories of metals and insulators. These materials are classified by the low temperature ordered phases these materials take on, and there may be several ordered phases interacting over the various regions of phase space. High temperature superconductors, for example, may also exhibit Mott insulator, charge density wave, spin glass, and pseudogap phases in their phase diagram. The current consensus in describing most strongly correlated electron systems is, at best, qualitative, and understanding these ordered phases, the mechanisms that drive them, and their relation to related emergent phenomena is necessary for developing a microscopic understanding of this class of materials.

The electron-electron interactions that drive the collective electronic state can be described by the dynamic charge susceptibility, $\chi(q, \omega)$. This quantity encodes information about the propagation of density fluctuations in a system—the collective “sloshing” of electrons—as mediated by bosonic excitations. In order to measure this quantity, we have developed a new experimental technique, momentum-resolved electron energy loss spectroscopy (M-EELS). As a part of this development, we derived the theoretical framework for describing the scattering cross section in terms of the imaginary part of the dynamic susceptibility, $\chi''(q, \omega)$, and implemented the software and hardware stack necessary to perform this measurement. Using this technique, we are able to measure finite momentum charge dynamics at 2 meV energy scales.

We used M-EELS to investigate materials in the Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) family of cuprate high temperature superconductors. In studying optimally doped crystals, we have performed a full energy and momentum characterization of the low-energy dynamic susceptibility. Our measurement identifies known phonon modes, as previously seen in Raman scattering, infrared spectroscopy, and
HR-EELS. Using a one-loop correction model, we have identified these modes as giving rise to the kinks in the electron spectral function as seen in ARPES, suggesting that these modes are related to the emergent phenomena exhibited in these materials. Furthermore, we observe a background in the optimally doped spectra that extends out to $\sim 1$ eV, consistent with a marginal Fermi liquid description of these materials.

In addition, from our measurements of the static component of the charge susceptibility, we have discovered diffuse, short-range charge order in optimally doped Bi2212. Proximity to the charge order state is suspected to be important in unconventional superconductivity, and has previously been seen in many families of high temperature superconductors, including underdoped Bi2212. At underdoping, we observe sharp elastic peaks consistent with previous charge order observations. At optimal doping, we observe diffuse scattering at low temperatures that exhibits a quasielastic broadening. This is a signature of the emergence of fluctuating order on a time scale of 180 fs.
To the memory of Luc Venema
Acknowledgments

Here, I will try to thank all the people who have helped get me to this point within a format and space constraint that cannot fully capture their full importance.

Foremost, I must thank Peter Abbamonte for guidance and support both as a scientist and an individual. His insightful and level-headed approach to scientific problems has made even the cuprates an engaging field. As a mentor and advisor, Peter has made it possible for me to succeed, shielding me from the political mess of the scientific sausage factory, while letting me catch a glimpse of what happens behind the curtains\textsuperscript{1}. I have learned a lot and benefited greatly from Peter’s passion for blue skies projects both in science and industry. His recognition and appreciation for the interesting problems outside of the basic sciences has been incredibly important to my development, yet is all too rare in the sciences.

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---

\textsuperscript{1}Peter Abbamonte. “How Laws, Sausages, and Science are Made: An inside view of how science really works.” Saturday Physics for Everyone, 24 October 2015. https://www.youtube.com/watch?v=UJaZs6UfnGw
to “Make the EELS Great Again,” a joke that has unfortunately become, well... sad.

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Chapter 1

Introduction

Understanding collective phenomena is currently one of the central pillars of condensed matter physics. By contrast, ordinary classes of materials, such as gasses, liquids, and perfect crystals, which fill the pages of standard solid state physics textbooks, are well understood materials. What makes these phases tractable is that in each, the many-body problem can be simplified to only needing to consider interactions between a single pair of the constituent particles. This formalism is able to be applied to a large number of materials, including the normal state of metals, which is treated in the Landau Fermi liquid formalism [1].

Fermi liquid theory allows us to treat metals not as a many-body electron system, but rather as a system of weakly interacting quasiparticles. This result is rather surprising, as the interactions between the individual electrons on their own is very strong, yet we are able to treat the dressed electrons in a single particle band theory picture.

Much of the recent work in condensed matter physics has been concerned with where these single particle pictures break down. Many-body systems will admit interesting phenomenology that emerges as a result of the collective effects, as is often stated and often parodied, “more is different” [2]. One simple example of this is in second order, or continuous phase transitions, where near the transition, the difference in free energy between the two phases can become negligible, in which case the system becomes sensitive to interactions over much larger distance scales, and hence much larger numbers of particles, even when the underlying interaction can be treated as a pairwise interaction. However, phase transitions are not necessary to cause this breakdown, as is seen in the heavy fermion systems, which shows qualitatively different behavior than is expected from a normal Fermi liquid [3]. Trying to sufficiently characterize the emergent behavior that arises in many body systems has vexed the community in all but a small handful of cases. One field of strongly correlated physics that is still unresolved, and the focus of this study, is the field of high
1.1 High temperature superconductivity

High temperature superconductivity has had a long and tumultuous history. While the identification of the first high temperature superconductor garnered a Nobel Prize in the following year, the subsequent 30 years has seen no consensus on the underlying mechanisms that drive high temperature superconductivity and we have reached a state where, just as a person with two watches is never sure of the time, a person who knows two condensed matter theorists is never sure of the theory of high temperature superconductivity.

In this time, so much has been said in articles, reviews, and books that one could hardly begin to give a reasonable background on the field in a thesis chapter, much less without offending someone, either by exclusion or inclusion. Review articles, with their respective biases, are better starting points for those wanting more information than is presented here [4–7]. I will present here the pertinent history and observations to motivate the development of momentum resolved electron energy loss spectroscopy (M-EELS) and the study at hand.

Conventional superconductivity is generally accepted to be those materials where the BCS electron-phonon mediated Cooper pairing holds. In these materials, the attractive interaction mediated by the lattice vibrations of the crystal allows for the formation of Cooper pairs, opening a single particle gap in the excitation spectrum. These classical superconductors are typically pure metals or simple crystal structures and generally have transition temperatures \( T_c \lesssim 25 \) K, as prescribed by their Debye frequency (though some more exotic BCS superconductors exist with higher transition temperatures, such as the two dimensional MgB\(_2\) and hydrogen-based materials).

While BCS superconductors are generally classified as “conventional”, this is a mostly historic point, as the conditions for BCS superconductivity to be seen are quite rare. By comparison, “unconventional” superconductivity spans several classes of materials, including cuprates, pnictides, fullerenes, organics, chalcogenides, ruthenates, and heavy fermion materials. In the cuprates alone, there has been hundreds of materials classified as superconductors. One of the keys to defining these systems as unconventional is that their superconducting transition is anomalously high compared to the energy scales in the material that would drive BCS, even in cases where the transition
Figure 1.1: BSCCO family of high temperature superconductors showing the homologous series, Bi$_2$Sr$_2$Ca$_n$Cu$_{n+1}$O$_{2n+2}$, which have optimally doped superconducting transitions at 2 K, 95 K, and 108 K, for $n = 1$, 2, and 3, shown in panels a, b, and c, respectively.

temperature is very low on an absolute scale (even in the mK range). Additionally, the unconventional superconductors generally break all of the empirical “Matthias’ rules” for searching for conventional superconductors.

Cuprate superconductors are two-dimensional layered ceramics, all of which contain eponymous CuO$_2$ layers that are generally regarded as being critical to their superconducting properties. The BSCCO homologous series of cuprate superconductors is shown in Figure 1.1; the subject of our study will be the Bi$_2$2212 compound, shown in Figure 1.1b.

From a band theory perspective, the parent compounds of the cuprates should be conductors, with the copper atom having an odd number of electrons, being in a 3d$^9$ configuration. However, these compounds are instead insulating antiferromagnets. This breakdown of the band picture is driven by strong electron-electron repulsion, wherein double occupancy, and thus conduction, is forbidden by the large on-site Coulomb repulsion. The classification for these materials is a Mott insulator. By doping a sufficient number of either electrons or holes into the crystal, we are able to turn the material into a standard Fermi liquid conductor. It is the transition from a Mott insulator that leads to the observed high-temperature superconductivity.

1Save the last rule, “Stay away from theorists”
Figure 1.2: Generic hole doped cuprate phase diagram, showing the Mott insulator parent compound, the low temperature superconducting dome which peaks around 18% doping, as well as nearby ordered states (CDW, SDW), as well as the pseudogap phase for under doped materials, the strange metal phase for optimally doped materials, and the Fermi liquid phase for over doped materials. Many of the qualitative features here are mirrored in the electron doped cuprate phase diagram.

insulator to a normal metal that we find the zoo of low temperature ordered phases, among them superconductivity, and sufficient work has gone into trying to build models in order to understand the physics in this regime [8]. The canonical cuprate phase diagram is shown in Figure 1.2.

We are interested in studying the many body electronic state of the cuprates in order to better understand the forces that drive the observed electronic interactions and the resulting broken symmetry states. In particular, we want to be able to directly probe the dynamics of the electronic state in order to elucidate the nature of the interactions that give rise to the emergent phenomena seen in these materials.

1.2 Characterizing Strongly Correlated Electronic Systems

Fully characterizing a many body system can be done with knowledge of two parameters [1]: the electron spectral function, $A(q, \omega)$, and the dynamic structure factor, $S(q, \omega)$. The spectral function is related to the single-particle Green’s function, $G(k, \omega)$, which describes the single particle dynamics in the system. This encodes information about the fermionic band structure and reveals
the existence of quasiparticles. The dynamic structure factor is related to the density Green’s function, $\chi(q, \omega)$, which describes the density response of the system to a charged perturbation. This encodes information about the interactions that drive collective behavior and the way these interactions dress any quasiparticles. While scientists have long written about the importance of the dynamic susceptibilities in understanding strongly correlated materials [9,10], this quantity has remained elusive in the high-$T_c$ materials.

The primary means to measure these correlation functions is with spectroscopic techniques. These are techniques wherein a material is probed using some particle (neutron, electron, photon, etc.) and by measuring the outgoing particle, we are able to deduce behavior of the material itself.

As it currently stands, there is a great deal of literature classifying the electron spectral function in the cuprates. This function can be measured using angle resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM). However, what is missing is the quantity that directly encodes the collective phenomena: the charge dynamic susceptibility.

### 1.3 Survey of Spectroscopic Techniques

In order to study the collective charge dynamics in the cuprates, we need a technique capable of measuring the charge dynamic susceptibility in this class of materials. There are some probes that are currently available that are able to measure the dynamic susceptibility, however, all of these probes fall short when it comes to the cuprates.

There are a few choices for the probe particle. Inelastic neutron scattering (INS), while it is able to probe energy scales down to the meV range and has the capability to measure finite momentum excitations is limited here because neutrons are not sensitive to the charge dynamics in the system. As such, INS measures the spin dynamic susceptibility, rather than the charge dynamic susceptibility. Switching over to photons, we have a choice of photon energy. With infrared (IR) spectroscopy measures the reflectivity, which can be related to the dielectric response function and in turn to the dynamic susceptibility. IR can achieve very high energy resolution, however, because of the low photon momentum at this energy, it is limited to $q \sim 0$ measurements. With inelastic X-ray spectroscopy (IXS), we are able to achieve both high energy resolution and wave vector tunability. However, X-rays couple to the electron density rather than the charge density.
The key difference between these two quantities is in how the nuclei are treated, which bears noting as the high-$T_c$ community has apparently forgotten about the existence of a lattice. For the electron density, the nuclei position will couple to the electron position, effecting the displacement of all electrons. However, in the case of charge density, the nuclei also act to cancel the core electrons, which screen the nuclei charge. As such, in materials like the cuprates in which there are typically several high-$Z$ elements, IXS will be primarily sensitive to the core electron states, which in turn reveals information about the lattice vibrations, rather than the valence electrons, which are generally of interest in the cuprates. IXS is further hindered in measuring the cuprates by X-ray adsorption, which scales as $Z^4$, lowering the count rate to near unworkable levels to study the relevant dynamics. Recent efforts in this area have focused on resonant techniques, such as resonant inelastic X-ray scattering (RIXS), which has the dual effect of coupling to the valence states and increasing the scattering cross section. However, not only is the energy resolution of this technique much worse ($\sim 50$ meV), the resulting cross section is not well understood and there is no clear way to relate the scattering intensity back to a density response function.

Finally, we turn to electrons as the probe particle. Electrons, unlike photons, are sensitive to charge, and so the core electrons serve to primarily screen the nuclei, such that the scattering is primarily a result of the valence electrons. When operated at high beam energies on thin film samples, transmission electron energy loss spectroscopy (EELS) is able to provide a strong signal with a clean correspondence to the charge dynamic structure factor. However, currently, the energy resolution of such systems is too high ($\sim 50$–$100$ meV) to study the low energy physics of the cuprates. While recent work has lowered the FWHM resolution of these techniques to near $10$ meV [11], there are still problems with heavy-tailed energy resolution and achieving momentum resolution.

### 1.4 Goals and Objectives

In order to address this shortcoming, we have adapted low energy reflection EELS to accomplish the goal of measuring the charge dynamic susceptibility using standard spectroscopic techniques. We have called this M-EELS to distinguish this technique of angle resolved low energy inelastic electron spectroscopic technique from other electron scattering techniques. We have adapted an ex-
isting high-resolution EELS (HR-EELS) spectrometer, which have been used primarily for studying surfaces of materials, to be able to perform the measurement of the charge dynamic susceptibility in the Bi2212 cuprate superconductor. By using a lower electron beam energy and the technology developed for HR-EELS, we are able to achieve \(\sim 2-4\) meV resolution while still having wave vector tunability across the Brillouin zone. Optimally doped Bi2212 is chosen as the focus of the study as these crystals are readily available, have an easily obtainable transition temperature, are easily cleaved in vacuum to expose a pristine surface, and (as a result of the last point) have been widely studied by ARPES and STM such that the fermionic characteristics of this material are well known and serve as a good benchmark to validate the technique.

This study will focus on measuring the dynamic susceptibility of Bi2212 and extracting the full amount of information out of it as possible. This includes characterizing the low energy excitation spectrum in this material, where we show that we are able to measure the collective modes that are responsible for the dispersion anomalies studied in ARPES. In addition, we can use M-EELS to probe larger energy loss values in order to study the electronic behavior in this sample out to the mid-infrared regime. Here, we see evidence generally supporting claims of the existence of a marginal Fermi liquid (MFL) state. Finally, we can use M-EELS to study the formation of ordered states, namely we identify a nematic charge order-like state in the optimally doped sample which exhibits fluctuations on the order of 160 fs.
Inelastic spectroscopic techniques are a valuable tool to provide a probe of the dynamics in many-body condensed matter systems. The basis of all such techniques involves the scattering of a beam of particles from one energy, $E_i$, and momentum, $k_i$, to a final energy, $E_f$, and momentum, $k_f$. By accounting for the change in energy and momentum from the scattering event, one is able to describe the dynamics of the target material. For example, when performing inelastic X-ray spectroscopy, the scattering cross-section can be related to the electron density-density correlation function, and for inelastic neutron scattering, the scattering cross-section can be related to the spin-spin correlation function.

### 2.1 M-EELS Cross-section

In M-EELS, a probe electron with well defined energy and momentum, $k_1$ and $\omega_1$, is incident on a sample surface, which is modeled as a semi-infinite plane, and scatters to a final state $k_2$ and $\omega_2$. The double differential cross-section for such a scattering event can be determined by time-dependent perturbation theory as the sum of all transition amplitudes multiplied by the density of states of the scattered electron:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{1}{\Phi} \sum_f w_{f\rightarrow i} \frac{\partial^2 N}{\partial \Omega \partial E}$$  \hspace{1cm} (2.1)
where $\Phi$ is the incident electron flux, and $\partial^2 N/\partial \Omega \partial E$ is the density of final states of the scattered electron. The term $w_{f \rightarrow i}$ is the transition probability from $f$ to $i$, as given by the equation:

$$w_{f \rightarrow i} = \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 = 2\pi \hbar |M|^2$$ (2.2)

where $|i\rangle$ and $|f\rangle$ are the initial and final states of the system of both the incident and final electron, respectively, and $H'$ is the perturbing Hamiltonian, which for the case of M-EELS, is the instantaneous Coulomb interaction:

$$H' = e^2 / 2 \int \hat{\rho}(\mathbf{R}_1) \hat{\rho}(\mathbf{R}_2) / |\mathbf{R}_1 - \mathbf{R}_2|$$ (2.3)

where $\hat{\rho}$ is the electron number density operator and the coordinate $\mathbf{R} = (\mathbf{r}, z)$, where $\mathbf{r}$ and $z$ are components parallel and perpendicular to the surface, respectively. In terms of this interaction, to determine the scattering cross-section for this process, we also define the matrix element:

$$M = -i \hbar \langle f | H'(0) | i \rangle$$ (2.4)

as the key quantity to compute to quantify the cross section.

The matrix element in Equation (2.4) can be written in terms of the Coulomb interaction Hamiltonian in Equation (2.3) as:

$$M = e^2 / 2 \int \langle n | \hat{\rho}(\mathbf{R}_1) | m \rangle \psi_s^*(\mathbf{R}_2) \psi_i(\mathbf{R}_2) / |\mathbf{R}_1 - \mathbf{R}_2|$$ (2.5)

where we have chosen to have $\mathbf{R}_1$ be a coordinate in the material, and $\mathbf{R}_2$ to be the coordinate of the probe electron. With $\psi_i$ and $\psi_s$ being the wave functions for the incident and scattered electron, respectively, and $|m\rangle$ and $|n\rangle$ are many-body eigenstates of the semi-infinite material. Note that in Equation (2.5), we have neglected exchange scattering, which can be important if the overlap between the probe and valence electron wave function is significant [12]. In so doing, we have neglected the possibility of spin-dependent scattering, which can be significant in materials exhibiting pronounced magnetic excitations, such as magnons.

Up until now, we have only considered the form of the interaction in a perturbative approach,
applying the Born approximation, which is generally valid for weakly interacting probes, such as hard X-rays. However, in M-EELS, multiple scattering effects are significant because of the strong interaction between the electrons in the material and the probe electron. One of the crucial milestones for this technique was the recognition that multiple scattering predominantly takes place in the elastic channel, rather than the inelastic channel. This suggests that the scattering can be accurately described by using wave functions for the probe electron that are modified from their nominally plane-wave form, and treating the inelastic scattering component in the Born approximation, which is formally described as the distorted wave Born approximation. As was argued earlier by Mills [13], the appropriate incident and scattered wave functions, $\psi_i$ and $\psi_s$, are:

$$
\psi_i(R) = N_i \left( e^{i\mathbf{k}_i \cdot \mathbf{r}} e^{ik_i^z z} + R_i e^{ik_i \cdot \mathbf{r}} e^{-ik_i^z z} \right) \theta(z) 
$$

$$
\psi_s(R) = N_s \left( e^{i\mathbf{k}_s \cdot \mathbf{r}} e^{ik_s^z z} + R_s e^{ik_s \cdot \mathbf{r}} e^{-ik_s^z z} \right) \theta(z).
$$

Here, we have adopted a notation that we will use throughout this work, in that lowercase momentum (here $\mathbf{k}$, but later as momentum transfer $\mathbf{q}$), will denote in-plane momentum transfers, and the out-of-plane component is explicitly denoted, e.g. $k_i^z$. In this expression, $R_i$ and $R_s$ describe the effect of the specular reflection of the incident and scattered plane wave off the sample surface, respectively, and the step function, $\theta(z)$, enforces that the wave functions do not penetrate into the material, which we take to fill the half-space $z < 0$. The factors $N_i$ and $N_s$ are normalizations constants that, if the phase shift due to the reflection is small, have the form [13,14]:

$$
N_{i,s} = \sqrt{\frac{2}{V \left(1 + |R_{i,s}|^2\right)}}.
$$

Inserting the above wave functions back into Equation (2.5) and evaluating the expression will result in four distinct terms which each contribute to the inelastic scattering cross section. These terms can be roughly characterized as the different ways in which a single inelastic scattering event can be made up of reflected and un-reflected particle trajectories, as sketched in Figure 2.1. As was shown by Mills, the matrix element is dominated by the cross terms, in which the inelastic scattering event involves a small momentum transfer on top of a single reflection from the surface. These terms end up involving single powers of $R_i$ and $R_s$. The schematic for these processes are
those in Figure 2.1b and 2.1c. Keeping only these terms, the matrix element is given by two terms, one involving each of $R_i$ and $R_s$, such that:

$$M = M_i + M_s \quad (2.9)$$

$$M_{i,s} = -\frac{ie^2}{2\hbar}NR_{i,s} \int \frac{\langle n|\hat{\rho}(r_1)|m\rangle e^{i\mathbf{q} \cdot \mathbf{r}_2} e^{\mp i(k_i^z+k_s^z)z_2}\theta(z_2)}{|r_1 - r_2|} |z_1 - z_2| \, dr_1^2 \, dz_1 \, dz_2 \quad (2.10)$$

where $N = \sqrt{N_i N_s}$ and $\mathbf{q}$ is the in-plane component of the momentum transfer, $\mathbf{k}_s - \mathbf{k}_i$.

If we express the above expression fully in terms of in-plane and out-of-plane components, we get:

$$M_{i,s} = -\frac{ie^2}{2\hbar}NR_{i,s} \int \frac{\langle n|\hat{\rho}(r_1, z_1)|m\rangle e^{i\mathbf{q} \cdot \mathbf{r}_2} e^{\mp i(k_i^z+k_s^z)z_2}\theta(z_2)}{\sqrt{(r_1 - r_2)^2 + (z_1 - z_2)^2}} \, dr_1^2 \, dr_2^2 \, dz_1 \, dz_2 \quad (2.11)$$

If we first consider the term $M_s$ and perform the $r_2$ integral, we get:

$$M_s = -\frac{i}{2\hbar}N^2R_sV_{2D}(q) \int \langle n|\hat{\rho}(r_1, z_1)|m\rangle e^{i(k_i^z+k_s^z)z_2} e^{i\mathbf{q} \cdot \mathbf{r}_1} e^{-q|z_1 - z_2|}\theta(z_2) \, dr_1^2 \, dz_1 \, dz_2 \quad (2.12)$$

where $q = |\mathbf{q}|$ and $V_{2D}(q) = 2\pi e^2/q$ is the Fourier transform of the two-dimensional Coulomb interaction. We then see that the $r_1$ integral is a Fourier transform of the $\hat{\rho}$ operator, such that
then we have:

\[ M_s = -\frac{i}{2\hbar} N^2 R_s V_{2D}(q) \int_{-\infty}^{0} dz_1 \langle n|\hat{\rho}(q, z_1)|m\rangle \int_{0}^{\infty} dz_2 e^{i(k_s^z+k_i^z)z_2} e^{-q|z_1-z_2|} \quad (2.13) \]

where we have used the step function and the fact that the material is semi-infinite to simplify the integrals, i.e. the \( z_1 \) integrand is non-zero only for \( z_1 < 0 \). The quantity \( z_1 - z_2 \) is always negative, so the \( z_2 \) integral may be readily done, which yields:

\[ M_s = \frac{N^2 R_s}{2\hbar} \frac{V_{2D}(q)}{k_s^z+k_i^z+iq} \int_{-\infty}^{0} \langle n|\hat{\rho}(q, z_1)|m\rangle e^{qz_1} \]  

When written in this form, we can more easily understand why the cross terms in Equation (2.10) dominate the scattering cross section. In high-energy, bulk sensitive EELS, the inelastic cross section \( \sim q^{-4} \), so it is a rapidly decreasing function of \( q \). In cross terms, such as Equation (2.14), however, the denominator contains the sum \( k_s^z+k_i^z \), rather than the difference \( q^z = k_s^z-k_i^z \), with \( q^z \) being the out-of-plane component of the momentum transfer. Hence, in this so-called “dipole” regime, in which measurements are carried out in near-specular geometry, \( k_s^z \approx -k_i^z \), so the sum approximately vanishes and the in-plane momentum transfer, \( q \), dominates the denominator. The overall effect is that the probe electron undergoes a large change in its out-of-plane component of the momentum transfer come “for free”, in the sense that it does not enter the Coulomb propagator, rather the momentum is being supplied by the reflectance from the sample surface, rather than the inelastic event. The same applies to other elastic scattering from the surface, namely Bragg peaks, which provide a large elastic signal from which the inelastic events can scatter.

The other component of the matrix element, \( M_i \), is identical to the above Equation (2.14), with \( R_s \rightarrow R_i \) and \( k_s^z+k_i^z \rightarrow -(k_s^z+k_i^z) \). This gives:

\[ M_i = \frac{N^2 R_i}{2\hbar} \frac{V_{2D}(q)}{-k_s^z-k_i^z+iq} \int_{-\infty}^{0} \langle n|\hat{\rho}(q, z_1)|m\rangle e^{qz_1} \]  

Combining the above Equations (2.14) and (2.15), the full matrix element, \( M = M_i + M_s \), is then:

\[ M = -\frac{i}{\hbar} N^2 R \frac{4\pi e^2}{(k_s^z+k_i^z)^2+q^2} \int_{-\infty}^{0} dz \langle n|\hat{\rho}(q, z)|m\rangle e^{qz} \]  

(2.16)
where we have assumed $R_s = R_i = R$, which is roughly valid for small energy losses in the inelastic scattering.

Returning now to the original expression we wrote for the cross section, Equation (2.1). We note that for a single non-relativistic electron travelling at $v$, $\Phi = v/V = \sqrt{2E_i/m/V}$, where $E_i$ is the incident electron kinetic energy and $V$ is the volume of all space. The density of final states is given by the usual expression:

$$\frac{\partial^2 N}{\partial \Omega \partial E} = \frac{V}{8\pi^3} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}. \quad (2.17)$$

Now, squaring the matrix element in Equation (2.16), the final result for the cross section is:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \sigma_0 \left[ V_{\text{eff}}(k_{z_i}^s, k_{z_s}^s, q) \right]^2 \int_{-\infty}^0 dz_1 dz_2 e^{q(z_1 + z_2)} \sum_{m,n} \langle n | \hat{\rho}(q, z_1) | m \rangle \langle m | \hat{\rho}(-q, z_2) | n \rangle \times P_m \delta(E - E_n + E_m) \quad (2.18)$$

where there is an overall constant:

$$\sigma_0 = \sqrt{\frac{E_f}{E_i} \frac{m^2}{2\pi^2 \hbar^4} \frac{|R|^2}{(1 + |R|^2)^2}} \quad (2.19)$$

and

$$V_{\text{eff}}(k_{z_i}^s, k_{z_s}^s, q) = \frac{4\pi e^2}{(k_{z_i}^s k_{z_s}^s)^2 + q^2} \quad (2.20)$$

is an effective Fourier transformed Coulomb interaction that describes how the probe electron couples to excitations near the surface of a semi-infinite system. From this result, we can already confirm the crucial observation, made previously by Mills, that the probe depth in M-EELS is not set by the penetration depth of the electrons, as it is in other electron spectroscopies such as angle-resolved photoemission spectroscopy (ARPES) or scanning tunneling microscopy (STM), but by the inverse of the in-plane component of the momentum transfer $1/q$ [13]. The reason is that M-EELS measures the dielectric response of the surface, which is coupled electromagnetically to layers deeper in the material. Hence, at low $q$, the technique can couple to features deep in the sample, via their influence on the dielectric response near the surface.
2.2 Fluctuation-Dissipation Theorem

We are now ready to establish a relationship between the cross section, Equation (2.18), and a correlation function for the density, and then ultimately a density response function. In complete generality, for a many-body system, the density correlation function is defined as [15]:

\[ S(R_1, R_2, \omega) = \frac{1}{\hbar} \sum_{m,n} \langle m| \hat{\rho}(R_1)|n\rangle \langle n| \hat{\rho}(R_2)|m\rangle P_m \delta(\omega - \omega_n + \omega_m) \]  

(2.21)

in real space. This quantity can also be expressed in momentum space:

\[ S(Q_1, Q_2, \omega) = \frac{1}{\hbar} \sum_{m,n} \langle m| \hat{\rho}(Q_1)|n\rangle \langle n| \hat{\rho}(-Q_2)|m\rangle P_m \delta(\omega - \omega_n + \omega_m) \]  

(2.22)

where for this quantity, we have adopted the momentum notation \( Q = (q, q_z) \), where \( q \) and \( q_z \) are the in-plane and out-of-plane components, respectively. To relate this quantity to the cross section, we consider here the mixed representation:

\[ S(q_1, z_1; q_2, z_2; \omega) = \frac{1}{\hbar} \sum_{m,n} \langle m| \hat{\rho}(q_1, z_1)|n\rangle \langle n| \hat{\rho}(-q_2, z_2)|m\rangle P_m \delta(\omega - \omega_n + \omega_m). \]  

(2.23)

In terms of this quantity, we can write the cross section from Equation (2.18) as:

\[ \frac{\partial^2 \omega}{\partial \Omega \partial E} = \sigma_0 [V_{eff}(k^z_1, k^z_2, q)]^2 \int_{-\infty}^{0} dz_1 dz_2 e^{i(z_1 + z_2)} S(q, z_1; q, z_2; \omega). \]  

(2.24)

this confirms the notion that M-EELS directly measures a correlation function for the charge density in the region near the surface of the material [14]. To complete our study, we must identify a relationship between this quantity and a causal response function.

The density response function is defined as [15]:

\[ \chi(R_1, R_2; t_1 - t_2) = -\frac{i}{\hbar} \sum_{m} P_m \langle m| [\hat{\rho}(R_1, t_1), \hat{\rho}(R_2, t_2)] |m\rangle \theta(t_1 - t_2) \]  

(2.25)

where [\( [-, -] \)] represents a commutator. In contrast to the correlation function, \( S \), the susceptibility, \( \chi \), is a propagator for the charge density, i.e. it represents the amplitude that a disturbance in the density at a location \( R_2 \) will propagate to \( R_1 \) after elapsed time \( t_1 - t_2 \). In contrast to the correlation
function, the propagator is a microscopic representation of the collective charge dynamics of the system, exhibiting causality enforced by the $\theta(t_1 - t_2)$ term, which mandates that disturbances in the density can only influence the state of the system at later times. Written out explicitly in the mixed representation, the response function has the form:

$$
\chi(q_1, z_1; -q_2, z_2; \omega) = \frac{1}{\hbar} \left[ \frac{\langle m|\hat{\rho}(q_1, z_1)|n\rangle\langle n|\hat{\rho}(q_2, z_2)|m\rangle}{\omega - \omega_n + \omega_m + i\eta} - \frac{\langle m|\hat{\rho}(q_1, z_1)|n\rangle\langle n|\hat{\rho}(q_2, z_2)|m\rangle}{\omega + \omega_n - \omega_m + i\eta} \right] \tag{2.26}
$$

To relate this quantity to the correlation function, we begin by taking its imaginary part. Using the relation:

$$
\text{Im} \left[ \frac{1}{x + i\eta} \right] = -\pi \delta(x) \tag{2.27}
$$

for infinitesimal $\eta$, we can write this as:

$$
\text{Im} \left[ \chi(q, z_1; -q, z_2; \omega) \right] = -\pi S(q, z_1; q, z_2; \omega) + \pi \hbar \sum_{m,n} P_n \langle m|\hat{\rho}(q, z_1)|n\rangle\langle n|\hat{\rho}(-q, z_2)|m\rangle \delta(\omega + \omega_n - \omega_m) \tag{2.28}
$$

where, in anticipation of a comparison to Equation (2.23), we have chosen the specific case $q_1 = -q_2 = q$. The first term in the sum of Equation (2.28) is identical to the correlation function in Equation (2.23), such that:

$$
\text{Im} \left[ \chi(q, z_1; -q, z_2; \omega) \right] = -\pi S(q, z_1; q, z_2; \omega) \tag{2.29}
$$

To handle the second term, we recognize that:

$$
P_n = P_m e^{-\beta(E_n - E_m)} = P_m e^{-\beta\omega}. \tag{2.30}
$$

Substituting this expression into Equation (2.29) and exchanging the indices $m$ and $n$ gives:

$$
\text{Im} \left[ \chi(q, z_1; -q, z_2; \omega) \right] = -\pi S(q, z_1; q, z_2; \omega) + \pi e^{\beta\omega} S(-q, z_1; -q, z_2; \omega) \tag{2.31}
$$
or equivalently:

\[ S(q, z_1; q, z_2; \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{\beta \hbar \omega}} \text{Im} [\chi(q, z_1; -q, z_2; \omega)] \]  

(2.32)

The final result in Equation (2.32) is a statement of the fluctuation-dissipation theorem relevant to high-resolution, electron energy loss spectroscopy. Its physical meaning is that the scattered intensity, which is directly proportional to the correlation function, \( S \), is also a measure of the dissipative, imaginary part of the Green’s function that describes the charge dynamics. The only assumption underlying this relationship is the presence of thermodynamic equilibrium and equipartition of energy. The proportionality factor, \( n(\omega) = \frac{1}{1 - \exp(-\beta \hbar \omega)} \), is the so-called Bose factor, which mandates that the excitations that contribute to \( S(q, \omega) \) exhibit Bose statistics, which is required for a two-particle response function.

The final expression for the cross section, from Equation (2.24), in terms of the dynamic susceptibility is:

\[ \frac{\partial^2 \omega}{\partial \Omega \partial E} = -\frac{\sigma_0}{\pi} [V_{\text{eff}}(k_i^z, k_s^z, q)]^2 n(\omega) \int_{-\infty}^{0} dz_1 dz_2 e^{q(z_1+z_2)} \chi''(q, z_1; -q, z_2; \omega) \]  

(2.33)

which we will write, suppressing the integral over the out-of-plane direction, as:

\[ \frac{\partial^2 \omega}{\partial \Omega \partial E} = -\frac{\sigma_0}{\pi} [V_{\text{eff}}(k_i^z, k_s^z, q)]^2 n(\omega) \chi''(q, \omega) \]  

(2.34)

2.3 Antisymmetrization of Dynamic Susceptibility

The relation of the M-EELS cross section to a response function suggests that this method, when combined with inverse methods such as those described in [16, 17], could be used to image the dynamics of electrons near surfaces.

As discussed earlier, however, M-EELS has very high energy resolution, and in the low-energy loss region will be sensitive to the non-trivial frequency region of the Bose factor, where there is a substantial difference between the correlation function, \( S(q, \omega) \), and the response function, \( \chi(q, \omega) \). To extract the latter, the Bose factor must be divided from the experimental data. In doing so, we encounter a problem. The cross section is proportional to \( n(\omega) \chi''(q, \omega) \), but the product is convolved with the resolution function of the spectrometer. On energy scales similar to the width
of this function, \( n(\omega) \) cannot be divided out, impeding the reconstruction of the electron dynamics.

In contrast to \( S \), we expect the dissipative part of response function to be odd in frequency, i.e. \( \chi''(q, \omega) = -\chi''(q, -\omega) \). The reason is that the charge density in real space and time must be real, so \( \chi^*(q, \omega) = \chi(q, -\omega) \). This is ultimately a statement of time invariance, and in the case that this would not hold, we would allow the real time dynamic susceptibility to have an imaginary component \([19]\). Hence, we expect that dividing a measured \( S(q, \omega) \) by \( n(\omega) \) should yield a function that is antisymmetric in \( \omega \).

To illustrate the point we show in Figure 2.2 an M-EELS scan taken in the dipole regime from the copper-oxide superconductor Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) at room temperature. The energy resolution for this scan was set to around 2 meV. Several collective modes are visible, which have been described previously by multiple authors \([20–24]\). In accordance with Equation (2.24), both Stokes and anti-Stokes features are visible when the temperature of the system is large relative to the energy resolution of the system. These energy gain peaks correspond to the probe electron creating or annihilating an excitation, respectively, with a weight described by \( n(\omega) \).

The result of the direct division of the Bose factor is shown in Figure 2.3a. At energy scales larger than the energy resolution, the division works remarkably well, with the antisymmetrized

\[ \text{Figure 2.2: Scattering cross section measured on optimally doped Bi2212 at both room temperature and in the superconducting state.} \]

\[ \text{Figure 2.3a: Direct division of the Bose factor.} \]

\[ \text{Figure 2.3b: Anti-Stokes features with temperature dependence.} \]

- Strictly speaking, this is only true for a system with inversion symmetry. See \([18]\)
Figure 2.3: Comparison and evaluation of the various methods for performing the calculation of \( \chi''(q, \omega) \) of Bi2212 from the \( q = 0 \) and 295 K spectrum shown in Figure 2.2. (a) The comparison of \( \chi''(q, \omega) \) computed via the direct method of Equation (2.34) to an antisymmetrized copy of \( \chi''(q, \omega) \). (b) The comparison of \( \chi''(q, \omega) \) as computed by the direct method and as computed by the antisymmetrization method of Equation (2.39).

energy loss and gain features overlapping to within the experimental statistics. In the region near the elastic line, however, the symmetry is lost, and a divergence occurs at \( \omega = 0 \). The divergence results from a rounding off of \( S(q, \omega) \) near zero energy due to the finite resolution, and represents the inability to distinguish between truly static correlations and finite frequency excitations lying within the elastic line. Customarily, such features are collectively referred to as “quasielastic scattering”.

One method to address this problem would be to fit and subtract a zero-loss line from the raw data [17, 25]. However, we have developed a method which exploits the antisymmetric nature of the propagator in order to write a closed form expression for the charge susceptibility in terms of the scattering intensity without the Bose factor, which more effectively accounts for the resolution problem without removing potentially important information about the quasielastic scattering.

For a single inelastic M-EELS spectrum, the electron scattering intensity is measured for various energy loss at some fixed momentum, \( q \), which we will denote \( I_q(\omega) \) for the scattering intensity.
We start from the result in Equation (2.32):

\[ S(q, \omega) = -\frac{1}{\pi} n(\omega) \chi''(q, \omega). \]  

(2.35)

We proceed in a way motivated by similar work for ARPES to symmetrize the response function [26], however, in the case of EELS, we use the fact that \( \chi''(q, \omega) \) is antisymmetric in energy, such that:

\[ S(q, \omega) - S(q, -\omega) = -\frac{1}{\pi} \left[ n(\omega) \chi''(q, \omega) - n(-\omega) \chi''(q, -\omega) \right] \]  

(2.36)

\[ = -\frac{1}{\pi} \chi''(q, \omega) \left[ n(\omega) + n(-\omega) \right]. \]  

(2.37)

It can simply be seen that:

\[ n(\omega) + n(-\omega) = \frac{1}{1 - e^{-\beta \hbar \omega}} + \frac{1}{1 - e^{\beta \hbar \omega}} = 1 \]  

(2.38)

such that:

\[ \chi''(q, \omega) = \pi [S(q, -\omega) - S(q, \omega)] \]  

(2.39)

This allows us to compute \( \chi''(q, \omega) \) from the scattering cross section directly without the complications of dividing the Bose factor and gives a function that is antisymmetric by construction. This method of computing the dynamic susceptibility is shown in comparison to direct division of the Bose factor in Figure 2.3b. Not only does this give a better representation of the propagator, but this allows us to compute the full energy dependence of the propagator at low temperatures, where the energy gain scattering signal is particularly small.

### 2.4 Kramers-Kronig and Fourier Transform Analysis

In order to describe the full dynamics of the system, we want to be able to extract \( \chi(q, \omega) \). However, the equation for the cross section that we have presented thus far gives us a means to determine the imaginary component of \( \chi(q, \omega) \). This is similar to the phase problem, as seen in inelastic X-ray scattering. Just as with X-ray spectroscopy techniques, we can resolve this by Kramers-Kronig analysis. The application of the Kramers-Kronig relations are derived from the fact that \( \chi(q, \omega) \) is
a causal function. The full Kramers-Kronig relations are:

\[
\chi'(q, \omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi''(q, \omega')}{\omega' - \omega} d\omega' \quad (2.40)
\]

\[
\chi''(q, \omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi'(q, \omega')}{\omega' - \omega} d\omega'. \quad (2.41)
\]

In our case, because M-EELS measures the imaginary component, we are most interested in Equation (2.40). Then, using the fact that \(\chi''\) is an odd function with respect to energy, we can write this Kramers-Kronig relation as:

\[
\chi'(q, \omega) = \frac{2}{\pi} \mathcal{P} \int_{0}^{\infty} \frac{\chi''(q, \omega') \omega'}{\omega'^2 - \omega^2} d\omega' \quad (2.42)
\]

where \(\chi'(q, \omega)\) is the real part of the dynamic susceptibility, and \(\mathcal{P}\) denotes the principal part of the integral.

With this relation, we are able to compute the full dynamic susceptibility for a given material from the scattering cross section. Note, however, that this requires an integral over the imaginary component of the susceptibility, which in practice requires sufficiently large energy scans to capture the excitations of interest and proper handling of the limiting behavior of the susceptibility. With the full susceptibility, it is possible to compute the real-space propagator, \(\chi(x, t)\), which describes the spatial and temporal evolution of the electronic system in response to disturbances in the charge density.
Chapter 3

Instrumentation

Prior to this work, the design and use of high-resolution EELS (HR-EELS) spectrometers, which is the basis for our measurement of $\chi''(q,\omega)$ as spelled out in Chapter 2, had been optimized for use in studying adsorbates and surface vibrations [14]. This technology has advanced such that it is capable of measuring energy losses in the single meV range [27]. As such, we are able to use an off-the-shelf spectrometer, the LK Technologies ELS5000, which is able to achieve the base requirements for this study. However, there are several additional modifications and considerations we have made in order to use this spectrometer to properly characterize the materials using the analysis from Chapter 2. The foremost of these concerns is achieving momentum resolution, and the hardware control development that went into that is described in Chapter 4. In this chapter, we will outline the instrumentation used, as well as the modifications and considerations taken to ensure proper use of the instruments for our applications.

3.1 Experimental Setup

In order to carry out this experiment, we had to design and construct a set of chambers for performing sample preparation, manipulation, and characterization capable of achieving ultra-high vacuum (UHV) conditions. High vacuum conditions are necessary as a requirement of running the electron filament, however it is primarily a concern because of surface contamination caused by adsorbates.

The experimental chamber setup consists of two chambers, the first is used for sample preparation and surface characterization and the second is used for performing the M-EELS measurement. In addition to the chambers themselves, there is also a sample transfer stage which allows us to move samples into and out of the sample preparation chamber under a high vacuum. A picture
Figure 3.1: Photograph of the chamber and instruments in the lab. On the left is the M-EELS and on the right is the sample preparation chamber, each with its associated pumps below and sample manipulation stage above, and on the far left and far right is the sample transfer and load lock stages.

showing the full layout of the laboratory at the time the measurements were performed is shown in Figure 3.1.

In order to achieve the base pressure, we use a series of ultra high vacuum capable pumps. On the sample preparation chamber, we have a 400 L/sec turbo pump which is backed by a scroll pump, and on the primary M-EELS chamber, we have both an ion pump capable of 400 L/sec pumping speed and a titanium sublimation pump with a liquid nitrogen cryoshield which is capable of 2000–5000 L/sec pumping speed at room temperature, depending on the gas, which can be improved by roughly a factor of 6.5 when cryogenically cooled. In the sample load lock, we also use a small turbo pump backed by diaphragm pump. In order to perform the necessary sample rotations (see Section 3.4), a differentially pumped rotary stage is used on the M-EELS sample stage, which also requires the use of a turbo pump backed by a scroll pump. In this configuration, both the primary
chamber and the sample preparation chamber have a base pressure of $1 \times 10^{-10}$ Torr once it has been baked using standard UHV protocol, while the load lock is able to achieve a $1 \times 10^{-6}$ Torr vacuum. In order to monitor the vacuum pressure, we use ion gauges on each chamber, in addition to both a residual gas analyzer (RGA) and vacuum quality motitor (VQM) on the sample prep and primary chambers, respectively.

Because the load lock cannot achieve UHV, in order to transfer samples between the load lock and the sample preparation chamber without contaminating the M-EELS chamber vacuum, a series of gate valves is installed between all of the components. This allows isolation of the various chambers while still enabling the required sample transfer capabilities. This allows for samples to be annealed *in situ* during sample preparation without compromising the vacuum for the M-EELS spectrometer.

In addition to the vacuum requirements, the M-EELS spectrometer requires low magnetic fields in the vicinity of the electron trajectory. This is necessary in order to achieve peak resolution and throughput because the stray magnetic fields will deflect the electron beam, particularly for low energy electrons. The ELS5000 instrument spec requires the magnetic field in the region of the spectrometer to be below 0.5 mG. In order to achieve this requirement, the spectrometer chamber has double mu-metal lined walls and custom shields to interface with the magnetic shielding on the spectrometer. Care was also taken with ion pumps, which contain large permanent magnets, and stepper motors, which use powerful electromagnets, to ensure their impact on the magnetic field is minimized.

### 3.2 M-EELS Spectrometer

The primary instrument used in this study is an Ibach-style HR-EELS system, built by LK Technologies for use in our system [27]. The instrument is capable of performing electron spectroscopy using an incident electron beam energy of 2–200 eV, with an energy resolution as low as 0.5 meV under optimal conditions. An overview schematic of the spectrometer is shown in Figure 3.2.

The electron source in the spectrometer is a LaB$_6$ thermionic emission source. This is operated at 1.75 A and provides 5 $\mu$A of current at 1850 K. A monochromatic beam is obtained by focusing and collimating the beam and passing it through a pair of toroidal electrostatic deflection
monochromators. The first monochromator is operated as a retarding monochromator and acts in conjunction with the second monochromator to optimize the total current throughput while maximizing the overall resolution. This is done by choosing appropriate values for the pass energies of each monochromator to properly account for space charge effects in each of the lenses. The single-pass analyzer stage allows for energy analysis of the scattered electron beam. This stage is mounted on a rotating platform to provide the angular information needed for our analysis. The electron beam energy is set by a symmetric pair of zoom lenses, positioned at the entrance and exit to the scattering chamber. A tightly collimated beam of the desired energy is obtained by floating the monochromator and analyzer system with respect to the grounded sample and using the zoom lens system to focus the beam to and from the sample which accelerating and decelerating it, respectively. Finally, the electron counting is performed by a Channeltron electron multiplier. The pulses from the Channeltron are then counted outside of the system using a discriminator to generate TTL pulses for direct counting.

The off-the-shelf ELS5000, as described above, required some minor modifications to function in the way we need. The primary modification from the stock unit was to motorize the electron analyzer rotation stage. As will be discussed in Section 3.4, this functionality is required to achieve proper momentum space scans in order to measure $\chi''(\mathbf{q}, \omega)$. As will be discussed in Chapter 4, the included EELS control hardware and software also needed to be overhauled to fully make use of this computerized control to perform the momentum space scans.

Figure 3.2: Schematic of the HR-EELS spectrometer, highlighting the key components of the spectrometer, including the electron gun, the electrostatic lenses, the energy dispersing elements, and the electron counting element.
Figure 3.3: Energy resolution of the HR-EELS spectrometer as used to perform the inelastic measurements at 7.4 eV beam energy, shown for both the direct beam geometry, which represents the base resolution of the spectrometer in the given configuration, and the specular geometry when the beam is reflected off the sample.

One of the key features of an electrostatic HR-EELS system is the ability to tune the spectrometer to trade-off energy resolution and signal. Higher resolution can be obtained by lowering the pass energy in the deflection stages and tuning the retarding monochromator to optimize the space charge effects in the system [27]. As such, when investigating inelastic effects, we operated with a high resolution 7 eV beam with roughly 2 meV FWHM, and when investigating elastic features, we operated with a lower resolution 50 eV beam with roughly 4 meV FWHM. The direct beam resolution and the resolution in specular reflecting geometry is shown in Figure 3.3.

The momentum resolution of the spectrometer is dependent on the angular acceptance of the various lens elements and the reduction of aberrations. By the construction of the deflection stages, the momentum resolution is best in the scattering plane, and can be tuned to be as low as 0.02 Å\(^{-1}\) with a 7 eV electron beam. The momentum resolution out of the scattering plane in such a configuration is roughly 0.1 Å\(^{-1}\). However, these values can vary, sometimes a lot, based on the beam energy and the particular voltage configuration of the optics. A specular scan giving the in-plane momentum resolution is show in Figure 3.4
Figure 3.4: Scan of the in-plane momentum transfer near the specular geometry showing the momentum resolution of the spectrometer in this direction.

3.3 Sample preparation and characterization

A critical step in the operation of the M-EELS is proper characterization, preparation, and alignment of the sample prior to being able to perform the measurement. Because of the surface sensitivity of this technique, we must be able to prepare pristine crystal surfaces \textit{in situ} in UHV conditions. Once prepared, we must be able to orient the sample properly in the scattering chamber in order to measure particular regions of momentum space.

Because of the highly layer nature of BSCCO crystals, the crystals used for this study were oriented with the sample surface in the (001) plane. In order to roughly orient the crystals, we use a back reflection Laue diffractometer. This quickly gives us an idea as to the quality of the crystal and the rough orientation of the crystal, both the copper-oxygen bond directions and the direction of the supermodulation, which appears along (110) but not (1T0). A typical Laue pattern for Bi2212 is shown in Figure 3.5.

In order to prepare the samples, they are affixed to sample pucks (see Section 3.4) using a conducting silver epoxy. This is used to ensure the sample is in electrical contact with the sample stage and does not charge. See Figure 3.6 for an image of a mounted sample. On top of the sample we glue down an aluminum post just large enough to fully cover the sample. Once the sample is passed into the sample prep chamber and a sufficiently low vacuum is obtained, we are then able
Figure 3.5: X-ray diffraction image of optimally doped Bi2212 captured using a Laue X-ray diffractometer. The superlattice which appears along (110) direction is oriented horizontally and can be seen as the streak through the middle of the image and in the creation of peaks displaced from the tetragonal Bragg peaks.

to knock this post off in order to cleave the sample in order to expose a pristine sample surface.

Once the sample is cleaved, we have a low-energy electron diffraction stage mounted to the chamber that is designed to focus on a sample in the sample preparation chamber. The LEED works by focusing an electron beam onto the sample and then imaging the reflected electrons onto a phosphorous screen. Using this instrument, we are able to demonstrate that the sample surfaces are sufficiently pristine to perform electron scattering measurements. An example LEED image is shown in Figure 3.7.

### 3.4 Sample manipulation

The foremost sample manipulation task is to be able to transfer the sample into the vacuum and between the two chambers. In order to do this, we have designed and installed a pair of gripper
Figure 3.6: Image of a typically mounted Bi2212 sample viewed under a microscope which is affixed to a copper puck using silver epoxy.

Figure 3.7: Image of LEED pattern taken on optimally doped Bi2212, note that the lines of peaks running roughly vertically across the image correspond to Bragg peaks from the superlattice modulation oriented along the (110) direction.
arms that can be extended and actuated by a magnetically coupled ring. A picture of this gripper is shown in Figure 3.8. One of the two grippers is for transferring from the load lock into the sample prep chamber while the main chamber is isolated from the relatively high vacuum, and the second gripper is for transferring between the chambers while the chambers are under UHV.

To work with the sample grippers, we also designed copper pucks for mounting the samples. OFHC copper is used here for its thermal and electrical conductivity and the ability to drive it to cryogenic temperatures. These pucks are designed to work with both the sample transfer system and the sample stages in both of the chambers. An image of a sample mounted on a puck is shown in Figure 3.9.

In the prep chamber, we have designed a sample holder in order to hold the samples while the surface is prepared before transferring the puck into the M-EELS chamber for analysis. In addition to acting as a stage for cleaving samples, the sample stage in the prep chamber is outfitted with a small button heater in order to anneal samples, allowing us to work with some refractory crystals and thin films. The sample stage itself is machined out of molybdenum, which is particularly well suited for heating. The button heater on its own has a maximum temperature of 1200°C, and when mounted, the maximum temperature measured on the sample holder is 350°C. The sample stage.
is mounted on the base of a steel rod attached to a rotating feedthrough and is designed such that the face of the sample will be at the center of rotation of this motion in order to perform the LEED measurement. A picture of the sample holder can be seen in Figure 3.10.

In the EELS chamber, we have another sample holder for both holding the pucks and for performing the necessary manipulations needed to perform the desired measurements. The sample goniometer provides two rotational degrees of freedom, a rotation normal to the face of the puck and another parallel to the face of the puck and normal to the scattering plane. The former is achieved by using an attocube rotation stage, which is a piezoelectric rotation stage with closed-loop positioning control. As such, the stage is composed of two parts, the base, which connects the feedthrough to the attocube and a seat which holds the puck on the attocube rotary stage. These components of the sample holder are machined from OFHC copper. In order to provide a good thermal contact between the base and the seat, there is a copper braid that connects the base and the seat. This sample holder, mounted with the attocube, can be seen in Figure 3.11.

In order to study properties of the samples related to superconductivity, we installed the sample holder on a Janis ST-400 UHV cold finger cryostat with closed-loop temperature control. In order to calibrate the cryostat, we fixed a silicon temperature diode to a sample puck and measured the relationship between the sample and cold finger temperature. The base temperature of the sample is 17 K when the cold finger is running at liquid helium temperature, which is sufficient to drive
Figure 3.10: Image of the sample holder for the sample preparation chamber. The ceramic is used to electrically isolate the sample holder from the thermocouple. The sample puck can be heated with the button heater visible in the back of the bottom hole. The upper hole provides both a thermal barrier and an additional location for placing a sample puck.

Bi2212, which has a $T_c = 92$ K, into the superconducting regime. The calibration curve is shown in Figure 3.13.

### 3.5 Sample positioning

Before discussing the details of the positioning of the sample in the M-EELS spectrometer, we must define the coordinate system for our angles. The sample geometry we use for inelastic electron spectroscopy is similar to the four circle sample geometry [28], which is defined by the scattering angle, $\gamma$, and the Euler angles defining the orientation of the sample. These goniometer angles, $\theta$, $\chi$, and $\phi$, are defined in the $z$-$y$-$z$ convention, respectively. These three angles are left-hand, right-hand, and left-hand rotations, respectively. In our case, the Cartesian axes of the lab are such that the $+y$–axis is parallel to the incident beam in the direction of travel and the $+z$–axis is defined as the left-hand rotation of the analyzer. The notable differences between this geometry and a standard four-circle geometry is the use of LRL-handed Euler angles, rather than RLR-handed, and the definition of the $+z$–axis by the left-hand, rather than right-hand rotation of the analyzer. These are based on the geometry of the LK Technologies ELS5000 HR-EELS spectrometer used in this study. A diagram showing the scattering angles as we have defined them with $\chi = 90^\circ$ can be
Figure 3.11: Image of the sample holder for the EELS shown mounted to the attocube rotation stage and mounted to the cryostat.

Figure 3.12: Schematic of the EELS sample goniometer highlighting the rotational degrees of freedom. The red arrow shows the electron beam trajectory reflecting off the sample surface. The sample stage provides the $\theta$ rotation by the rotating feedthrough and the $\phi$ rotation by the attocube stage by piezoelectric actuation, and the $\gamma$ rotation is provided by the rotating analyzer. The $\chi$ angle for the sample is not shown, but is fixed by the construction of the sample holder to be $90^\circ$, seen in Figure 3.12.

One of the key developments in formulating M-EELS, in particular in differentiating it from HR-EELS, is the precise locating of centers of rotation for both the $\theta$ and $\gamma$ angles and moving these centers of rotation to be coincident. This precise positioning is required to specify the exact location in reciprocal space being measured and to be able to perform continuous scans on the same position on the sample surface. In order to achieve this, we must have two independent $x$–$y$ translation stages, one to translate the sample relative to the $\theta$ center of rotation, and one to move the $\theta$ center of rotation relative to the chamber. Locating the center of rotation of $\theta$ is accomplished by using a USB camera with a set of crosshairs to check the motion of the sample through a full
180° rotation of $\theta$. With the sample face coincident with the center of rotation of $\theta$, we make the $\theta$ and $\gamma$ centers of rotation coincident by searching for the location at which the specular reflection is maximized at an angle $\gamma = 2\theta$. This relationship is only linear with a slope of 2 precisely at the point where the centers of rotation are coincident. In order to be able to ensure these centers of rotation are coincident before every measurement, we have a pair of USB cameras pointed into the scattering chamber, each with a crosshair fixed on the sample face. Using parallax between the two cameras, we are able to reproducibly position the sample such that the face is at the center of rotation of the analyzer in every configuration.

In order to use properly perform M-EELS, given any incident beam energy and energy loss, we must be able to transform between the goniometer angles that we have defined in designing the sample holder and the momentum transfer, $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$. The design of the goniometer is based on a standard four circle design commonly used in inelastic X-ray spectroscopy. However, in the case of X-rays, the incident photon energy is large in comparison to the energy losses that are considered, and as such $k_f \approx k_i$. In our case, the electron energy loss is not necessarily negligible on the order of the incident energy. As such, we have derived the functions that do this transformation for arbitrary $k_f$ and $k_i$. For both the incident and reflected beam, we can define the magnitude of the
electron momenta in terms of the electron energy:

\[ k_{i,f} = \sqrt{\frac{2m_e E_{i,f}}{\hbar}} \]  \hspace{1cm} (3.1)

for \( m_e \) the electron mass and \( E_{i,f} \) the incident or final electron energy, respectively.

Now, given a particular incident and scattered energy, we can define the transformation from \( \mathbf{q} \) to a given goniometer geometry. For simplicity, we have assumed that the normal to the sample face is always in the scattering plane, the four circle equivalent of \( \chi = 90^\circ \), as this is always the case with the current sample holder. This can be done because the standard four circle geometry has an extra degree of freedom, and so our choice is to fix \( \chi \). Note that this precludes some corner case values for \( \mathbf{q} \) and forces the \( \Gamma \) point to always lie in the scattering plane. Even with this constraint, there are, in general, two equivalent scattering geometries that give the same value of \( \mathbf{q} \), as shown in Figure 3.14 which correspond to the choice of having either the incident or the scattered beam being more grazing. For convenience, we define the angle the \( \mathbf{q} \) vector makes with the \( x-y \) plane to be \( \alpha \), and can be computed as:

\[ \tan \alpha = \frac{q_z}{q_{xy}} \]  \hspace{1cm} (3.2)

for \( q_z \) and \( q_{xy} \) the signed \( z \) and in-plane components of the momentum transfer, respectively, for choosing the proper branch of the tangent function. From this, the two possible goniometer
(a) Overview of full scattering geometry, including incident and reflected beams

(b) View parallel to both sample face and scattering plane

(c) View normal to face of sample

Figure 3.15: Schematics showing how the momentum vector \( \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \) is decomposed into its components, \( q_i \), in the coordinate system of the sample, \( \mathbf{q}_i \), for a general four circle goniometer position, as defined by \( \theta, \gamma, \chi, \) and \( \phi \).

The geometries are:

\[
\cos \gamma = \frac{k_i^2 + k_f^2 - q^2}{2k_i k_f} \quad \quad \cos \gamma = \frac{k_i^2 + k_f^2 - q^2}{2k_i k_f} \quad (3.3)
\]

\[
\tan \phi = \frac{q_x}{-q_y} \quad \quad \tan(\phi - \pi) = \frac{q_x}{-q_y} \quad (3.4)
\]

\[
\theta = \pi - \alpha - \arccos \left( \frac{k_i^2 - k_f^2 + q^2}{2k_i q} \right) \quad \quad \theta = \alpha - \arccos \left( \frac{k_i^2 - k_f^2 + q^2}{2k_i q} \right) \quad (3.5)
\]

where the left and right equations correspond to the geometry in Figure 3.14a and Figure 3.14b, respectively, and in Equation (3.4), the \( q_x \) and \( q_y \) are signed components of \( \mathbf{q} \) with the negative sign given to set the proper branch for \( \phi \).

Next, for any incident and scattered electron energies, given the goniometer geometry, we must be able to determine the momentum transfer vector \( \mathbf{q} \). In this case, the momentum transfer is uniquely determined by the scattering geometry, and it is straightforward to consider the \( \chi \) angle in full generality.

In order to perform this calculation, we consider the components of the momentum vector parallel and perpendicular to the incident beam direction, and transform those components into the coordinate system of the sample. This is then rotated by \( \theta \) to give the component of \( \mathbf{q} \) parallel...
to and perpendicular to the sample if aligned at $\chi = 90^\circ$:

\[
q_\parallel = k_f \sin \gamma \sin \theta - (k_i - k_f \cos \gamma) \cos \theta
\]

\[
q_\perp = k_f \sin \gamma \cos \theta + (k_i - k_f \cos \gamma) \sin \theta
\]

where we are careful to note that the definitions of parallel and perpendicular here do not account for the $\chi$ rotation, see Figure 3.15a.

Next, we note that only $q_\perp$ contributes to the $q_z$ component, which can be found by considering the projection of this vector normal to the surface of the sample rotated by $\chi$, see Figure 3.15b. The component of $q_\perp$ in the plane of the sample as well as $q_\parallel$ contribute to the in-plane components of the momentum transfer. In the $\phi = 0^\circ$ geometry, the $q_\perp$ projection lies along the $+\hat{q}_y$ direction, see Figure 3.15c. As such, considering the rotation of these components by $\phi$, and combining with the result from above, we can write the momentum transfer as:

\[
q_x = -k_f \sin \gamma (\cos \phi \cos \chi \cos \theta - \sin \phi \sin \theta) - (k_i - k_f \cos \gamma)(\cos \phi \cos \chi \sin \theta + \sin \phi \cos \theta)
\]

\[
q_y = -k_f \sin \gamma (\sin \phi \cos \chi \cos \theta + \cos \phi \sin \theta) - (k_i - k_f \cos \gamma)(\sin \phi \cos \chi \sin \theta - \cos \phi \cos \theta)
\]

\[
q_z = k_f \sin \gamma \sin \chi \cos \theta + (k_i - k_f \cos \gamma) \sin \chi \sin \theta.
\]

Thus, with Equations (3.3)–(3.5) and (3.8)–(3.10) we are able to perform the transformation between the goniometer position and reciprocal space of the sample. On top of this transformation, in order to consider an arbitrary alignment of the crystal, another treatment would be needed to determine the UB matrix, which defines this transformation. However, to do this, we used standard X-ray diffraction software outfitted with our custom geometry code. See Section 4.9 for the details of this implementation.
Chapter 4

M-EELS Control Hardware and Software

To control the LK Technologies ELS5000 spectrometer, we had to develop a suite of in-house software and hardware. Existing hardware and software is designed with surface chemistry in mind, where a small number of energy loss spectra are taken at fixed scattering geometries. Our interest in M-EELS is in performing energy loss scans at constant in-plane momentum transfer while sweeping the momentum across the Brillouin zone. This necessitates a redesign of the control system to achieve true momentum resolution. This chapter describes the design of these software and hardware packages and their relation to the information reverse engineered from the stock EELS hardware. This chapter is organized in a bottom-up fashion, such that, we will build up from the basic design of the ELS5000 spectrometer control circuits, to the interfacing control hardware, to the protocol layer, and ultimately to the control software.

4.1 Motivation for Replacing Stock Implementation

Before we dive into the details of how all of the hardware and software fits together, we will enumerate some of the key shortcomings of the included hardware and software stack that led us to abandon it in favor of the in-house developed solution that we describe below. Future work to either upgrade, reimplement, or replace the current implementation should keep the following points in mind:

- Coordinated momentum space control

Arguably the crowning achievement of this implementation, we have implemented a system capable of performing coordinated momentum space measurements. This enables us to perform scans at fixed points in momentum space by varying the sample orientation as a function of energy. The stock implementation offers no such control or calculations.
• Hardware motor and temperature control integration

In conjunction with the previous point, we have integrated the control of the other various hardware components into the same software frontend that runs the spectrometer itself. This not only allows us to precisely set our momentum space position, but also to scan other sample orientation and positioning motors while measuring the scattering intensity. The previous interface offered no functionality to interface with other hardware components.

• Standard communication interface

The ELS5000 control box, as we will see communicates over a TTL level signal which directly drives digital integrated circuits. As such, there is no standard interface to communicate between a computer and the control box. Instead, a computer needs to have a PCI digital I/O card, with its associated driver, in order to generate signals to send to the control box. Beyond that, from discussions with the company, we have learned their software will vary over time because of the difficulty in obtaining the same Keithley digital I/O board as old boards fall out of production, requiring new drivers and new hardwired software. This makes the software non-portable, and also opens us up to issues when faced with hardware failure. We have abstracted this component of the control out and exposed a common USB serial interface for the control hardware.

• Simple API

As we will see in the following sections, the application programming interface (API), or the commands needed to perform some action, for the ELS5000 control box is extremely complicated, requiring specific knowledge of the design and construction of the control interface at the level of individual circuit components. We have hidden this calculation in a dedicated hardware microcontroller, which sits behind the USB interface, and which accepts simple serial commands to set the voltages on the various optics elements.

• Software fault tolerance

One thing anyone will learn in dealing with the stock control software that ships with the ELS5000 is that it is highly prone to crashing. This will happen not only during scans, but even if it is left open and idle for too long. This has been a non-issue for the company because
of the way typical HR-EELS measurements are run, which typically do not involve a series of long-running scans. With our new software, we are able to achieve software stability capable of running our system indefinitely.

- **Continuous data saving**

  One big annoyance with the stock software is that it does not by default save any scans or any data. All data must be manually saved before being cleared, and there is a distinct lack of warnings when clearing un-saved data. This problem is compounded when taken in conjunction with the previous point about the stability (or rather instability) of the software. By interfacing our software with spec, we are able to get continuous data logging by default.

- **Automated logging of state**

  Beyond the complications of saving the data, when the data is saved using the stock software, it only gives energy loss, count rate, and integration time. No information is provided along side the data unless manually entered. This has led to having files with a series of numbered scans where all of the information about what each scan is has to be looked up in a table in the logbook. With spec, we are able to control what is automatically logged with the files for each scan. We are able to automatically log all of the voltages on the spectrometer, the orientation of the sample, and the temperature of the sample, in addition to the scattering information in the scan itself.

  As another part of this point, when tuning the spectrometer with the stock software, while changing voltages, there is no way to undo an operation or to know where a voltage was before the change occurred. As such, the only way to return to a previous state in the tuning process is to save at every voltage change. By logging changes of state, we are able to trivially address this problem.

- **Signal and cable fault tolerance**

  Because the input signal to the ELS5000 control hardware is at logic level and it is wired directly to the integrated circuit elements, the system is highly susceptible to problems arising from spikes or drops in the signal line. This sort of behavior could potentially come about by power cycling the interface connected to the ELS5000, unplugging or plugging in the cable, or
from spurious noise. Any one of these conditions may cause improper commands to be issued to the EELS, causing voltages to be improperly set or relays to be improperly triggered. By using USB connections, we get the built in signal and cable fault tolerance built into the USB standard. Thus, we have removed this issue from our primary signal interface, and in particular the connection most susceptible to these types of problems listed.

- Signal validation and error checking

In conjunction with the previous point, spurious signals that are received are not detected in any way, and can cause side effects in the configuration of the spectrometer. In our working with the ELS5000, we have on multiple occasions triggered some unknown state by some combination of power cycling and plugging/unplugging connections that has damaged electrical components in the control box. This is ultimately a result of the dumb circuitry in the control box, which has a distinct 1970’s character, which can be understood entirely from Chapters 1–8 of Horowitz and Hill, and in particular containing no microcontroller components. Our USB interface provides a microcontroller to receive and parse the incoming commands, perform validation and safety checks on the received commands, determining the corresponding output commands, and relaying these output commands to the control circuitry.

- Query-able state

An extension of the above point, there is absolutely no way to query the state of the EELS. The information flow between the control box and the controlling interface is strictly one directional. The only way to determine the voltages on the components or the beam voltage is to use a voltmeter and there is no way to determine the state of the relays used to measure electrical current. This is particularly problematic when working with the included control software, as it does not remember the previous state of the spectrometer when the program is closed (or, as noted above, when the software crashes). As such, it is easy to lose the state of the current tune (see above about not logging the state), as there is no way to recover it from the running spectrometer. Too address this, we make the microcontroller interface store the state of the system as it issues commands, such that it can be queried by the control software on the computer over the standard USB control interface.
• State recoverability across power cycles

In conjunction with the previous point, the spectrometer itself does not remember its state across power cycles. This, in conjunction with the inability to query the state to detect such misconfiguration, exposes potential problems if the spectrometer is power cycled. Not only is this in losing the particular tune configuration of the spectrometer, but also in setting the spectrometer in a state that may lead to problems with the spectrometer itself if the electron beam is running. To address this, we provided flash storage to the microcontroller which is read on reboots and restores the most recent state of the EELS spectrometer.

• Script-ability

The stock program can only be controlled through the Windows GUI. This makes setting up a series of scans, performing an iterated series of scans, or setting some easily reproduced series of scans a grueling manual task. In moving the programming interface to Spec, we move to a command line based interface which natively supports scripting, enabling these long running scans.

• Improved plotting

The plotting functionality included in the stock program is terrible. When performing energy scans, axes are neither labeled nor drawn. When performing tuning, the plotting functionality also does not provide any axes or labels, does not clearly display either the measured beam current or the current voltage, and will sometimes not update during the scanning process. The built-in plotting functionality of Spec is sufficient to address all of these plotting issues.

4.2 ELS5000 Hardware Description

Before diving into the control system, it is important to understand how the function of the hardware in the EELS spectrometer and how this function drives the electron optics. As outlined in Section 3, the spectrometer in use for this study uses electrostatic electron optics to achieve energy and momentum selection [27]. The electrostatic components can be broadly classified as one of the following:

• Single voltage lens
This is the simplest electrostatic lens, composed of a single conducting element with a slit or hole which is held at a uniform fixed voltage.

- **Split dual voltage lens**
  These lens elements are similar in shape to a single voltage lens, but they are composed of two halves, split either horizontally or vertically, allowing steering of the electron beam by creating an electric field between the two halves. These are controlled by two voltages, the mean voltage of the two halves and the voltage difference between the two halves.

- **Cylindrical deflection monochromator**
  The workhorse of the EELS, the monochromators are primarily composed of toroidal or cylindrical deflection plates. Like split lenses, these are controlled by two voltages, for the mean voltage and the voltage difference between the inner and outer shell. The mean voltage here sets the energy of the electron (typically called the pass energy) and the voltage difference establishes the electric field to deflect the electron beam. Additionally, there are top and bottom plates that terminate the electric field and shield the beam. Here again, there are two voltages to control the cover plates, a mean offset of the plates relative to the pass energy and a voltage difference, which provides minor out-of-plane steering of the beam.

In addition to the lens elements, the EELS control hardware must be able to scan the analyzed electron energy. Because electron energy is changed by changing the surrounding electrostatic potential, the method to change the scattered energy is to bias the voltage of the lenses and analyzer downstream of the scattering chamber. In doing so, all of the electron focusing optics are able to work with the same pass energy in the analyzer, but total electron energy accepted is changed by shifting the analyzer potential.

Along with the control of the voltage elements, the ELS5000 has the capability to monitor the electron beam current at various points along the electron path through the instrument, which is vital to the tuning procedure of the electron optics. These elements are selected by a series of controllable relays.

Ultimately, the control hardware is designed to adjust the voltages for both tuning and scanning, and adjust the relays to aid in the tuning process. The following sections outline how these voltages
are set, starting from the circuits used to set the voltages.

### 4.3 Setting Lens Voltages

The basic control of the lens voltages in the ELS5000 is controlled through a series of digital-to-analog converters (DACs) connected to low noise, low drift, low offset op amp voltage amplifier circuits. This section outlines the means by which the voltages on the spectrometer are set by the DAC values, starting with the basic operation of the DACs, then specifying the circuits by which the DACs set the lens voltages, as well as some specific cases that are important to address in the context designing the EELS.

#### 4.3.1 Basic DAC Operation

All of the DACs used to control the EELS are buffered multiplying DACs, either 12- or 16-bit input. More details on the operation of DACs can be found in Horowitz and Hill §9.16 and §10.06 [29], or the relevant data sheets (AD7545 for the 12-bit and LTC1597 for the 16-bit DACs). The DACs are buffered, meaning they will only change the output value when a pair of input latches are set low. This allows all of the DAC input lines to share the same parallel data bus and the DACs to be individually addressed. Each DAC has a reference voltage, $V_{\text{ref}}$, which sets the maximum output voltage of the DAC. Typically, the reference voltage is $+10$ V or $-10$ V, but some of the DACs, namely the scan DACs, use other DAC outputs as their reference voltage. The output voltage, $V_{\text{out}}$, is given in terms of the input digital value, $D_{\text{in}}$ as

$$V_{\text{out}} = V_{\text{ref}} \frac{D_{\text{in}}}{D_{\text{max}}}$$

where $D_{\text{max}}$ is the maximum digital value, for an $n$-bit DAC, this is $2^n$. The reference voltage as well as the number of bits for each of the DACs in the EELS is shown in Table 4.1 and Table 4.2. The correspondence between the lenses and their location in the geometry of the EELS spectrometer is shown in Figure 4.2.

The DAC output is routed to the lens voltage circuits. Each lens element circuit may be one of couple different configurations, whether it is a single voltage lens element, or a dual voltage lens
4.3.2 Single voltage circuits

The simplest voltage circuit to control are the single voltage lens elements. The voltage on the lens is set by op amp circuits. The circuit diagram for these single voltage lens elements is shown in Figure 4.1a, which is a simple summing (inverting) amplifier. For more information on op amp circuits, see Horowitz and Hill §4.2 [29]. The output voltage on the lens element is:

\[ V_{\text{out}} = -R_f \left( \frac{V_{DAC}}{R_0} + \frac{V_1}{R_1} \right) \] (4.2)

where the resistances and voltages are as outlined in the above mentioned figure. From this, we see a given choice of \( R_f/R_0 \) sets the range over which the lens voltage can vary, and \( R_f/R_1 \) sets the value of the offset that is applied to the lens, as the voltage \( V_1 \) is typically held constant and may be either positive or negative. There may be multiple offset voltages, \( V_i \), and corresponding amplifier resistors, \( R_i \). The full table showing all of the component value for all of the single voltage lenses is shown in Table 4.1.

4.3.3 Dual voltage circuits

Split lens elements are typically single electron optics elements split either horizontally or vertically, composed of two voltage. The EELS control electronics sets these voltages by controlling the median voltage and the voltage difference. The mean voltage is obtained using the same circuit that is used by the single voltage electron optics components, shown in Figure 4.1a. The voltage difference about the mean voltage is obtained by the circuit shown in Figure 4.1c. In this case, the voltages output to the two elements are:

\[ V_{\text{out},1} = -V_{\text{in}} - R^* \left( \frac{V_{\Delta DAC}}{R_0} - \frac{V_{\text{offset}}}{R_1} \right) \] (4.3)
\[ V_{\text{out},2} = -V_{\text{in}} + R^* \left( \frac{V_{\Delta DAC}}{R_0} - \frac{V_{\text{offset}}}{R_1} \right) \] (4.4)

where \( V_{\text{in}} \) corresponds to the output from Equation (4.2) and the other voltages and resistances are as defined in Figure 4.1c. We can see that the two output voltages are centered at \( -V_{\text{in}} \), differing
Figure 4.1: Op amp circuits used to set lens voltages based on various DACs. (a) A summing amplifier is used for the standard lens elements to set the base voltage for the lens, given an input DAC voltage and a set of offset voltages. (b) A high-voltage amplifier used for high voltage lenses, including some of the focusing lenses and all of components of the analyzer. (c) A pair of summing amplifiers used for split lenses, where the output from a summing amplifier is connected into $V_{in}$, and the outputs are $V_{in} \pm \Delta V$, where $\Delta V$ is determined by the $\Delta DAC$. The parameters for each of the lenses is given in Table 4.1.
by \(2R_1 \left( \frac{\text{DAC}}{R_0} - \frac{V_{\text{offset}}}{R_1} \right) \). This voltage difference corresponds to the “delta voltage” in the software interface, and is used to create a steering electric field between the two lens components. The full table showing all of the component value for all of the dual voltage lenses is shown in Table 4.2.

### 4.3.4 Monochromator circuits

Not its own unique circuit, the monochromator circuits is composed of the above two circuits. All of the voltages in the monochromator are given with respect to a reference voltage defined relative to the beam energy which acts as the pass energy. This voltage defines the voltage along the median point between the inner and outer cylindrical deflecting plates. Each monochromator is then made up of: inner and outer deflector voltages, entrance and exit slits, and top and bottom cover plates. The cylindrical deflection plates are defined as a split lens element relative to the central voltage, which establishes the electric field between the inner and outer plates. Likewise, the top and bottom plates are split lens elements, such that they are biased relative to the pass energy, and a small voltage difference is setup between them. The entrance and exit slits are both single voltage elements, but each is defined relative to the central voltage.

### 4.3.5 High-voltage amplifiers

The output voltage from the above circuits can be varied up to the \(V_{cc}\) value for the op amp, which for the op amps circuits used in the ELS5000 is 15 V. However, in several cases, a larger voltage is required in order to run the EELS, to set larger voltages on the lenses, to set the beam energy, and as a bias voltage for the inelastic measurements to scan energy loss beyond 15 eV. In order to accomplish this, the output from the circuits described above are routed into a high voltage amplifier. This is done using a non-inverting amplifier, shown in Figure 4.1b. The voltage output from such a circuit is given by:

\[
V_{\text{out}} = V_{\text{in}} \left( 1 + \frac{R_2}{R_1} \right)
\]  

(4.5)

where the input voltage, \(V_{\text{in}}\) is the output from the relevant low energy circuit, \(V_{\text{out}}\) in either the single voltage or the dual voltage circuits in Equation (4.2) or Equation (4.4), respectively, and the other resistances as defined in Figure 4.1b. The full table showing all of the component value for all of the high-voltage amplifiers is shown in Table 4.3.
### DAC

<table>
<thead>
<tr>
<th>Name</th>
<th>Bits</th>
<th>$V_{ref}$ (V)</th>
<th>$R_0$ (kΩ)</th>
<th>$R_f$ (kΩ)</th>
<th>$V_1$ (V)</th>
<th>$R_1$ (kΩ)</th>
<th>$V_2$ (V)</th>
<th>$R_2$ (kΩ)</th>
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<td>+10</td>
<td>6.19</td>
<td>15</td>
<td>−10</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Repeller</td>
<td>12</td>
<td>−10</td>
<td>10</td>
<td>20k</td>
<td>+10</td>
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<td>+10</td>
<td>10</td>
<td>10</td>
<td>+10</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>+10</td>
<td>10</td>
<td>10</td>
<td>−10</td>
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<td>+10</td>
<td>10</td>
<td>20</td>
<td>−10</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>16</td>
<td>+10</td>
<td>10</td>
<td>20</td>
<td>−10</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1-slit</td>
<td>16</td>
<td>−10</td>
<td>10</td>
<td>10</td>
<td>+10</td>
<td>20</td>
<td>$V_{M1}$</td>
<td>10</td>
</tr>
<tr>
<td>M1-cov</td>
<td>16</td>
<td>+10</td>
<td>30.1</td>
<td>20</td>
<td>−10</td>
<td>13.3</td>
<td>$M1$</td>
<td>10</td>
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<tr>
<td>M2†</td>
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<td>20</td>
<td>10</td>
<td>−10</td>
<td>39.2</td>
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<td></td>
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<tr>
<td>M2‡</td>
<td>16</td>
<td>+10</td>
<td>10</td>
<td>20</td>
<td>−10</td>
<td>20</td>
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<td>16.9</td>
<td>10</td>
<td>−10</td>
<td>13.3</td>
<td>$M2$</td>
<td>20</td>
</tr>
<tr>
<td>M2-cov‡</td>
<td>16</td>
<td>+10</td>
<td>31.1</td>
<td>20</td>
<td>−10</td>
<td>13.3</td>
<td>$M2$</td>
<td>10</td>
</tr>
<tr>
<td>M2-exit</td>
<td>16</td>
<td>−10</td>
<td>10</td>
<td>10</td>
<td>+10</td>
<td>20</td>
<td>$V_{M2}$</td>
<td>10</td>
</tr>
<tr>
<td>B1</td>
<td>12</td>
<td>+10</td>
<td>10</td>
<td>20</td>
<td>−10</td>
<td>39.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>16</td>
<td>−10</td>
<td>10</td>
<td>15</td>
<td>+10</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shield</td>
<td>12</td>
<td>+10</td>
<td>4.99</td>
<td>10</td>
<td>−10</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>12</td>
<td>+10</td>
<td>6.19</td>
<td>10</td>
<td>−10</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>16</td>
<td>−10</td>
<td>10</td>
<td>15</td>
<td>+10</td>
<td>200</td>
<td>B3ramp</td>
<td>30.1</td>
</tr>
<tr>
<td>B4</td>
<td>12</td>
<td>+10</td>
<td>20</td>
<td>20</td>
<td>−10</td>
<td>100</td>
<td>B4ramp</td>
<td>10</td>
</tr>
<tr>
<td>An1†</td>
<td>16</td>
<td>+10</td>
<td>49.9</td>
<td>10</td>
<td>−10</td>
<td>100</td>
<td>$V_{loss}$</td>
<td>10</td>
</tr>
<tr>
<td>An1‡</td>
<td>16</td>
<td>+10</td>
<td>22.1</td>
<td>10</td>
<td></td>
<td></td>
<td>$V_{loss}$</td>
<td></td>
</tr>
<tr>
<td>An1-slit†</td>
<td>16</td>
<td>−10</td>
<td>25.5</td>
<td>10</td>
<td>+10</td>
<td>49.9</td>
<td>$V_{An1}$</td>
<td>10</td>
</tr>
<tr>
<td>An1-cov†</td>
<td>16</td>
<td>+10</td>
<td>45.3</td>
<td>10</td>
<td>−10</td>
<td>34.8</td>
<td>An1</td>
<td>49.9</td>
</tr>
<tr>
<td>C1†</td>
<td>16</td>
<td>+10</td>
<td>30.1</td>
<td>10</td>
<td>−10</td>
<td>60.4</td>
<td>C1ramp</td>
<td>4.99</td>
</tr>
<tr>
<td>C2†</td>
<td>12</td>
<td>−10</td>
<td>20</td>
<td>20</td>
<td>+10</td>
<td>39.2</td>
<td>C2ramp</td>
<td>10</td>
</tr>
<tr>
<td>C3†</td>
<td>12</td>
<td>+10</td>
<td>30.1</td>
<td>10</td>
<td>−10</td>
<td>60.4</td>
<td>C3ramp</td>
<td>4.99</td>
</tr>
<tr>
<td>Exit grid†</td>
<td>16</td>
<td>−10</td>
<td>25.5</td>
<td>10</td>
<td>+10</td>
<td>49.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Box</td>
<td>12</td>
<td>+10</td>
<td>10</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cone</td>
<td>12</td>
<td>−10</td>
<td>15</td>
<td>10k</td>
<td>−$V_{loss}$</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3ramp</td>
<td>12</td>
<td>$V_{loss}$</td>
<td>30.1</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B4ramp</td>
<td>12</td>
<td>−$V_{loss}$</td>
<td>10</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1ramp†</td>
<td>12</td>
<td>−$V_{loss}$</td>
<td>4.99</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2ramp†</td>
<td>12</td>
<td>$V_{loss}$</td>
<td>10</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3ramp‡</td>
<td>12</td>
<td>−$V_{loss}$</td>
<td>4.99</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scan</td>
<td>16</td>
<td>+10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>12</td>
<td>Scan</td>
<td>100</td>
<td>20</td>
<td>10</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Offset</td>
<td>12</td>
<td>+10</td>
<td>100</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: The parameters of for all single lens element circuits as outlined in Section 4.3. Voltages denoted $V_{lens}$ are the values output from the amplifier circuit, while voltages denoted DAC are the voltages output from the DAC corresponding to that lens. The $V_{loss}$ voltage corresponds to the energy loss, as defined in Equation (4.6). † specifies lenses available for spectrometers equipped with Channeltron analyzers, ‡ signifies lenses available for spectrometers equipped with MCA analyzers.
### Table 4.2: The parameters for all split lens element DAC and opamp circuits used to set the lens voltages as outlined in Section 4.3, see Table 4.1 for notation used in this table.

<table>
<thead>
<tr>
<th>Name</th>
<th>Bits</th>
<th>$V_{ref}$ (V)</th>
<th>$R_0$ (kΩ)</th>
<th>$R^*$ (kΩ)</th>
<th>$V_1$ (V)</th>
<th>$R_1$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta A1$</td>
<td>12</td>
<td>−10</td>
<td>121</td>
<td>10</td>
<td>+10</td>
<td>243</td>
</tr>
<tr>
<td>$\Delta A2$</td>
<td>12</td>
<td>−10</td>
<td>121</td>
<td>10</td>
<td>+10</td>
<td>243</td>
</tr>
<tr>
<td>$\Delta A3$</td>
<td>12</td>
<td>−10</td>
<td>20</td>
<td>10</td>
<td>+10</td>
<td>39.2</td>
</tr>
<tr>
<td>$\Delta M1$</td>
<td>12</td>
<td>−10</td>
<td>20</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta M1$−$\text{cov}$</td>
<td>12</td>
<td>+10</td>
<td>39.2</td>
<td>10</td>
<td>−10</td>
<td>80.6</td>
</tr>
<tr>
<td>$\Delta M2^\dagger$</td>
<td>12</td>
<td>−10</td>
<td>39.2</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta M2^\ddagger$</td>
<td>12</td>
<td>−10</td>
<td>20</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta M2$−$\text{cov}$</td>
<td>12</td>
<td>+10</td>
<td>39.2</td>
<td>10</td>
<td>−10</td>
<td>80.6</td>
</tr>
<tr>
<td>$\Delta B1$</td>
<td>12</td>
<td>−10</td>
<td>39.2</td>
<td>10</td>
<td>+10</td>
<td>80.6</td>
</tr>
<tr>
<td>$\Delta B4$</td>
<td>12</td>
<td>−10</td>
<td>100</td>
<td>10</td>
<td>+10</td>
<td>200</td>
</tr>
<tr>
<td>$\Delta An1^\dagger$</td>
<td>12</td>
<td>−10</td>
<td>100</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta An1$−$\text{cov}$</td>
<td>12</td>
<td>+10</td>
<td>25.5</td>
<td>10</td>
<td>+10</td>
<td>49.9</td>
</tr>
<tr>
<td>$\Delta C1^\dagger$</td>
<td>12</td>
<td>−10</td>
<td>20</td>
<td>10</td>
<td>+10</td>
<td>39.2</td>
</tr>
<tr>
<td>$\Delta C3^\dagger$</td>
<td>12</td>
<td>+10</td>
<td>20</td>
<td>10</td>
<td>−10</td>
<td>39.2</td>
</tr>
</tbody>
</table>

### Table 4.3: The parameters for all lens elements that have a corresponding high voltage amplifier as outlined in Section 4.3. All elements corresponding to any given lens have the same amplification and lenses not listed are output without amplification.

<table>
<thead>
<tr>
<th>Name</th>
<th>$R_1$ (kΩ)</th>
<th>$R_2$ (kΩ)</th>
<th>Name</th>
<th>$R_1$ (kΩ)</th>
<th>$R_2$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam</td>
<td>10</td>
<td>100</td>
<td>$C1^\dagger$</td>
<td>30.1</td>
<td>50</td>
</tr>
<tr>
<td>A1</td>
<td>20</td>
<td>100</td>
<td>$C2^\dagger$</td>
<td>30.1</td>
<td>50</td>
</tr>
<tr>
<td>A2</td>
<td>20</td>
<td>100</td>
<td>$C3^\dagger$</td>
<td>30.1</td>
<td>50</td>
</tr>
<tr>
<td>B2</td>
<td>15</td>
<td>121</td>
<td>Exit$^\dagger$</td>
<td>30.1</td>
<td>50</td>
</tr>
<tr>
<td>B3</td>
<td>15</td>
<td>121</td>
<td>Range</td>
<td>30.1</td>
<td>50</td>
</tr>
<tr>
<td>B4</td>
<td>30.1</td>
<td>50</td>
<td>Offset</td>
<td>30.1</td>
<td>50</td>
</tr>
<tr>
<td>An1</td>
<td>30.1</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 4.3.6 Beam energy

The voltages specified for the various lens elements are typically given relative to the electron filament. However, the voltage of these elements relative to ground is offset by the beam voltage. As such, the beam energy itself is set using a standard single voltage circuit, as outlined above, however this voltage then serves as the reference ground for all of the lens elements. This is done so beam energy changes only require changes in the configuration of the zoom lenses, while the behavior and performance of the instrument in all other regards is unchanged. Certain non-lens
elements, namely the filter box, the sample, and the scattering chamber shield, are referenced to earth ground, rather than the filament ground.

4.3.7 Energy loss

Similar to the fact that beam energy is set by offsetting all of the voltages in the spectrometer by a certain values, energy loss is set by offsetting all of the lens elements downstream of the scattering chamber by the desired energy loss. This is accomplished using several DACs, which are specified by LK Technologies as the “scan”, “range”, and “offset” DACs. The scan and range DACs are chained together, where, using notation from Equation (4.1), the $V_{out}$ from the scan DAC serves as $V_{DAC}$ for the range DAC. Because the overall energy range of the energy loss is relatively large, having these DACs chained increases the granularity of the energy loss. The convention with these DACs is to specify the range as the allowed range for a given loss scan, which is between 0 V and about 53.2 V, and the scan DAC gives a value from 0 to 1, corresponding to the ratio of the DAC digital input value to the maximum digital value. The offset DAC adds to this value, taking any value in the range $-2.66$ V to $2.66$ V (after accounting for the high voltage amplifiers), allowing energy gain features to be scanned. Using this convention, the resulting equation for the electron energy loss measured for a given system configuration is:

$$V_{loss} = V_{range} \times \text{SCAN} + V_{offset}$$

(4.6)

where $V_{range}$ and $V_{offset}$ specify the voltages as described above, and $\text{SCAN}$ is the parameter corresponding to the scan DAC value as described above.

4.4 DAC and Relay Addressing

We have thus far established the functioning of the DAC circuits and the relationship between the digital value on the DAC and the voltage output on the corresponding lens elements. Now, we establish the means by which the different DACs are addressed and selected. As noted previously, all of the DACs used in the EELS are buffered. That is to say, in order for the digital input signal to be used to set the corresponding analog output, an input latch must be pulled low. While this
Figure 4.2: Schematic of the HR-EELS electron optics elements unfolded along the beam trajectory. This is a top-down view of the spectrometer, such that the page is in the scattering plane. Not shown are the cover plate voltages on the monochromators and analyzers, which lie parallel to the page above and below the beam in each of the deflecting elements for the top and bottom cover plates, respectively.
input pin is high, the DAC maintains its most recent output value. This allows all of the DACs to be on a common parallel data bus for the DAC input values.

In order to perform the DAC selection outlined above without requiring a separate input bit for each of the DACs, we use a pair of 1-of-8 decoders, see Horowitz and Hill §8.14 for a general overview, or see the relevant data sheet for the 74HC138. The configuration for the two decoders is shown in Figure 4.3, where the labeled inputs are the address inputs and the labeled outputs run to the latches on the DACs. We use 6 bits here to select the DAC, three for each of the decoders, with bits \( DB_5-DB_0 \) selecting the specific DAC, and \( DB_7 \) enabling the decoders. The naming of these bits will be used later when we specify the digital signal structure.

This naturally gives rise to a 8-bit address for each of the DACs. The hexadecimal address is given for each of the DACs in Table 4.4.

We take a brief moment to mention the relays and their addressing. The relays are used to measure the current to various components of the EELS during initial alignment. Note in Figure 4.3 that setting the \( DB_7 \) bit low enables the decoders. This is chosen such that setting this bit high will disable the DAC configuration, which allows up to enable the relay selection circuits. Thus, addressing the relay drive is done with an address of \( 0x80 \). Though the lower 7-bits do not actually
Table 4.4: A list of all of the DACs, the name of every DAC as specified by the Arduino API, and the 8-bit addresses of each of the DACs in the EELS given in hexadecimal format. † signifies lenses only available for spectrometers equipped with Channeltron analyzers, ‡ signifies lenses only available for spectrometers equipped with MCA analyzers.

<table>
<thead>
<tr>
<th>DAC</th>
<th>Name</th>
<th>Adr.</th>
<th>DAC</th>
<th>Name</th>
<th>Adr.</th>
<th>DAC</th>
<th>Name</th>
<th>Adr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam</td>
<td>beam</td>
<td>0x38</td>
<td>∆M2-cov</td>
<td>m2covd</td>
<td>0x18</td>
<td>C1†</td>
<td>c1</td>
<td>0x33</td>
</tr>
<tr>
<td>Repeller</td>
<td>rep</td>
<td>0x0C</td>
<td>M2</td>
<td>m2</td>
<td>0x08</td>
<td>C2†</td>
<td>c2</td>
<td>0x0B</td>
</tr>
<tr>
<td>A1</td>
<td>a1</td>
<td>0x10</td>
<td>B1</td>
<td>b1</td>
<td>0x13</td>
<td>C3†</td>
<td>c3</td>
<td>0x1B</td>
</tr>
<tr>
<td>∆A1</td>
<td>a1d</td>
<td>0x10</td>
<td>∆B1</td>
<td>b1d</td>
<td>0x23</td>
<td>∆C3†</td>
<td>c3d</td>
<td>0x1C</td>
</tr>
<tr>
<td>A2</td>
<td>a2</td>
<td>0x11</td>
<td>B2</td>
<td>b2</td>
<td>0x01</td>
<td>Exit grid‡</td>
<td>exit</td>
<td>0x05</td>
</tr>
<tr>
<td>∆A2</td>
<td>a2d</td>
<td>0x21</td>
<td>B3</td>
<td>b3</td>
<td>0x02</td>
<td>Box</td>
<td>box</td>
<td>0x1D</td>
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<tr>
<td>A3</td>
<td>a3</td>
<td>0x12</td>
<td>B4</td>
<td>b4</td>
<td>0x14</td>
<td>Cone</td>
<td>cone</td>
<td>0x0D</td>
</tr>
<tr>
<td>∆A3</td>
<td>a3d</td>
<td>0x22</td>
<td>∆B4</td>
<td>b4d</td>
<td>0x24</td>
<td>B3ramp</td>
<td>b3ramp</td>
<td>0x28</td>
</tr>
<tr>
<td>M1</td>
<td>m1</td>
<td>0x30</td>
<td>Shield</td>
<td>shield</td>
<td>0x39</td>
<td>B4ramp</td>
<td>b4ramp</td>
<td>0x2A</td>
</tr>
<tr>
<td>M1-slit</td>
<td>m1slit</td>
<td>0x04</td>
<td>Sample</td>
<td>sample</td>
<td>0x3A</td>
<td>C1ramp‡</td>
<td>c1ramp</td>
<td>0x2B</td>
</tr>
<tr>
<td>M1-cov</td>
<td>m1covd</td>
<td>0x19</td>
<td>An1</td>
<td>an1</td>
<td>0x32</td>
<td>C2ramp‡</td>
<td>c2ramp</td>
<td>0x29</td>
</tr>
<tr>
<td>∆M1</td>
<td>m1d</td>
<td>0x03</td>
<td>An1-slit‡</td>
<td>an1slit</td>
<td>0x05</td>
<td>C3ramp‡</td>
<td>c3ramp</td>
<td>0x2C</td>
</tr>
<tr>
<td>M2</td>
<td>m2</td>
<td>0x31</td>
<td>An1-cov‡</td>
<td>an1cov</td>
<td>0x16</td>
<td>Scan</td>
<td>scan</td>
<td>0x34</td>
</tr>
<tr>
<td>M2-slit</td>
<td>m2slit</td>
<td>0x06</td>
<td>∆An1-cov‡</td>
<td>an1cova1</td>
<td>0x1A</td>
<td>Scan</td>
<td>scan</td>
<td>0x34</td>
</tr>
<tr>
<td>M2-cov</td>
<td>m2covd</td>
<td>0x17</td>
<td>∆An1</td>
<td>an1d</td>
<td>0x0A</td>
<td>Relay</td>
<td>0x80</td>
<td></td>
</tr>
</tbody>
</table>

matter, they are set to zero by convention.

The 16 digital input lines that set the values of the DACs also run the relay selection circuit. The circuit which selects the relay is another decoder, this one a 1-of-16 latched decoder. Just as with the buffered DACs used to set lens voltages, the input that is sent to the DACs can be sent in parallel to the decoder to select the appropriate relay when the input latch is pulled low. In this case, the signal for the input latch is the inverted DB7 input. The digital values that correspond to each of the various relay components is given in Table 4.5. The current measuring relays are disabled and the spectrometer put in pulse counting mode when the Counts relay is set.

4.5 Example Voltage Computations

We have to this point established the format in which the ELS5000 receives commands (Section 4.4) and the correspondence between these commands and the voltages on the optics elements (Section 4.3). Here, we will show some examples of this calculation, effectively summarizing the details of the previous sections. For this exercise, we will start from a given command and compute the
Table 4.5: All of the relays available to measure, along with the name used to identify the relay in the Arduino API and the 16-bit values in hexadecimal format used to enable the various relays when the relay address is specified (cf. Table 4.4), † signifies relays only available for spectrometers equipped with Channeltron analyzers, ‡ signifies relays only available for spectrometers equipped with MCA analyzers.

<table>
<thead>
<tr>
<th>Relay</th>
<th>Name</th>
<th>Value</th>
<th>Relay</th>
<th>Name</th>
<th>Value</th>
<th>Relay</th>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counts</td>
<td>counts</td>
<td>0x000F</td>
<td>An1 slit</td>
<td>an1slit</td>
<td>0x0006</td>
<td>An1 out</td>
<td>an1out</td>
<td>0x0007</td>
</tr>
<tr>
<td>M1 slit</td>
<td>m1slit</td>
<td>0x0000</td>
<td>M2 exit</td>
<td>m2exit</td>
<td>0x000A</td>
<td>C1 down</td>
<td>c1down</td>
<td>0x0008</td>
</tr>
<tr>
<td>M1 out</td>
<td>m1out</td>
<td>0x0001</td>
<td>B2</td>
<td>b2</td>
<td>0x0004</td>
<td>Exit grid</td>
<td>exit</td>
<td>0x0006</td>
</tr>
<tr>
<td>M2 slit</td>
<td>m2slit</td>
<td>0x0002</td>
<td>Sample</td>
<td>sample</td>
<td>0x0005</td>
<td>Cone†</td>
<td>cone</td>
<td>0x0009</td>
</tr>
<tr>
<td>M2 out</td>
<td>m2out</td>
<td>0x0003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

voltages that such a command corresponds to, the inverted process should follow directly from this. For the point of this exercise, we will assume all of the following commands are issued together in order.

### 4.5.1 Command: 0x38016F

First for this command, we must determine which lens element we are effecting. Looking up in Table 4.4, we see that the address for this command, 0x38, corresponds to the beam energy. Now, we decode the value used to set the voltage of the beam, that is 0x016F. For this, we use Table 4.1.

First, we note that the beam is driven by a 12-bit DAC. As such, the voltage output from the DAC will be $V_{DAC} = (10 \text{ V}) (0x16F/0x1000) = 0.896 \text{ V}$. Then, we use the equation for a single lens element, Equation (4.2), in conjunction with the information in the table to determine the voltage from the low power op amps:

$$V_{out} = -(15 \text{ k}\Omega) \left( \frac{0.896 \text{ V}}{6.19 \text{ k}\Omega} + \frac{-10 \text{ V}}{100 \text{ k}\Omega} \right) = -0.671 \text{ V} \quad (4.7)$$

Finally, we see from Table 4.3 that the beam voltage also has applied a high voltage amplification. Here, we use Equation (4.5) to compute the final beam energy:

$$V_{out} = (-0.671 \text{ V}) \left( 1 + \frac{100 \text{ k}\Omega}{10 \text{ k}\Omega} \right) = -7.38 \text{ V} \quad (4.8)$$

Note that the voltage of the filament is negative, such that the negatively charged electrons will have a net kinetic energy of 7.38 eV when they reach the sample at ground. However, the software
will read this off as a positive beam energy, rather than the negative voltage.

### 4.5.2 Command: 0x110712–0x21093B

Next, we will cover the above two commands. We see by examining Table 4.4 that we need to consider both commands as the addresses in the two commands, 0x11 and 0x21, correspond to A2 and ΔA2, respectively. In order to determine the voltages on each of the A2 lens elements requires knowing both of these voltages. Starting with the first command for A2, we have a value 0x0712. The voltage on the A2 DAC will be $(10 \text{ V}) (0x712/0x1000) = 4.42 \text{ V}$. As above, we compute the single lens value for A2 as:

$$V_{\text{out}} = -(10 \text{ k}\Omega) \left( \frac{4.42 \text{ V}}{10 \text{ k}\Omega} + \frac{-10 \text{ V}}{20 \text{ k}\Omega} \right) = 0.58 \text{ V}. \quad (4.9)$$

We continue to the high voltage op amp circuit, as above, and for A2 this gives a final value of:

$$V_{\text{out}} = (0.58 \text{ V}) \left( 1 + \frac{100 \text{ k}\Omega}{20 \text{ k}\Omega} \right) = 3.49 \text{ V}. \quad (4.10)$$

This is the voltage that would be set for A2 through the software interface. Note, however, that this exact voltage is not physically realized in the control hardware, as A2 is a split lens, and so each the low voltage op amps to set the voltage difference enter the circuit before the high voltage amplifier circuit.

To actually determine the voltages of the individual lens elements, as would be read off on the voltmeter, we need to also include the voltage difference between the two A2 lens elements, as what we have is the central voltage. In order to do this, we use the second command. The value for this command, 0x93B, gives a voltage on the ΔA2 DAC as $V_{\text{out}} = (-10 \text{ V})(0x93B/0x1000) = -5.77 \text{ V}$. Then, referencing Table 4.2, the voltages for the two components, as determined by Equation (4.4), can be found to be:

$$V_{\text{out},1/2} = -(0.58 \text{ V}) \pm (10 \text{ k}\Omega) \left( \frac{5.77 \text{ V}}{121 \text{ k}\Omega} - \frac{10 \text{ V}}{243 \text{ k}\Omega} \right) = 0.65 \text{ V}, \ 0.52 \text{ V} \quad (4.11)$$

where we note that we have used the $V_{\text{in}}$ value from the A2 low voltage op amp circuit of 0.58 V in Equation (4.9), as this circuit sits before the high voltage op amp. Now, when these voltages are
passed through the high voltage op amp, giving measured voltages of:

\[
V_1 = (0.52 \text{ V}) \left( 1 + \frac{100 \text{ k}\Omega}{20 \text{ k}\Omega} \right) = 3.09 \text{ V}
\]

\[
V_2 = (0.65 \text{ V}) \left( 1 + \frac{100 \text{ k}\Omega}{20 \text{ k}\Omega} \right) = 3.88 \text{ V}.
\]

The delta between these voltages, 0.78 V, is the value that is set in the software for $\Delta A_2$. We note that these voltages are as measured with respect to the beam energy. As such, we compute the voltage of each lens element relative to ground to be $-3.50 \text{ V}$ and $-4.29 \text{ V}$.

### 4.5.3 Command: 0x31C660–0x17B6DA–0x1807C8

At this point, we have covered all three types of circuits with examples. However, the monochromator circuits are themselves special. For example, with the above sequence of commands, we see we are dealing with M2, M2 cover plates, and the delta on the M2 cover plates. While the inner and outer shells of the M2 monochromator behave as a split lens element, yielding a computation similar to the one performed in the previous section, the other M2 voltages, namely the cover plates and the entrance and exit slits, each are treated in software as their own lenses, but are actually referenced to the M2 voltage, rather than directly to the beam voltage.

With this in mind, we compute the voltages resulting from the above sequence of commands. The M2 value, given by the 0x31 command, has a value of 0xC660. Following the same prescription as above, for a Channeltron EELS system, this corresponds to a voltage of 1.32 V as read in the software. Now, the cover plate voltages are set by M2-cov and $\Delta M2$-cov, which are commands 0x17 and 0x18, respectively, corresponding to the second and third commands in the sequence we are analyzing. Taken as an independent split lens element with values of 0xB6DA and 0x07C8, we would compute voltages of $-0.74 \text{ V}$ and $0.1 \text{ mV}$ for the software values of M2-cov and $\Delta M2$-cov, respectively. That is to say, that is the result when we compute the values of the M2 cover plates relative to the M2 voltage. Note that we must treat M2-cov carefully because it has as one of its input the DAC output from M2, and so the offset applied to go from the DAC value to the actual value of M2 must be applied in the opposite direction to get M2-cov relative to the output value of M2. Other than this wrinkle, the calculation is the same as above. With this in hand, we see that, because the cover plate voltages are relative to M2, the actual voltages of the cover plates, as
measured by the built-in voltmeter, will be 0.58 V for both the top and bottom plates, measured with respect to the beam voltage. Here, because the delta voltage is essentially 0, the top and bottom are the same, though this is not true in general. Measuring relative to ground, we thus see that the voltage output to the M2 cover plates in this configuration would be −6.80 V.

4.6 ELS5000 Command Structure and Protocol

As we have established, to control all of the circuitry of the EELS requires 8-bits for addressing DACs and as many as 16-bits (though some lenses only use 12 and selecting relays only uses 4) to set the values of the DACs themselves. Each command is thus naturally takes the form of a 24-bit command, composed of two sections, an 8-bit address and a 16-bit value. Starting at the most-significant bit (MSB), the first 8 bits specify the recipient of the command: whether it sets a DAC, and if so which DAC it sets, or whether it sets a relay, as outlined in Section 4.4. The last 16 bits encode the value sent to the command recipient: the DAC value to set the particular lens voltage as outlined in Section 4.3, or the relay to activate. This data is transferred over the wire least significant bit (LSB) first. A schematic representation of the bit structure and the order is given in Figure 4.4. All values written in this reference, notably Tables 4.1, 4.4, and 4.5, follow this convention.

Communication with the EELS control hardware is done by passing these binary commands directly into the circuitry. Note that there is no error checking or fallback mechanisms to this communication—all digital pulses sent over the wire are routed directly to the EELS voltage cir-
Figure 4.5: The connectors used in the EELS wiring, a. The Mil-Spec connector to the National Instruments breakout box b. The DIN connector to the EELS control box. Writing NI DAC line–NI DAC pin–Mil-Spec pin–DIN pin, the EELS TTL lines are hooked up as: Data D0.0–52–A–2, Clock D0.1–17–B–5, Load D0.2–49–D–4, +5 V +5V–14–C–1

circuit. Not only must care be taken when creating programs to control the EELS, but also when changing or powering/unpowering the control interface, circuits have been destroyed by changing signal cables with the control circuits powered.

Now that the digital command specification is established, we must establish how to communicate these commands to the EELS control box. In particular, we must establish the protocol of sending the required 24-bits. The main control component of the EELS is a 24-bit buffered shift register created by chaining three 8-bit buffered shift registers. There are five wires that run into the EELS control box. Three of the five control lines are used to send digital signals to the shift register, with the fourth and fifth line being +5 V and ground reference lines, $V_{CC}$. In summary, digital control lines are:

1. Data TTL line: sends the digital values corresponding to commands
2. Clock TTL line: on rising clock edges loads the data line into the register
3. Load TTL line: pushes the data in the register to the output
4. +5 V line
5. Digital ground

The outline of the connectors used and the wiring connections is shown in Figure 4.5. The specifics of how the registers act as an interface along with examples are detailed below.

Commands are sent to the EELS by loading the buffer in serial using the data and clock lines; on a rising clock edge, the data in the buffer is shifted over one and the current value of the data line is placed in the buffer. The load line pushes the buffered value to the output; on a rising
edge of the load, the values in the buffer are pushed to the output. See Figure 4.6 for a schematic representation of this process. For a general overview of shift registers, see Horowitz and Hill §8.26, and for the specific implementation used in the spectrometer, see a data sheet for an appropriate shift register, SN54HC595.

After pushing the buffer of the shift register, the load signal also triggers the execution of the command given by the value in the register. This command will be to either set the voltage of a DAC (which will set the various lens voltages) or to activate a specific relay, the structure of these commands is outlined in Section 4.6.

4.7 Arduino Control Hardware and Protocol

The above digital communication is the protocol that is implemented by the ELS5000 spectrometer control electronics. This complexity of the protocol and the implementation of the circuitry in the controller make communication difficult and dangerous. In order to address this problem, we have developed and constructed a hardware component designed to communicate directly with the ELS5000 and expose a proper serial communication interface. The interface not only allows the voltages and settings to be modified, but also preserves the state of the spectrometer across power cycles and exposes an API that allows users to query parameters over the serial interface.

For ease of extensibility, the core of the hardware module is built around an Arduino Mega board. This provides simple in-circuit programming, robust and well-designed circuitry, and easily configurable external interfaces. In addition to the Arduino, we have built in an SPI flash EEPROM, which provides persistent memory to store and recall voltage configurations. Outputs from the Arduino to the EELS control box are buffered using opamps in order to ensure signal integrity between the Arduino and the circuits in the control box. Also, a high-voltage interlock is provided so the Channeltron high voltage power supply can be disabled in the case of either: activation of the relay to measure current to the Channeltron cone or a user specified event, namely when the analyzer is brought close to the direct beam geometry. The circuit diagram for the hardware interface is provided in Figure 4.7 and the diagram showing how the Arduino shield is wired is provided in Figure 4.8. The entire circuit is built into a NIM module and powered by the NIM backplane.
Figure 4.6: Operation of the buffered shift register for the given input. The time reflected in the register is given by the vertical dashed line and the arrows denote the action that was taken at the given time frame. a) Changing the value of the data line has no effect, b–e) On each rising clock edge, the values in the buffer are shifted one position and the current data TTL value is loaded into the MSB, f) On a rising load edge, the buffer is copied to the output values, at this point the specified command will be run, g–h) Continue loading in new values on rising clock edges, note the buffer is not reset or cleared, new values are added as before.
Figure 4.7: Schematic of the Arduino shield used to interface between the computer and the ELS5000 control hardware.

The code for the hardware interface is written in to the C++11 standard to take advantage of modern C++ features and type safety. The codebase is compatible with the most recent version of the Arduino IDE as of this writing (version 1.8.1).

The hardware control system is designed to compute the correct digital value for any lens voltage, output the proper digital sequence to the ELS5000 control box, and return queries for the current state of the spectrometer via input commands it receives on the USB serial line, configured as 115200/8-N-1. The USB exposes an FTDI USB-to-serial adapter which sends and receives standard serial commands. The table outlining the API for the serial interface is given in Table 4.6. Successful query commands will return the value queried in the same format used to set the cor-
Figure 4.8: Board schematic of the Arduino shield used to interface between the computer and the ELS5000 control hardware, including wiring to switches, LEDs, pin headers, and connectors not on the shield.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Query command</th>
<th>Set command</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lens voltage</td>
<td>v?lens</td>
<td>vlens=voltage</td>
<td>lens is case insensitive, voltage is a float</td>
</tr>
<tr>
<td>DAC value</td>
<td>v?lens</td>
<td>vlens=value</td>
<td>lens is case insensitive, value is an integer</td>
</tr>
<tr>
<td>Relay</td>
<td>R?</td>
<td>R=relay</td>
<td>relay is case insensitive</td>
</tr>
<tr>
<td>HV interlock</td>
<td>HV?</td>
<td>HV=enable</td>
<td>enable is 0 or 1</td>
</tr>
<tr>
<td>Board reset</td>
<td></td>
<td>RESET</td>
<td></td>
</tr>
<tr>
<td>Board status</td>
<td></td>
<td>STATUS</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6: Serial command API for the Arduino interface. The user-defined parameters shown in italics. In all cases, the names of the lenses and relays are not case sensitive and the names are as given in Table 4.4 and Table 4.5.

responding parameter. Successful set commands will return 0, while failures will return a negative integer based on the reason for failure.

### 4.8 Voltage-to-Frequency Converter

In addition to the Arduino interface, we have also designed and built a voltage-to-frequency (V/F) converter. This component is needed to perform current mode measurements with the EELS in spec. The picoammeter provides a voltage output proportional to the current, and this signal must be converted to a series of pulses to be measured as a count rate in spec. Like the Arduino, this
component is built into a NIM module and powered from the NIM bin backplane.

The V/F converters are based on the VFC100 integrated circuit. For redundancy, the V/F converter module provides three V/F converter inputs and outputs as BNC connections. The board layout for the V/F converter is shown in Figure 4.9 and the schematic for the circuit is shown in Figure 4.10.

4.9 spec Interface

The user interface for all controlling the spectrometer is exposed through spec, a standard X-ray spectroscopy software package. We use spec because it exposes built-in functionality for many of the standard tasks needed to run a spectrometer. On the hardware side, spec includes drivers to interface with various motors, communicate with temperature controllers, interface with digital acquisition hardware to perform pulse counting, as well as provide methods to integrate user-defined motors and devices, allowing easy integration with serial devices. On the software side, spec is able to perform the geometry calculations needed to perform spectroscopy, transforming from motor space to the reciprocal space of the crystal using custom defined geometries and built-in UB matrix
Figure 4.10: Circuit schematic for the V/F converter showing the connections between the various elements on the board and the connections to both power, input, and output elements in the NIM module not on the circuit board.
In order to adapt spec to our needs, there are several modifications that are taken before installing it. For the custom geometry of the M-EELS spectrometer, we have integrated Equations (3.3)–(3.5) and Equations (3.8)–(3.10) into our custom spec deployment. These equations are encoded into the `geo_eels.c` file. In addition to these functions, this file defines all of the motors needed for the M-EELS spectrometer, which includes the goniometer angles, \( \theta \), \( \chi \), and \( \phi \) and the analyzer angle, \( \gamma \), as well as the beam energy and the energy loss in electron volts, which are treated as motors for the purposes of scanning. In order to expose these functions and parameters to the spec read-eval-print loop (REPL) environment, we add functionality to the `u_hook.c` file. In order for the installation script for spec to be aware of the M-EELS geometry and how to compile it, we modify the `geometries` file to specify the geometry file and the compilation options. Because we are defining a new geometry, we also must include a `macros/eels.src` file. This file integrates some of the core spec functionality with the geometry we have defined, hooking the C functions for the geometry up to standard spec macros. In addition, this file implements basic macros for adjusting lens voltages, setting relays, performing scans, and running automated tuning procedures. Important here is the `lossscan` macro, which performs energy loss scans at a constant value of the momentum transfer. Finally, there are also several macro files that are included in `macros/` that are installed into the `SPECd` directory. This includes several macros:

- **eels-motors.mac**: the macros needed to communicate with the Arduino interface over the serial line and expose the manipulation of these voltages as macro motors
- **tth-motor.mac**: macros for the analyzer rotation motor (in particular, the non-linear relationship between the stepper motor position and the analyzer angle)
- **temperature.mac**: macros to communicate with the temperature controller
- **mca-scans.mac**: macros for performing scans on the multichannel analyzer version of the ELS5000
- **z-th_limits.mac**: safety macros for ensuring the sample stage does not collide with the spectrometer.
Chapter 5

Characterization of Low Energy Collective Excitations

First, we focus on characterizing the low energy excitations in optimally doped Bi2212. The single particle spectral function, $A(k, \omega)$, has been extensively studied in the cuprates, and in BSCCO in particular, in momentum space by angle resolved photoemission (ARPES) and in real space by scanning tunneling spectroscopy. This work is largely responsible for establishing what we know about the low energy charge dynamics in the cuprates. Namely, the existence of a hole-like Fermi surface, establishing the existence of a 40 meV superconducting gap, the existence of the “pseudogap” state in which part of the Fermi surface near the antinode begins to open, the emergence of fermion quasiparticles below $T_c$, and the “ubiquitous” anomalies in the electron dispersion at 70 meV, 50 meV, and 10 meV. These measurements have been shown to be consistent with dispersionless collective modes [30]. The energies of these modes appear to be modulated in free space by the superconducting gap [31]. In this field, there has been a great deal of work trying to establish the relationship between these observations and various collective modes in this low energy regime. This includes more standard textbook excitations, such as phonons [32] and spin fluctuations [33,34], but also includes more exotic excitations arising from various features related to the collective electronic behavior, including $d$-symmetry density waves [35], Mottness [36], and smectic stripes [37].

In this study, we M-EELS to characterize the properties of the low energy electron dynamics of optimally doped Bi2212. We will perform a full momentum space mapping of the dynamic susceptibility in order to elucidate the nature of the collective excitations that exist below 100 meV, which is where we expect to see collective modes that are related to the emergent phases of matter.
5.1 Low Energy Scattering Cross Section

Our study of the collective modes in Bi2212 was performed primarily on optimally doped crystals. We collected the inelastic spectra through an octant of the two dimensional Brillouin zone along the (HK7) plane. To map reciprocal space, we performed measurements along radial cuts of the Brillouin zone along the node, antinode, and two additional cuts in between at 15° and 30° from the antinodal direction. Assuming C4 crystal symmetry, we can then reconstruct the dynamics for the entire Brillouin zone. For this measurement, because we are primarily interested in obtaining high energy resolution, we tuned the incident beam energy to 7 eV, which yielded a direct beam resolution of 2 meV. We performed measurements at both 20 K, which is into the superconducting state, and 295 K.

The raw dispersion scans for the nodal and anti-nodal cuts are presented in Figure 5.1. We have chosen for this study to perform the scan along the nodal direction to be in the direction of the supermodulation wave vector. For all of these scans, each momentum cut is performed on the same sample cleave and would last as must as 20 hours after the initial cleave. Because of sample degradation occurring as a result of surface adsorbates, the overall scattering intensity decays as a function of time, however, we verified that the over these time scales, only the relative intensity of these features changes. To account for this, each of the momentum cuts has a time dependent normalization determined by fitting the decrease in intensity to an exponential decay. To compare the different momentum cuts, because each cut is taken on a new sample cleave, we also need to normalize between cuts. To do this, we compared the intensity of the 80 meV feature at $q = 0$ and normalized to the height of this peak. Note that we do not choose the elastic peak, because this will be strongly dependent on the fine grained alignment of the sample and any slight tilting of the sample out of the scattering plane.

The primary features we note in Figure 5.1 are the peaks visible at roughly 80 meV, 48 meV, 24 meV, and 15 meV. The modes do not shift appreciably in energy between normal state at room temperature and the superconducting state at 20 K. The full energy and momentum plot for this data can be seen in Figure 5.2. The modes that we observe are mostly dispersionless out to the momenta at which we are no longer able to perform fits to the mode because of the loss of scattering signal at large momentum transfer.
Figure 5.1: Nodal and antinodal spectra on Bi2212 taken at both 20 K and 295 K.
Figure 5.2: Heatmap of the M-EELS scattering intensity of Bi2212 at 20 K measured at L=7 along four directions between the antinode and the node, as denoted in the insert. The green circles are fits to the observed peaks in the data, the triangles are the observed modes as reported in [24].

While the bulk of this study centers on optimally doped Bi2212, we also performed some measurements on $T_c = 55$ K underdoped samples for comparison. The specular loss scan is shown in comparison to the data collected on the optimally doped crystal in Figure 5.3. While the different dopings are qualitatively similar, namely the existence of collective modes around 80 meV and 50 meV, the 50 meV peak shows evidence for being composed of multiple modes, evidenced by the lowering of the energy of one of the modes. As we will see in the discussion, we believe these peaks are composed of many underlying modes and as such, assignment to any particular mode is not feasible.

5.2 Calculation of Dynamic Susceptibility

With this survey of the scattering intensity throughout the first Brillouin zone, we can use Equation (2.39) to compute the imaginary part of the dynamic susceptibility of Bi2212 at the measured temperatures. Constant energy cuts of this data is shown in Figure 5.4. This represents the study of the charge dynamic susceptibility of a large region of the first Brillouin zone in this material.
Figure 5.3: Comparison of the specular low temperature scattering intensity of optimally doped Bi2212 (a) to under doped Bi2212 with $T_c = 50$ K (b). We note that what seems to be one diffuse mode at 48 meV in the optimally doped sample seems to appear as two different modes at 41 meV and 53 meV in the under doped sample.

From $\chi''(q, \omega)$, we can perform a Kramers-Kronig transformation using Equation (2.42) in order to compute the real part of the dynamic susceptibility, $\chi'(q, \omega)$. In particular, here we are interested in computing the real part of the dynamic susceptibility as $\omega = 0$. Because of the resolution anomalies that arise in computing the imaginary part of the susceptibility [38], we set $\chi''(q, \omega)$ to 0 for all values of $\omega$ less than the half-width at half-max of the elastic peak. This is sufficient to eliminate the resolution anomalies in $\chi''(q, \omega)$, at the cost of eliminating any information of quasielastic scattering taking place at these energy scales. The real part of the dynamic susceptibility at zero frequency as a function of momentum is shown in Figure 5.5b.

5.3 Comparison to Other Techniques

Many of the modes that we observe in our study have been observed before using standard HR-EELS techniques [20, 21, 23, 39]. Our results are largely consistent with this previous work, and both with the specular spectra in the case where the dispersion of the modes is studied [24]. These works largely cite Bi-O bond buckling modes as the source of these modes.

While this is the first extensive study of the charge dynamic susceptibility in this material, there are other probes capable of measuring the charged density response of materials in some
Figure 5.4: Constant energy cuts of $\chi''(q,\omega)/q^2$ for optimally doped Bi2212 at 20 K as a function of momentum. The first quadrant of data is obtained by reflecting the data shown in Figure 5.2 according to the tetragonal symmetry of the crystal. The quadrant shown contains the superlattice modulation, visible as bright peaks along the (11) direction. Additional scattering can also be seen along the (10) direction. These bright spots are enhanced at the energies corresponding to the peaks in the spectral function, roughly 50 meV (e) and 80 meV (h).

region of energy and momentum space, as noted in Chapter 1. In addition to M-EELS, inelastic X-ray spectroscopy (IXS) and inelastic neutron spectroscopy (INS) are capable of measuring lattice excitations in similar families of superconductors. IXS studies of Bi$_2$Sr$_2$CuO$_{6+\delta}$ (Bi2201) have shown the existence of nearly dispersionless modes at roughly the energy of the 80 meV peak we observe which is attributed to the Cu-O bond stretching phonon [40]. INS studies of HgBa$_2$CuO$_{4+\delta}$ (Hg1201) have shown the existence of a dispersionless magnetic excitation around 50 meV [41].

In addition to INS and IXS, which measure momentum resolved density response functions for spin and electrons, respectively, we can also compare our measurements to infrared spectroscopy, a $q = 0$ probe of the dielectric function $\epsilon(\omega)$, and by extension the charge dynamic susceptibility. As shown in Figure 5.6, there is a strong correspondence between the $E \parallel c$-axis response function
Figure 5.5: Plots showing $\chi''(q,\omega)$ and $\chi'(q,\omega)$ for optimally doped Bi$_2$212 in panels a and b, respectively. For $\chi''(q,\omega)$, we show specular data taken at specular ($q = 0$) for both 20 K and 295 K, the dashed lines show the original spectra, which are antisymmetrized to give $\chi''(q,\omega)$. For $\chi'(q,\omega)$, we show the susceptibility at 20 K and $\omega = 0$.

Figure 5.6: Comparison of the $q = 0$ component of the $\chi''(q,\omega)$ in Bi$_2$212 at 20 K we measure with M-EELS compared to the $E \parallel c$-axis component of the loss function $\text{Im}[-1/\epsilon(\omega)]$ measured with IR spectroscopy [42].
measured by IR and the \( q = 0 \) response function we measure with M-EELS. In particular, the
peaks measured are at nearly the same energies. The key difference is that M-EELS measures a
constant background, which is discussed in Chapter 6.

Using other techniques as a basis of comparison, in light of contradicting explanations and many
different excitations at play in this energy regime [24, 30, 42–47], we do not assign the modes we
observe to any particular lattice vibration or excitation. In particular, studies of Bi2201 and Bi2212
using Raman spectroscopy to identify various lattice vibrations identify even more vibrational
modes below 100 meV with assignments to all of the layers of the material [47].

5.4 Relationship to ARPES Kink

In order to characterize the possible importance of the modes observed in this study, we relate them
to the dispersion anomalies, typically referred to as kinks, observed ubiquitously in the spectral
function of high-temperature superconductors [48]. The presence of kinks in an electronic dispersion
are signatures of a coupling to a bosonic collective mode. However, the mode itself need not be
exotic. In fact, in the presence of a phonon mode, a Hartree-Fock analysis, where the change in
the quasiparticle dispersion is of the form:

\[
\Delta E_k(\omega) = -\int \frac{d\mathbf{k'}}{(2\pi)^3} \frac{V_{\text{eff}}(\mathbf{k} - \mathbf{k'})}{\epsilon^L(\mathbf{k} - \mathbf{k'}, \omega)}
\]  

for the effective propagator, \( V_{\text{eff}}(q) \), and the longitudinal dielectric function, \( \epsilon^L(q, \omega) \), using the
full forms of these quantities in which we include the both electronic and ionic contributions to the
screening results in an anomaly in the dispersion near the Fermi energy within a window \( \hbar \omega_D \) [49].

This leads to qualitatively the same kink feature as observed in the cuprates.

In the cuprates, the kinks and their relationship to the superconducting and related ordered
states have been thoroughly studied [31, 50, 51]. In particular, in Bi2212, these dispersion anomalies
have been observed at around 70 meV, 50 meV, and 10 meV [32]. These kinks have varying behavior
along the nodal and antinodal directions and vary through the superconducting transition [30].

While the ARPES kink has been studied extensively, the anomaly itself is a result of the
interaction that is encoded in the dielectric function or dynamic susceptibility. Other than M-
Figure 5.7: Comparison of the electronic dispersion in Bi2212 as measured with ARPES [52] to the renormalized dispersion we compute from a one-loop correction to the bare dispersion using the measured excitations.

EELS, there are no direct probes of the electronic dynamic susceptibility with both the energy resolution to observe features on the relevant energy scales and the wavevector tunability to map any significant fraction of the Brillouin zone. However, with the data presented in Figure 5.5, we are able to investigate the relationship of the collective modes observed in Bi2212 to the kinks.

In order to study this relationship, we compute the self-energy correction that from this interaction in a one loop approximation, where we take:

$$\Sigma(k, i\omega) = g_{bf}^2 T \sum_{q} \int_{\Omega} G(k - q, i\omega - i\Omega) D(q, i\Omega)$$  \hspace{1cm} (5.2)

where $T$ is the temperature and $g_{bf}$ is the boson-fermion coupling constant. The variables $k$ and $q$ are the momenta and $\omega$ and $\Omega$ are Matsubara frequencies for the fermion and bosons, respectively. This leads to an expression for the imaginary part of the self energy:

$$\Sigma''(k, \omega) = -g_{bf}^2 \sum_{q} \chi''(q, \omega - \xi_{k-q}) \left[ n(\omega - \xi_{k-q}) + f(-\xi_{k-q}) \right]$$  \hspace{1cm} (5.3)

for $\xi_k$ the bare fermion dispersion, and $n$ and $f$ the Bose and Fermi functions, respectively. The bare dispersion for the fermions is determined from a tight binding dispersion fit to match the Fermi surface measured in ARPES [52].
In this model, we can use three fitting parameters to characterize the effect of the measured collective modes on the fermion self energy. First, we adjust the bare Fermi velocity to match the ARPES spectrum at high energy, then the electron-boson coupling constants for each of the two primary modes observed in the M-EELS spectra are chosen to reproduce the low energy Fermi velocity. The resulting dispersion along the nodal direction computed by considering this interaction compared to the measured ARPES spectrum is presented in Figure 5.7. Here, we see excellent qualitative agreement between the measured and computed electron dispersion, despite the simplistic form of the model used in this computation. The resulting estimate for the total electron-boson coupling constant gives \( \lambda = 0.7 \), which is consistent with previous estimates [53].

5.5 Imaging Density Perturbations

With a map of the full density response function, we can construct the response of the system to charged perturbations. In so doing, we can determine the real time and space electron dynamics of the system. Under a linear response framework, the density fluctuations induced by an external charged perturbation is described by the susceptibility in reciprocal space as [54]:

\[
n_{\text{ind}}(\mathbf{q},\omega) = V(\mathbf{q})\chi(\mathbf{q},\omega)n_{\text{ext}}(\mathbf{q},\omega)
\]

for \( n_{\text{ind}} \) and \( n_{\text{ext}} \) the induced and external charge density, respectively, and \( V(\mathbf{q}) \) the Coulomb propagator, which in our case is the two-dimensional propagator \( V(\mathbf{q}) = \frac{2\pi e^2}{q} \).

The charge disturbance induced by an point source of unit charge is found by taking the external charge density to be \( n_{\text{ext}}(\mathbf{x},t) = \delta^{(2)}(\mathbf{x})\delta(t) \), which is equivalent to the Fourier transformed expression \( n_{\text{ext}}(\mathbf{k},\omega) = -e \). Thus, \( n_{\text{ind}}(\mathbf{q},\omega) = -V(\mathbf{q}\chi(\mathbf{q},\omega)) \). While inverse Fourier transforming the induced density fluctuation, while M-EELS only measures the imaginary component of the dynamic susceptibility, we use the Kramer-Kronig relation, noted in Equation (2.42), as well as the symmetry properties of \( \chi'(\mathbf{q},\omega) \) and \( \chi''(\mathbf{q},\omega) \) to write:

\[
n_{\text{ind}}(\mathbf{q},t) = -4V(\mathbf{q})\theta(t) \int_0^\infty \sin(\omega t)\chi''(\mathbf{q},\omega) \, d\omega = eV(\mathbf{q})\chi''(\mathbf{q},t)
\]

where we define \( \chi''(\mathbf{q},t) = -4\theta(t) \int_0^\infty \sin(\omega t)\chi''(\mathbf{q},\omega) \, d\omega \). Performing the inverse Fourier transform
Figure 5.8: Real space electron density fluctuations in optimally doped Bi2212 at 20 K as a function of time induced in response to a point like charged disturbance as computed in a linear response framework. Note the increased response along the (10) and (11) directions. These images have resolutions of roughly 1.9 Å and 13 fs.
of the spatial component, assuming C\textsubscript{4} crystal symmetry, gives the final expression:

\[
  n_{\text{ind}}(x, t) = 4 \int_0^\pi dq_x \int_0^\pi dq_y \ V(q) \chi(q_x, q_y; t) \cos(q_x x) \cos(q_y y).
\]  

(5.6)

In order to perform this calculation without introducing spurious features, we fit a Lorentzian tail to the data to interpolate out to high energy. This is done to avoid truncation problems, which can introduce features in the Fourier transform at time scales related to the cutoff frequency.

Performing this calculation, the resulting induced charge density is shown in Figure 5.8. Using this formulation, we can extract time domain information out to a maximum time of \( t_{\text{max}} = 2\pi/\Delta\omega \), for \( \Delta\omega \) the energy step size of our scans, at time intervals of \( \Delta t = \pi/\omega_{\text{max}} \), for \( \omega_{\text{max}} \) the largest scanned energy loss. In our case, we can measure time scales of roughly 4.1 ps at a resolution of 14 fs.

In addition, we can consider the static screening of a charged impurity in this linear response framework. In this case, we consider an external charge density:

\[
  n_{\text{ext}}(x, t) = \delta^{(2)}(x)
\]  

(5.7)

\[
  \Rightarrow n_{\text{ext}}(k, \omega) = \delta(\omega).
\]  

(5.8)
In this case, because only the real part of the dynamic susceptibility is non-zero at $\omega = 0$, the induced static charge density depends solely on the $\chi'(\mathbf{q}, \omega)$ as:

$$n_{ind}(\mathbf{q}) = V(\mathbf{q})\chi(\mathbf{q}, \omega = 0) = V(\mathbf{q})\chi'(\mathbf{q}, \omega = 0)$$

(5.9)

Therefore, in this case, we are required to compute $\chi'(\mathbf{q}, \omega)$ explicitly using Equation (2.42). As above, the resulting real space form of the induced density perturbation is given as:

$$n_{ind}(\mathbf{x}) = 4 \int_0^{\pi} \int_0^{\pi} dq_x dq_y V(q)\chi'(\mathbf{q}_x, \mathbf{q}_y; \omega = 0) \cos(q_x x) \cos(q_y y).$$

(5.10)

The resulting plot for this is shown in Figure 5.9.

In the above figures, we see the linear response theory description of the density fluctuations in Bi2212. The key feature to observe in these is the distinct peaks in the density fluctuations along the antinodal direction (10) and the nodal direction (11). These fluctuations are closely tied to the charge ordering of the system, as we will discuss in detail in Chapter 7.
Chapter 6

Observation of Marginal Fermi Liquid Continuum

In addition to work that has gone into studying the microscopic low-energy excitation spectrum, we are also able to study the mid-infrared characteristics of Bi2212. There has been a great deal of work that has gone into developing an understanding of the dynamics of the cuprates at these higher energy scales and using this behavior to drive our understanding of these high correlated systems [55–57].

The work that we have done in studying optimally doped Bi2212 is focused on observing and quantifying marginal Fermi liquid (MFL) continuum. Marginal Fermi liquid theory is a phenomenological framework that seeks to describe the breakdown of the Fermi liquid behavior near optimal doping. The motivation for studying the MFL continuum is to establish constraints on the details of any proposed theories to describe the high temperature superconductivity. Work in this area has focused on describing the transport properties in the breakdown of Fermi liquid theory that is believed by its practitioners to arise as a result of the proximity to quantum critical behavior [58].

The MFL theory is characterized by a lack of quasiparticles at the Fermi energy [59]. The central assumption of MFL theory is that the dissipative part of the fluctuation spectrum takes the following form:

\[
\chi''(q, \omega) = \begin{cases} 
-\chi''_0 \omega / T & \omega \ll T \\
-\chi''_0 \text{sgn}(\omega) & \omega_c \gg |\omega| \gg T 
\end{cases}
\]

(6.1)

for \(\chi''_0\) a bare single-particle density of states and \(\omega_c\) some cutoff frequency. That is to say, at very low energies, the dynamic susceptibility will be roughly linear in energy, and for energies up to the cutoff, the susceptibility will be constant. This cutoff frequency will be something on the order of \(v_F q\), for \(v_F\) the Fermi velocity and \(q\), the measured momentum. For sufficiently long wavelength, however, we expect the dynamic susceptibility to go as \(q^2\) in order for the fluctuations of conserved quantities.
Starting from the MFL theory, the computed normal state transport properties are generally in good agreement with experimental evidence. One of the more prominent features of the normal state strange metal phase is $T$ linear resistivity, which arises from MFL theory from a logarithmically singular contribution to the electron self-energy [60]. These self energy effects can be measured directly using ARPES, which is generally consistent with the qualitative temperature and momentum dependence of scattering rates [58]. In the seminal paper [59], evidence for the MFL continuum was obtained using Raman spectroscopy, which sees a temperature and frequency independent background out to roughly 0.5 eV. However, Raman spectroscopy is limited to $q = 0$ measurements and does not admit a clear relationship to the dynamic susceptibility.

Using M-EELS, we will investigate the existence of this marginal Fermi liquid continuum in optimally doped Bi2212. In the optimally doped compound, we expect to see the clearest MFL signature because of the proximity to the quantum critical point. M-EELS is well suited to this study, as it couples directly to the charge degrees of freedom, as well as having wave vector tunability and a clear relationship to the dynamic susceptibility, allowing us to investigate the qualitative description posed by marginal Fermi liquid theory.

### 6.1 Collapsing M-EELS spectra

In order to perform this study, we measure the scattering cross section of the optimally doped Bi2212 crystals as a function of energy loss out to 2 eV. We perform the measurement as a function of momentum to investigate the momentum dependence of the continuum. Because we are measuring energy losses out to 2 eV, we use an incident electron beam with a 50 eV beam energy. Using this higher energy beam lowers the energy resolution of the spectrometer to 4.6 meV, however, because we are focused on the high energy behavior of the system, this loss of resolution does not negatively effect this measurement. We perform this measurement at 20 K with a base pressure of $1 \times 10^{-10}$ Torr.

The raw M-EELS spectra taken as a function of energy for different momenta is shown in Figure 6.1. Here we can qualitatively see the existence of a energy independent background that extends out to roughly 1 eV, but for with a cutoff that varies as a function of momentum.

In order to show that the M-EELS spectra are consistent with the MFL form of $\chi''(q, \omega)$ given in
Figure 6.1: High energy dynamic structure factor of Bi2212 measured at 20 K. The measured momentum is along the (10) direction.

Equation 6.1, we fit the spectra to a functional form that captures the correct qualitative behavior. Given that we are at 20 K and the width of our elastic line is $\sim 12$ meV, we do not expect to see the $\omega/T$ linear regime of the dynamic susceptibility. Out to the cutoff, we expect $\chi''$ is roughly constant, at which point there is a crossover to a regime where $\chi'' \propto q^2$. Such a function can be written:

$$\chi''(q, \omega) = -\chi_0'' \tanh \left( \frac{a^2}{x^2} \right)$$

where we define the dimensionless crossover parameter $x = \omega/v_Fq$, $\chi_0''$ is the density of states $N(0)$, and $a$ is a constant $O(1)$. Now, we can relate this to our measurement by using the expression:

$$S(q, \omega) = -\frac{\chi''(q, \omega)}{|\epsilon(q, \omega)|^2}$$

In order to write the dielectric function, $\epsilon(q, \omega)$, we again use an interpolation function between the static limit of:

$$|\epsilon(q, \omega)| \sim \epsilon_0 + \left( \frac{q_s}{q} \right)^2$$
Figure 6.2: The dynamic structure factor for optimally doped Bi2212 computed from the data presented in Figure 6.1 by scaling the data according to Equation (6.6) such that all of the curves roughly collapse to the same line. Here, \(a\) and \(c\) are the two fit parameters leading to the collapsing of the data into this functional form and \(y = q/q_s\), as defined in the main text.

at low \(q \ll q_s\) for \(q_s\) the Thomas-Fermi screening length and a constant \(|\epsilon(q, \omega)| \to \epsilon_0\) over the full range of \(\omega\). As such, our interpolation function can be written:

\[
|\epsilon(q, \omega)|^{-2} = \frac{1}{\epsilon_0^2} \left( \frac{c^2 y^2}{1 + c^2 y^2} \right)^2
\]  

(6.5)

where we have defined a dimensionless crossover parameter \(y = q/q_s\) and \(c\) is a constant \(O(1)\).

We can now write our full expression for the functional form we expect the measured dynamical structure factor, combining Equation (6.2), Equation (6.3), and Equation (6.5) to take as a function of the dimensionless quantities \(x\) and \(y\) as:

\[
S(x, y) = \frac{\chi_0}{\epsilon_0^2} \left( \frac{c^2 y^2}{1 + c^2 y^2} \right)^2 \tanh \left( \frac{a^2}{x^2} \right).
\]

(6.6)

From Figure 6.1, it can be seen that the spectra qualitatively match this functional form. We perform these fits and use the fitted parameters to scale the data. The rescaled data is presented
Figure 6.3: The fit parameter $a$ used to generate the collapse shown in Figure 6.2 plotted as a function of momentum. We see here three distinct regions, for low momentum near the specular reflection, the prescription we have taken here breaks down, this may be a result of the strong elastic scattering signal, or it may be a result of the mid-infrared plasmon, which is more pronounced at low momentum, disrupting the continuum fits. There is then a hydrodynamic regime, in which the $a$ constant is roughly constant $O(1)$, then at large momentum, there is a cross over to a Fermi liquid behavior, where the constant $a \propto (v_F q)^{-2}$.

In Figure 6.6. This presentation of the data shows that our measurement qualitatively matches the functional form presented for the marginal Fermi liquid.

In order to perform the fitting leading to the collapse in Figure 6.2, we perform a fit to the two parameters $a$ and $c$ in Equation (6.6). We are able to get a global fit for the $c$ parameter, however, in order to obtain a good fit to the data, we fit a separate $a$ parameter for each momentum point. For the fits, we get a value for $c$ of 2.1, which is consistent with the initial assumption that it is a constant $O(1)$. The fits for $a$ as a function of the momentum point is shown in Figure 6.3. As noted in the Figure, we see a region of momenta consistent with the ansatz developed in Equation (6.6). However, for larger momenta, the data follows the same functional form, but the cutoff point for the constant background no longer has the same qualitative behavior.

From this initial study we have done, we see that M-EELS is able to provide key measurements of the dynamic susceptibility as a function of energy and momentum. This expands on previous studies carried out with Raman spectroscopy at $q = 0$. We have thus demonstrated that continued study of this continuum features as a function of energy, momentum, temperature, and doping will
provide strict limits on the validity of the marginal Fermi liquid model and in turn on the form of an allowable microscopic description of the cuprates.
Chapter 7

Charge Order and Quasielastic Scattering

In addition to the superconducting state itself, high temperature superconductors exhibit an array of related collective phenomena. Understanding and characterizing the broader collective dynamics is likely to play a key role in understanding the superconducting state itself. Since the identification of long range spin and charge order in the La$_{1.6-\delta}$Nd$_{0.4}$Sr$_{\delta}$CuO$_4$ (LNSCO) high temperature superconductor [61], the importance of the various broken symmetry states has garnered a great deal of attention and importance in the drive to understand the strongly correlated electron physics at play in these materials.

Neutron scattering and resonant X-ray scattering (RXS) have been able to identify several families of cuprates as exhibiting this stripe ordering, in which spin and charge degrees of freedom separate and form a periodically modulated ordered phase. In addition to the discovery in LNSCO, static long range charge and spin order has been observed in La$_{2-x}$Ba$_x$CuO$_4$ (LBCO) [62], both of which are able to be grown as large crystals, suitable for neutron scattering. Quantum oscillation [63] and thermoelectric transport [64] on YBa$_2$Cu$_3$O$_{6+\delta}$ (Y123) gave evidence for the existence of a stripe ordered state in these materials. This ordering is typically related to the 1/8-anomaly, a reduction of the the superconducting transition near 12% doping as a result of the formation of the static stripe phase.

In addition to the static stripe order, a great deal of research has gone into understanding the fluctuating order parameter related to the stripe state. Such fluctuating order arises because of the proximity to the ordered state [65]. These fluctuations are important as they may important to the understanding of the strange metal phase which appears above the superconducting dome and is characterized by $T$ linear resistivity. The fluctuations of the stripe phase are interpreted as being related to the existence of a nematic electronic liquid crystal phase [66], and the onset of this nematic order generally coincides with the onset of the pseudogap state [67]. Further evidence
for the existence of an electronic nematic state has been seen with scanning tunneling microscopy in both cuprate [68] and iron-based [69] superconductors. Still, the smoking gun for fluctuating charge order has been difficult to establish because of the difficulty in measuring a clear experimental signature [65, 70].

Understanding the various non-superconducting broken symmetry states exhibited by the high temperature superconductors has generated a great deal of interest. In particular, understanding interplay between the various ordered phases, charge density wave (CDW), spin density wave (SDW) and superconductivity, as a pair density wave (PDW) state [71]. Evidence for the observation of such a state has been seen in scanning tunneling microscopy (STM) on Bi2212 [72].

With the current rise of resonant X-ray probes, there has been increased effort to establishing CDW order in the cuprates. Charge ordering has been identified using resonant X-ray scattering on underdoped Bi2201 [73], underdoped Bi2212 [74], HgBa2CuO4+δ [75], and even on electron-doped (Nd,La)2−δCeδCuO4 [76], which along with previous work with neutron and X-ray scattering suggest a ubiquity of charge ordering in the cuprates. Short range charge order has also been observed with RIXS in optimally doped Bi2201 [77] and Pb-Bi2212 [78]. It should be noted, however, that RXS is an energy integrated technique and cannot identify scattering as elastic, and even RIXS, which energy resolving, has a typical energy resolution of 100 meV, which is much too large to make very definitive claims on the elastic nature of observed scattering, precluding any statement on the fluctuating nature of the observed order.

In this study, we will focus on the use of M-EELS to investigate the charge ordering and fluctuating charge order as it exists in optimally doped Bi2212. In particular, we are able to use M-EELS to investigate the low-energy structure factor and the dynamic susceptibility, which have been key missing features in the study of this material as it relates to the broader question of CDW ordering [9, 65].

7.1 Elastic scattering and change order

First, we look at the static charge order of optimally doped Bi2212. For these studies, we used a 50 eV incident electron beam with a FWHM of 4 meV in the direct beam geometry. By using a relatively high energy beam here, we are able to survey a larger section of the Brillouin zone, in
Figure 7.1: Elastic scattering maps of optimally doped Bi2212 at 295 K and 20 K, respectively taken with a 50 eV incident electron beam. The intensity scales are identical between the two images. Dashed lines are the Brillouin zone boundary, and the high symmetry points are labelled according to the orthorhombic convention. Upon cooling, we see the increase in the elastic scattering oriented along the (10) and (11) directions, but which is very diffuse radially.

particular allowing us to reach the (1,0,0) Bragg peak. While we sacrifice some energy resolution by using a higher energy beam, the chosen resolution is sufficient to survey elastic scattering because the elastic scattering is the dominant scattering term. At this higher momentum, we took all HK scans at $L=20$. All of the scans are performed with a $1 \times 10^{-10}$ Torr base pressure. While full two-dimensional surveys of the elastic scattering is investigated for optimally doped Bi2212, we also look at (10) scans of under doped samples for comparison.

Data showing the elastic scattering at both 295 K and 20 K is shown in Figure 7.1. This data is collected by taking a series of radial elastic scans. The scans cover a 60° wedge of the Brillouin zone, with scans taken between 5° and 15° apart. The radial spacing of the points sampled is 0.02 rlu. The wedge that was chosen fully captures the (10) direction, including the Bragg peak at (1,0), and the superlattice direction.

At room temperature, Figure 7.1a, as with the inelastic data, we see the superlattice modulation along the (11) as well as the (1,0) Bragg peak. Satellite peaks along the (10) direction appear around both (0,0) and (1,0) peaks as a result of (11) superlattice, which is seen because of the large out-of-plane momentum resolution.

However, upon lowering the temperature, shown in Figure 7.1b, in addition to the elastic features
Figure 7.2: Comparison of the elastic scattering intensity as a function of momentum along the \((10)\) direction between optimally doped and under doped samples. We see the diffuse ordering in the optimally doped material forms into a well defined peak in the under doped material. Measurements were taken with an incident beam energy of 50 eV.

we see at room temperature, we also see the emergence of a band of quasielastic scattering along the \((10)\) and \((11)\) directions. This additional scattering is diffuse radially but sharp in angle. This scattering is reproducible upon cooling and warming cycles and has been observed on separate runs taken on different Bi2212 crystals, indicating that this is not a result of a particular sample cleave or the collection of surface adsorbates.

In addition to verifying the reproducibility of this observation, we compared this data to a scan taken on an under doped sample with a \(T_c\) of 50 K. For the underdoped sample, shown in Figure 7.2, we see that the diffuse scattering forms into a more well defined peak. This further shows that the observed enhancement in the scattering intensity is not an artifact of surface adsorbates, as the exposed Bi-O surface of both under doped and optimally doped is similar and the data was acquired in a similar vacuum state. While there is a difference in the exact wavevector of the ordering, the formation of a more well defined peak is qualitatively consistent with previous RXS measurements on underdoped Bi2201 samples [73]. In our study, we see the peak at roughly 0.38 rlu along the \((10)\) direction.
7.2 Quasielastic scattering observation

Using M-EELS, we are able to perform the first measurement on the nature of the CDW scattering observed in the BSCCO family of superconductors on the sub-10 meV scale. In order to study the quasielastic nature of this scattering, we return to a 7 eV electron beam. With the greater energy resolution of 2 meV FWHM in direct beam, we are able to better characterize the low-energy scattering we observe in the optimally doped sample in order to determine if there is actually quasielastic scattering caused, perhaps, by fluctuations of nearby charge ordered state.

In order to perform this analysis, we used inelastic spectra we used previously for studying inelastic loss features, which had been measured along four radial directions between the nodal superlattice direction and the antinodal direction. For this measurement, we look at the shape of the elastic line in the low energy loss regime. Referring back to Figure 5.2, we see that at low temperatures, the elastic line is not resolution limited, but rather exhibits some additional scattering near $\omega = 0$.

To fully characterize this quasielastic scattering, we fit the spectra near the elastic line as the sum of two Gaussian functions, one for the sharp elastic peak and another for the quasielastic tail. The energy cuts about $\omega = 0$ showing shape of the normalized the elastic line as a function of momentum is shown in Figure 7.3. While both Figure 5.2 and Figure 7.1 show that the elastic scattering intensity is highly modulated by the diffuse charge ordering, when the data is normalized, the spectra show a similar broadening behavior across the Brillouin zone.
Figure 7.4: Absolute scattering intensity of quasielastic scans shown for various momenta shown in Figure 7.3, as well as the two-component fits to the shape of the elastic line. The individual fits are shown as the short dashed lines, and the sum of the two fits is shown as the long dashed line. The momenta are measured along radial cuts at the specified angle $\phi$ from the (10) direction.

Figure 7.5: The full width at half maximum (FWHM) of the two-component fits to the elastic line, as shown in Figure 7.4, as a function of momentum. The different panels show different radial cuts, with the labels a–d showing the fit parameters for the corresponding panels of Figure 7.3.
Figure 7.6: The real part of the static structure factor, $-\chi'(q, \omega = 0)$, for optimally doped Bi2212 plotted as a function of momentum along radial cuts of the Brillouin zone, with the given $\phi$ angle relative to the (10) direction. We see an increase in the static susceptibility along (11) arising from the supermodulation as well as along (10) which is related to the charge ordering in this direction.

We can perform the fits to the two components of the elastic peak, as shown in Figure 7.4. Extracting the widths from these fits, the momentum dependence of the quasielastic broadening is shown in Figure 7.5. Not only is the existence of fluctuations visible at all momentum points, but the width of this quasielastic broadening is roughly constant throughout momentum space. Extracting from this data a characteristic broadening, the fluctuations give rise to an average broadening of $23\pm5$ meV. At 20 K, this is much larger than could be explained by any thermal broadening effect. From this, the time scale on which we see these fluctuations is roughly $\tau = 2\pi \hbar / 23$ meV = 180 fs.

### 7.3 Static susceptibility

Finally, we use these M-EELS spectra to analyze the static susceptibility, that is $\chi'(q, \omega = 0)$. This quantity reveals CDW instabilities, where in the one-dimensional Peierls CDW instability, the static susceptibility diverges at the momentum of the CDW modulation as the system approaches the CDW transition temperature [79]. We can compute this quantity by evaluating the Kramers-Kronig transformation given in Equation (2.42).

The result of this is shown in Figure 7.6. Here, we see an increase in static susceptibility along the (10) ($\phi = 0^\circ$) and (11) ($\phi = 45^\circ$) directions. From this plot, we can see that the peaks
Figure 7.7: The real part of the static structure factor, $-\chi'(\mathbf{q}, \omega = 0)$, for 50 K under doped Bi2212 measured as a function of momentum along the (10) lattice direction. The measurement is performed at both 20 K and at room temperature and is done using an incident beam energy of 50 eV.

along the (11) direction arise as a result of the supermodulation. However, the increase in the static susceptibility in the (10) direction at the same momentum we see a peak in the fluctuations suggests a connection between the fluctuations and the CDW ordering seen in the underdoped cuprates.

Similarly, we can look at the static susceptibility for the underdoped Bi2212 crystal along the (10) direction. Performing the same Kramers-Kronig transformation, we compute the static susceptibility shown in Figure 7.7. Here, while we are not at the probable CDW transition temperature, however, we can still see the formation of a more well defined peak in the susceptibility, suggestive of proximity to the ordering transition.
Chapter 8

Conclusion

Here we will summarize the key achievements and findings arising from this work.

First, we have developed momentum resolved electron energy loss spectroscopy into a modern spectroscopic technique, capable of measuring the dynamical structure factor of materials across energy and momentum space. This work has built upon the successes of existing HR-EELS instrumentation and techniques. However, existing hardware required retooling in order to function correctly for the desired measurements. In order to make full use of these hardware enhancements, we have also implemented new experimental techniques. This has included the design and construction of the sample goniometer, modifications to the spectrometer to allow for motorized control, and experimental procedure to align and run this upgraded system. In addition, to the enhancements to the spectrometer, we have done a ground up redesign and rewrite of the spectrometer control interface, enshrining the author with the title of “the grad student with the Arduino.” This includes a full stack software and hardware development, tying together frontend interfaces with backend control systems. The sum total of this development has been the ability to measure the low energy dynamical structure factor, $\chi''(q, \omega)$, with wave vector tunability across the Brillouin zone.

We have used this technique to study the low energy electron dynamics of the optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) high temperature superconductor. First, we have identified the low energy excitations present in this material, seeing modes at 17 meV, 24 mev, 49 meV, and 80 meV, mapping their dispersion across the first Brillouin zone. Using the modernized expressions we have written for computing the dynamical structure factor, we have written $\chi''(q, \omega)$ for this material in both the normal and superconducting state. This is the quantity that we argue is key to quantifying the electron dynamics of this strongly correlated electron system. We see that even under simple assumptions, our measured dynamical structure factor is able to reproduce the dispersion anomalies.
seen in ARPES, suggesting we are measuring the modes that are responsible for the kinks. Further study of the dynamical structure factor in this low energy regime will be able to guide the study of possible theories to describe the many body state of the cuprates.

In addition to the low energy phenomena, we have used M-EELS to observe an energy independent background in optimally doped Bi2212 that is qualitatively consistent with the marginal Fermi liquid phenomenology to describe the cuprates. We have been able to map the momentum dependence of this background, see previously at $q = 0$ in Raman spectroscopy. Additional studies in this energy regime will not only provide tests for such phenomenological theories, but will also test other theories of high temperature superconductivity that are tied to the behavior of the midinfrared charge dynamics, such as the midinfrared scenario.

Finally, we have used M-EELS to provide the first direct observation of static charge ordering and charge fluctuations in optimally doped Bi2212. We have observed a radially diffuse band of elastic scattering along the antinodal direction that appears upon cooling below the superconducting transition. With underdoping, this additional scattering becomes a more well defined peak with wave vector of roughly 0.38 rlu. Because of the energy and momentum sensitivity of M-EELS, we have also observed quasielastic scattering indicative of fluctuations of this ordered state. Both the collective modes that we observe in the dynamic susceptibility and these fluctuation are modulated by the charge ordering that we observe. This suggests that these fluctuations are related to the formation of the charge density wave state, and provide can provide further insight into the relationship between the various ordered phases that we see in the cuprates.
References


