Abstract

Optical spectroscopy of two-dimensional electronic materials

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This thesis presents optical studies of several low-dimensional electronic materials. Reflectance, transmittance, ellipsometry and Raman scattering were employed to measure the fundamental excitations of the materials under study. The electrodynamics of BSCCO two-dimensional atomic crystals were investigated as a function of thickness. The thickness dependence of the optical response indicates a tendency of the BSCCO surface to become insulating. Furthermore, the characteristic energy scale of magnetic fluctuations was observed to increase in the atomic crystals. A series of superconducting Cu$_x$Bi$_2$Se$_3$ crystals with different Cu content were also studied using optical spectroscopy. These measurements revealed a change in the conduction band mass with doping and have implications for the superconductivity in this material. Finally, the electronic and magnetic excitations of the spin-orbit coupled Mott insulator $\alpha$-RuCl$_3$ were examined in a combined optical and Raman study. Spin-orbit coupling was found to play an important role in determining the electronic structure and therefore the optical spectra. Finally, unusual magnetic fluctuations were identified via Raman scattering.
Dedication

To my grandmother Cynthia.
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Chapter 1

Introduction

1.1 Collective behaviour in low dimensions

A persistent theme in condensed matter physics is that the interactions between microscopic entities, such as electrons and phonons, conspire to dictate the macroscopic and collective behaviour of a solid state system. The quintessential example of this paradigm is magnetism, where interactions between electrons mediated by the Coulomb force favour a macroscopic spin polarization. Another example is the electron-phonon interaction, which can lead, in some cases, to either a charge density wave (a static modulation of both the electron density and crystal lattice) or a superconducting state. These effects become especially pronounced in low dimensions (e.g. when the electrons are constrained to move in plane or a line, rather than a three dimensional volume)[1]. Indeed, the cuprates, where CuO$_2$ planes give rise to a quasi-two dimensional electronic structure, display a variety of spectacular collective behaviour, including a Mott insulating state, antiferromagnetism, charge density wave order, and high transition temperature superconductivity[2].

Anticipating or understanding such collective or emergent behaviour from knowledge of the microscopic participants remains a difficult problem [3, 4]. Experimentally, the
approach in condensed matter physics is to measure the effect of varying some parameter of the material system, such as the chemical composition or electron density, on the collective behaviour. The resulting effect, if any, can serve to discriminate between different theoretical proposals. For instance, the sensitivity of the superconducting transition temperature in some elemental metals to the mass of the atoms (varied though isotope substitution) was an important piece of evidence for phonon-mediated superconductivity in these compounds[5].

The development of collective behaviour is typically accompanied by a pronounced rearrangement of the low-energy excitations of the material. For instance, the onset of superconductivity in certain metals is accompanied by the development of a gap in the spectrum of electron-hole excitations, as well as the emergence of new collective modes associated with the superconducting order itself [5]. Optical spectroscopy provides access to these excitations and is therefore an powerful technique for studying collective behaviour in the solid state[6]. Here the interaction of electromagnetic radiation with a given material is measured and then used to infer information about the spectrum of excitations in the material. Optical spectroscopy directly probes the electronic structure by creating electron-hole pairs either within the conduction band, as in a metal, or between bands, as in a semiconductor. The energies and lifetimes of collective modes, such as phonons or magnons, can also be accessed with this technique.

1.2 Scope of thesis

In this thesis, we present optical and Raman spectroscopic measurements of a variety of low dimensional electronic materials where collective behaviour is known to play a decisive role. Specifically, we focus on several topical van der Waals solids, materials whose crystal structure consists of stacks of covalently-bonded layers weakly held together by van der Waals forces. Because of the weak interlayer interactions, the electronic structure of these
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materials is extremely two-dimensional as the electrons move more easily within the layers than between them. The materials systems studied are Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (BSCCO), Cu$_x$Bi$_2$Se$_3$, and α-RuCl$_3$. These compounds evince a variety of collective behaviour. In particular, BSCCO and Cu$_x$Bi$_2$Se$_3$ host unusual superconducting states, while both BSCCO and α-RuCl$_3$ show evidence for magnetism and the tendency to become (Mott) insulating due to electron-electron interactions. We investigate the effects of several important parameters, namely the dimensionality, the chemical composition, and spin-orbit coupling on the single particle and collective behaviour in these compounds.

We start in chapter 2 by describing how the interaction of light and matter can be used to study the elementary excitations of a material. We then describe the experimental techniques employed in the thesis to measure this interaction. Specifically, we provide details on the instruments and methods used for reflectance, transmittance and Raman scattering measurements.

In chapters 3 and 4, we focus on the electronic and magnetic excitations of exfoliated two-dimensional (2D) atomic crystals of the high-T$_c$ superconductor Bi$_2$Sr$_2$CaCu$_2$O$_8$ (BSCCO). 2D atomic crystals refers to a class of ultra-thin (few layer) films that can be isolated from a parent van der Waals solid through the technique of mechanical exfoliation[7]. Prominent examples of 2D atomic crystals include graphene (derived from bulk graphite) and single layer MoS$_2$. These materials can have properties that differ markedly from the bulk parent. For instance, single layer MoS$_2$ is a direct gap semiconductor with a strongly spin-orbit split split valence band, while its bulk analogue is a conventional indirect gap material[8]. Bulk BSCCO is a prototypical high-T$_c$ cuprate and has therefore attracted enormous experimental effort. Depending on chemical content, the cuprates can display a spectacular variety of collective effects including Mott insulating behaviour, antiferromagnetic and charge density wave order, and high T$_c$ superconductivity[2, 9]. However, it is not clear how strongly correlated materials such as BSCCO, whose physics is dominated by collective behaviour, will behave in the few layer
limit. Intriguingly, single layer BSCCO, derived from a metallic bulk parent, was found to be insulating, implying a drastic change in the electronic structure[7]. By studying a series of samples with different thicknesses, we can investigate the role of dimensionally in the BSCCO system. In chapter 3, we describe methods for isolating and characterizing 2D atomic crystals of BSCCO. Using Raman microscopy, we demonstrate that the crystal symmetry of these materials is not altered while the magnetic excitations are significantly hardened. In chapter 4, we report the results of a synchrotron-based infrared microscopy study of 2D atomic crystals of BSCCO. This study identified a pronounced suppression of the optical conductivity $\sigma_1(\omega)$ with decreasing sample thickness. Using an effective medium approximation, we attribute this effect to an insulating surface layer, demonstrating that the insulating behaviour observed in BSCCO 2D atomic crystals is an extrinsic effect. Furthermore, we are able to identify a subtle change in the charge dynamics of BSCCO 2D atomic crystals that suggests a hardening of the electron-boson spectral function $\alpha^2 F(\omega)$. This function contains information about the coupling between electronic and magnetic degrees of freedom and so is consistent with the results of our Raman microscopy that show a hardening of the magnetic excitations. Taken together with X-ray studies of the structure of exfoliated BSCCO[10], our results can be understood in terms of a subtle modification of the average Cu-O bond angle in these samples, rather than a change in dimensionality.

In chapter 5, we report on the optical spectra of a series of superconducting Cu$_x$Bi$_2$Se$_3$ crystals. Due to the importance of Bi $p$ orbitals in this material, spin-orbit coupling (SOC) plays a decisive role in determining the electronic structure. Indeed, the strong SOC is known to cause a topological insulating state in this compound. The Bi$_2$Se$_3$ structure consists of a stack of quintuple layers made up of Se and Bi that are weakly bound by van der Waals interactions. Importantly, Cu atoms can be intercalated in the van der Waals gap between the weakly bound layers[11]. Cu doping is thought to influence the number of free carriers and the disorder level in this compound. This renders
the material superconducting and SOC is believed to strongly influence the nature of the resulting superconducting state. Indeed, various theoretical and experimental works have suggested that Cu$_x$Bi$_2$Se$_3$ hosts an unusual, odd parity superconducting state\cite{12, 13, 14}. Our measurements reveal unexpected changes in the electronic structure with Cu doping. Specifically, we show that the conduction band effective mass $m_b$ progressively increases with Cu doping, while the disorder level and carrier density $n$ remain relatively constant. This demonstrates that one of the principal pieces of evidence for unconventional superconductivity in Cu$_x$Bi$_2$Se$_3$, namely the anomalous doping dependence of the superfluid density $\rho_s$\cite{15}, is in fact a band structure effect. These results therefore cast doubt on the possibility of odd-parity superconductivity in Cu$_x$Bi$_2$Se$_3$ and highlight the complex nature of Cu doping in this material.

SOC is also expected to drive a number of exotic magnetic states in systems when electron-electron interactions are also important\cite{16, 17, 18}. To date, most studies of these phenomena have focussed on compounds containing 3$d$ transition metals where SOC is a small energy scale. Indeed, the consequences of the combined effect of SOC and electron-electron interactions is not well-established. In chapters 6 and 7, we report the results of Raman and optical spectroscopy of RuCl$_3$, a layered Mott insulator on the honeycomb lattice. As discussed in chapter 6, we consider in detail the electronic excitations of this material and demonstrate the importance of SOC in driving the Mott insulating state. Our measurements are in good agreement with the \textit{ab initio} band structure calculations, provided SOC is properly accounted for and suggest that RuCl$_3$ is an excellent candidate system for exploring the combined effects of SOC and electron correlations. In chapter 7, we discuss Raman scattering from lattice and magnetic excitations in RuCl$_3$. Most prominently, we identify a broad magnetic continuum which we discuss in relation to the SOC. We also identify signatures of spin-phonon coupling in this compound.

In chapter 7, we present our conclusions and also suggest future experiments for furthering the understanding of the materials studied in this thesis.
Chapter 2

A primer on optical spectroscopy

2.1 Introduction

In an optical spectroscopy experiment, the response to electromagnetic radiation of the material under study is measured. This response includes quantities such as the reflectance, transmittance or scattered intensity and is typically extrinsic, in that it is influenced by the sample geometry, the measurement configuration and so on. In order to compare results obtained from different optical techniques, as well as to relate these results to theory, the experimental data must be converted to an intrinsic property of the material. For an optical measurement, this intrinsic quantity is the complex optical conductivity $\hat{\sigma}(\omega)$, a linear response function. Alternatively, $\hat{\sigma}(\omega)$ can be recast in terms of a complex dielectric function $\hat{\epsilon}(\omega)$ or a complex index of refraction $\hat{n}(\omega)$. Below we describe how $\hat{\sigma}(\omega)$ relates to the elementary excitations of a material. We also discuss the optical techniques employed in the remainder of the thesis and how $\hat{\sigma}(\omega)$ can be extracted from experimentally accessible quantities.

The interaction of light with matter is most succinctly expressed through the complex optical conductivity $\hat{\sigma}(\omega)$, which relates the current density $j(\omega)$ to the electric field $E(\omega)$ at frequency $\omega$: 
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\[ j(\omega) = \hat{\sigma}(\omega)E(\omega). \] (2.1)

Alternatively, \( \hat{\sigma}(\omega) \) can be expressed as the dielectric function \( \hat{\varepsilon}(\omega) = 1 + 4\pi i \hat{\sigma}(\omega)/\omega \), where \( \hat{\sigma}(\omega) \) is in CGS units. Moreover, \( \hat{\sigma}(\omega) \) represents how easily charge can be moved about and is therefore intimately related to the charge excitations. To see this more explicitly, consider the following derivation adapted from reference [19]. We start by considering an electronic system described by the Hamiltonian \( H_s \), eigenstates \( |s\rangle \), and eigenvalues \( \hbar \omega_s \). In the Coulomb gauge and for wave vector \( q = 0 \), the interaction of light and matter can be approximated by the following perturbation to \( H_s \):

\[ H_{\text{int}} = -\frac{1}{c} \mathbf{j} \cdot A(\omega). \] (2.2)

Here \( c \) is the speed of light, while \( \mathbf{j} \) is the transverse quantum mechanical current operator and \( A(\omega) = -(ic/\omega)E(\omega) \) is a classical transverse vector potential. Detailed discussions of \( H_{\text{int}} \) and the Coulomb gauge can be found in references [19] and [20] respectively. To first order, \( H_{\text{int}} \) will induce transitions between initial state \( |s\rangle \) to final state \( |s'\rangle \) and Fermi’s golden rule can be used to evaluate the rate of such a transition:

\[ W_{s,s'} = \frac{2\pi}{\hbar^2} |\langle s'|H_{\text{int}}|s\rangle|^2 \delta(\omega - (\omega_s' - \omega_s)). \] (2.3)

The total rate of transitions induced by \( E(\omega) \) is then \( W = \sum_{s,s'} W_{s,s'} \), where the sum runs over all initial states \( |s\rangle \) and final states \( |s'\rangle \). Since each transition involves an increase in the electronic system energy of \( \hbar \omega \), we can identify the absorbed power \( P = \sigma_1(\omega)|E(\omega)|^2 \) with the quantity \( \hbar \omega W \). Using the fact that \( |\langle s'|H_{\text{int}}|s\rangle|^2 = \frac{1}{c^2} |E(\omega)|^2 |\langle s'|\mathbf{j}|s\rangle|^2 \) and then cancelling the \( |E(\omega)|^2 \) term yields the following:

\[ \sigma_1(\omega) = \frac{2\pi}{\omega^2} \sum_{s,s'} |\langle s'|\mathbf{j}|s\rangle|^2 \delta(\omega - (\omega_s' - \omega_s)). \] (2.4)
This expression encapsulates the microscopic factors that determine $\sigma_1(\omega)$. Due to the sum and delta function, $\sigma_1(\omega)$ will reflect the density of excitations at a given $\omega$. The matrix element $\langle s'|j|s \rangle$ is also important as it determines which combinations of initial and final states can contribute (i.e. selection rules) and is determined by the symmetry of the excitation. As an aside, $\hat{\sigma}(\omega)$ is a linear response function and so $\sigma_2(\omega)$ can be computed from $\hat{\sigma}(\omega)$ via a Kramers-Kronig transform of $\sigma_1(\omega)$.

The effects of $H_{int}$ can also be evaluated to second order, a procedure that results in inelastic or Raman scattering. This yields a Raman transition matrix element $H_{s,s'}^R$ given by

$$H_{s,s'}^R = \sum_i \frac{\langle s'|H_{int}|i \rangle \langle i|H_{int}|s \rangle}{\hbar \omega - (E_i - E_s)},$$

where the sum is over intermediate states $i$. Raman scattering also provided information about the spectrum of excitations of a solid. However, because $H_{int}$ appears twice in $H_{s,s'}^R$, Raman scattering has selection rules that are more complex than and distinct from those relevant to optical spectroscopy. To illustrate this, consider the specific case of inversion symmetry. The states of an inversion symmetric system can be classified according to their parity. Since the current $j$ is a vector and has odd parity, $H_{s,s'}^R$ will connect states of like parity, while $\langle s|j|s' \rangle$ (relevant to $\sigma_1(\omega)$) will connect states of opposite parity. Raman scattering therefore probes even parity excitations, while $\sigma_1(\omega)$ is sensitive to odd parity excitations.

### 2.2 Anatomy of an optical spectroscopic measurement

In this thesis we employ a number of optical techniques including broadband reflectance, transmittance, and ellipsometric measurements of $\hat{\sigma}(\omega)$, as well as synchrotron-based
Figure 2.1: Schematic depiction of light impinging on a vacuum-solid optical processes discussed in this thesis. The figure and accompanying discussion are adapted from reference [21].

infrared microscopy and Raman scattering. Because of this diversity, we will describe here in general the optical processes and techniques relevant to this thesis and leave the experimental details to the individual chapters.

As depicted in figure 2.1, several processes can occur when a sample surface is exposed to light of intensity $I_i(\omega)$. First, a portion of the light is reflected with some intensity $I_r(\omega)$ due to differences in the optical constants of the sample and vacuum. The remaining, transmitted portion $I_t(\omega)$ of the signal then propagates through the sample, where it can either be absorbed, following equation 2.4, or be inelastically scattered due to $H_{s,s'}^{R}$. In a typical optical measurement, the reflectance $R(\omega) = I_r(\omega)/I_i(\omega)$ or transmittance (through a finite sample) $T(\omega) = I_t(\omega)/I_i(\omega)$ are measured using a suitable optical arrangement and with $I_i(\omega)$ spanning a broad frequency range. The appropriate use of Maxwell’s equations allows these quantities to be related to the optical conductivity $\hat{\sigma}(\omega)$. For instance, the reflectance $R(\omega)$ for light incident parallel to the surface normal is given by
\[ R(\omega) = |(1 - \hat{n})/(1 + \hat{n})|^2 \] (2.6)

where the index of refraction \( \hat{n}(\omega) = n(\omega) + i\kappa(\omega) = (\hat{\epsilon}(\omega))^{1/2} \). Similarly, the transmittance through some sample length \( l \) is given by

\[ T(\omega) = e^{-\alpha(\omega)l}, \] (2.7)

where reflectance at any the sample-vacuum interfaces has been ignored and the absorption coefficient \( \alpha(\omega) = 4\pi\kappa(\omega)/\lambda_o \) for vacuum light wavelength \( \lambda_o \). Absorption and reflection are first-order processes and so in measuring \( R(\omega) \) and \( T(\omega) \) other second-order optical processes that affect the measured intensities (e.g. Raman or photoluminescence) are ignored. Care must taken, however, to avoid spurious intensity loss due to surface roughness or other geometric factors. In a Raman measurement, \( I_i(\omega) \) is ideally monochromatic with frequency \( \omega_o \) and is typically sourced from a laser. The Raman scattered intensity \( I_S(\omega) \) is then measured and plotted in terms of a Raman shifted frequency \( \omega_r = \omega - \omega_o \). Since it is experimentally challenging to measure all inelastically scattered photons, Raman measurements are usually reported in arbitrary intensity units.

### 2.2.1 Reflectance and transmittance

The experimental arrangement used to collect the reflectance and transmittance data contained in chapters 5 and 6 is shown schematically in figure 2.2. Although some details vary, the basic arrangement is the same for the measurements described in chapter 4.

The sample and an appropriate reference are mounted on a cold finger inside the evacuated cryostat sample space. For a transmittance reference, this can be a suitably sized aperture while for a reflectance measurement a gold mirror of similar area to the sample is employed. The sample and reference are arranged vertically so that the z-axis translator can move the sample and reference in and out of the beam focus as required.
Chapter 2. A primer on optical spectroscopy

Figure 2.2: Schematic of a reflectance or transmittance measurement. The sample and reference is mounted inside a cryostat on a z-axis translator (out of page direction). Light from a broadband thermal source (yellow regions) is modulated by an FTIR spectrometer and directed onto the sample using flat mirror M1, and parabolic mirrors PM1 and PM2. For a reflectance measurement, the reflected light is collected and focused onto a detector using PM3, M2 and PM5. The sample can be translated upwards to a thermal evaporator setup (not shown) for \textit{in situ} gold coating. For a transmittance measurement, M2 can be flipped and light is instead collected from behind the sample using PM4, M2 and PM5. The dashed lines represent the transmitted light.
For low temperature measurements, care must be taken to ensure good thermal contact between the sample and the cold finger. Typically, this means using a high thermal conductivity epoxy suitable for low temperatures and high vacuum.

As shown in 2.2, the reflectance or transmittance data are collected by directing light from a thermal source modulated by a Bruker 80v spectrometer onto the sample and then measuring the intensity of the reflected or transmitted light. Covering a broad spectral range requires different combinations of optical components, detectors and sources in different spectral regions. For instance, a measurement in the mid-infrared region would typically employ a HgCdTe detector, a heated SiC rod (Globar) as a thermal source, and KBr windows and beamsplitter. The entire optical arrangement is also enclosed in a vacuum box. This is to minimize thermal drift of the sources and detectors and also to reduce absorption due to atmosphere (principally H$_2$O).

Reflectance and transmittance measurements are absolute measurements and therefore need to be properly referenced. For a transmittance measurement, this can be accomplished by placing the sample under study behind an aperture. A similar sized aperture can then be used as the reference. For a reflectance measurement, the procedure is more complex. Reflectance is very sensitive to the sample surface roughness and geometry, making the preparation of an identically shaped reference prohibitively difficult except in cases where large and optically flat samples are available (such as with some thin film samples). Therefore, an in situ gold coating procedure is usually employed[22]. In this approach, the sample reflectance is first measured with respect to an arbitrary reference, typically a gold mirror of similar area to the sample. The sample is then coated with a thin layer of gold using a thermal evaporator setup incorporated into the cryostat. The gold-coated sample reflectance can then be measured, again with respect to the reference mirror. The ratio of the bare surface reflectance to the gold-coated surface reflectance then gives the intrinsic reflectance of the vacuum-sample interface referenced to the vacuum-gold interface, with geometric effects as well as the reference mirror di-
viding out. At energies above about 1 eV, the optical properties of gold are temperature dependent, meaning *in situ* silver evaporation is preferred. A useful check of the data is to compare the values measured using different optical components in the region of overlap. Both the slopes and magnitude of these should match. Ellipsometry can also be used to estimate the reflectance and therefore provides a similar consistency check.

A key step in an optical spectroscopy experiment is converting the measured response into the optical conductivity $\hat{\sigma}(\omega)$. For a reflectance measurement, this is complicated by the fact that the measurement records a scalar quantity $R(\omega) = |r(\omega)|^2$ at each frequency, while the actual reflectivity $\hat{r}(\omega) = |r(\omega)|e^{i\theta(\omega)}$ is a complex function. An additional constraint is therefore required. For a pure reflectance measurement, this can be accomplished through a Kramers-Kronig (KK) transform $\theta(\omega) = \frac{\omega}{\pi} \mathcal{P} \int_0^\infty d\omega' \ln(R(\omega')/R(\omega))/(\omega^2 - \omega'^2)$ that relates the phase of $\hat{r}(\omega)$ to its magnitude[23]. Once $\hat{r}(\omega)$ is known, the optical conductivity $\hat{\sigma}(\omega)$ can be computed by inverting equation 2.6. Since the KK transform runs over all frequencies, this requires measuring over as large a frequency range as possible and then using suitable extrapolations at low and high frequencies. These extrapolations usually involve conductivity data obtained from other techniques (for instance microwave, DC transport, or UV spectroscopy) and the use of physically motivated model functions (such as the Drude model). The resulting $\hat{\sigma}(\omega)$ can be sensitive to the details of the extrapolation and so this method is not ideal[23]. Alternatively, if both $R(\omega)$ and $T(\omega)$ are known $\hat{\sigma}(\omega)$ can be computed directly from the data without recourse to the KK transform. This approach is taken in chapter 4 of this thesis. A second alternative is to employ spectroscopic ellipsometry to directly measure $\hat{\sigma}(\omega)$. Briefly, ellipsometry measures the complex ratio of $r_p$ to $r_s$, where $s$ and $p$ refer to $s$- and $p$ polarized light. Since two quantities are measured at each frequency, $\hat{\sigma}(\omega)$ can be directly computed from the data. Ellipsometry is experimentally difficult below 0.75 eV and at low temperatures and so it is typically combined with reflectance or transmittance measurements. Indeed, as was shown by Bozovic[24], the $\hat{\sigma}(\omega)$ obtained
from ellipsometry can be used to constrain the phase of $\hat{\sigma}(\omega)$, obviating the need for the full KK transform. This can be accomplished using a KK-consistent parameterization of $\hat{\sigma}(\omega)$ that is simultaneously fit to both the ellipsometry and $R(\omega)$ or $T(\omega)$ data\[^2\text{5}\] , a procedure that is applied in chapters 5 and 6 of this thesis.

### 2.2.2 Raman scattering

As described previously, light can be inelastically or Raman scattered by the elementary excitations of a solid. The experimental setup used to measure this scattering is shown in figure 2.3. Monochromatic light from a laser is focussed onto the sample surface using mirror M1, the dichroic beamsplitter, and the microscope objective. The back scattering geometry is employed, where the same objective is used to collected scattered light from the sample. This light is directed through a pair of notch filters using M2. These filters are designed to reflect light from the excitation laser and transmit other frequencies. Finally, the scattered light is coupled to a grating spectrometer where its spectrum can be recorded.

The setup described above also allows for the analysis of the polarization dependence or selection rules of the Raman scattering process. This is accomplished in two ways. First, an analyzer polarizer P2 is placed before the entrance to the grating spectrometer, meaning only a single polarization state (denoted by X) is measured. Second, the polarization of the incident laser light can be rotated with respect to X by using the half-wave plate WP1 and polarizer P1. Before entering the objective and being focussed onto the sample, the laser light passes through a Fresnel rhomb. This allows the polarization of the laser light to be rotated with respect to the sample. The returning Raman scattered light then passes back through the rhomb and restores the polarization to the 'instrument reference frame'. For example, light initially polarized along X would be rotated by the rhomb to some polarization $X'$ before impinging on the sample. Raman scattered photons of $X'$ polarization would then be rotated back to X upon passing through the
Figure 2.3: Schematic depiction of the Raman scattering experiment. Mirror M1, a dichroic beam splitter, and the objective are used to focus 532 nm laser light onto a sample mounted in a cryostat. Mirror M2 then directs the scattered light to a grating spectrometer. Between M1 and the spectrometer, a pair of Ondax notch filters are used to reject reflected or elastically scattered light from the laser. The polarization state of the incident and collected light with respect to the sample can be selected using the half-wave plate WP, polarizers P1 and P2 and the Fresnel rhomb.
rhomb in the opposite direction. This is particularly useful for the 2D atomic crystals describe in chapter 3 where the atomic crystal orientation with respect to the substrate is not known. By a suitable arrangement of WP1, P1 and the Fresnel rhomb the scattered intensity in both the XX and XY geometries can be measured with respect to an arbitrary direction in the plane defined by the sample surface.

Common experimental difficulties in Raman scattering include local heating due to the laser and the possibility of spurious features due to stray light or photoluminescence. These problems can be checked by examining both the Stokes (red) and the Anti-Stokes (blue) shifted Raman spectra. At temperatures comparable to or larger than the frequency $\omega_o$ of a given Raman-active excitation, this feature should appear at both $\omega_o$ and $-\omega_o$ with respect to the laser line[26]. If a feature does not appear on both sides of the line, it is likely not due to a Raman process. Additionally, in time-reversal invariant systems, the relative ratio of the Stokes and anti-Stokes intensities $I_S$ and $I_{AS}$ are related by $I_{AS}/I_S = e^{-\hbar\omega_o/k_bT}[26]$. Therefore, the local temperature implied by the ratio of $I_{AS}/I_S$ can be compared to the temperature measured by the cryostat thermometer. A final check of any laser heating is to vary the incident power and detector integration times. For instance, halving the laser power and doubling the integration time should produce no change in the measured spectrum (after correcting for detector dark counts) in the absence of laser heating.
Chapter 3

Magnetic excitations of Dy-BSCCO

2D atomic crystals

3.1 Introduction

Cuprate thin films are an appealing platform for devices as well as exploring the roles of dimensionality, disorder, and free carrier density in strongly correlated materials[27, 28]. Mechanical exfoliation has proven to be an effective way of producing a variety of thin crystals[7, 29, 30], although it has mostly been applied to graphene[31, 32] and dichalcogenides[8, 33]. Compared to traditional techniques, mechanical exfoliation allows a large variety of deposited materials and substrates. To determine the viability of this approach in the cuprates, we have produced thin cuprate crystals on oxidized Si substrates via mechanical exfoliation and characterized them with atomic force microscopy (AFM) and Raman microscopy. The measured Raman spectra of these exfoliated samples suggest differences in the magnetic properties versus bulk and provides a critical tool for monitoring sample quality. This is particularly relevant given the previous observation of insulating behaviour in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (BSCCO) 2D atomic crystals[7].
3.2 Mechanical exfoliation of BSCCO

Here we describe the procedure for the isolating BSCCO 2D atomic crystals from a parent van der Waals bulk crystal. This technique is typically referred to as mechanical exfoliation or the ‘Scotch tape’ method. We have also used this technique to produce few-layer samples of the charge density wave compounds TiSe$_2$ and TbTe$_3$, the topological insulator Bi$_2$Se$_3$, and the spin-orbit assisted Mott insulator RuCl$_3$. Mechanical exfoliation also obviates the need for lattice matching which is required for many film growth techniques (e.g. molecular beam epitaxy) and so the techniques allows for a variety of substrates as well. Besides the standard oxidized silicon, we have deposited 2D atomic crystals of BSCCO on bare silicon, GaAs, the magnetic semiconductor (Ga,Mn)As, and mica. A warning is that interference effects in the oxide layer of the standard substrates makes identifying extremely thin crystals possible. For instance, we found that BSCCO 2D atomic crystals are no longer visible on GaAs, with no oxide layer, once the BSCCO thickness is reduced below 20 nm.

The details of the mechanical exfoliation technique are as follows. We focus on the specific case of Bi$_2$Sr$_2$Dy$_x$Ca$_{1-x}$Cu$_2$O$_{8+δ}$ (Dy-BSCCO) with silicon substrates coated in 280 nm of thermal oxide, but the procedure is general. Ideally, the exfoliation process is performed in a dry or N$_2$ atmosphere inside a glove box. For the samples considered later in this chapter, N$_2$ was used. Prior to the exfoliation process, the substrates are baked at 450 K in order to minimize the amount of adsorbed H$_2$O.

Before deposition, a bulk crystal must be selected. In our experience, thin plate-like samples with thicknesses of approximately 10 µm are ideal. Large, flat faces allow for the crystal to be pressed flush to the substrate. If a suitable crystal is unavailable, one may be obtained by cleaving a larger crystal using adhesive tape or a razor blade. The bulk crystal is placed between two pieces of adhesive tape, with the adhesive oriented inwards towards the crystal. The two pieces of tape are then peeled apart and the exposed crystal faces are immediately pressed to the substrate. The adhesive tape around the crystal
edges will adhere to the substrate as well. The back of the adhesive tape/crystal ‘stack’ is then gently rubbed. For this step, we found that the back side of the tip of a pair of carbon fiber tweezers was most effective, at least compared with the metal and Teflon tweezers that were also tried. Too much pressure or the use of sharp tweezers will result in scratching the substrate and deposited crystals that appear to have been crushed. After rubbing for roughly 60 seconds, the tape/crystal stack is removed. The substrate is then inspected with an optical microscope in order to locate any 2D atomic crystals.

We found that ‘pre-cleaving’ a crystal (i.e. peeling part the two adhesive tape layers and then reapplying tape to the exposed faces prior to the actual exfoliation) several times can improve the yield of large and thin 2D atomic crystals. Furthermore, the bulk crystal remaining on the adhesive tape after deposition can also be reused, provided a fresh crystal surface can still be obtained by cleaving.

Due to interference effects in the 2D atomic crystals and the oxide layer (if present), the reflectivity of the 2D atomic crystals is sensitive to thickness. This allows for the identification of thin crystals as well as roughly characterizing their thickness. Indeed, we have identified crystals of Dy-BSCCO as thin as three unit cells (∼9 nm) in this manner. Example samples of a variety of thicknesses (and thus colours) are shown in figure 3.1. After being identified optically, potentially thin crystals were then examined using a Digital Instruments Nanoscope III AFM operating in contact mode to measure their dimensions. An example AFM image is shown in figure 3.2. These exfoliated crystals can be tens of microns across and as thin as three unit cells. As seen in figure 3.2, samples tend to be planar (RMS roughness < 1.5 nm comparable to the bare substrate roughness) and have well-defined edges. The small thickness and large cross-sectional area of these samples makes them promising candidates for studies of electrostatic doping and the effects of dimensionality.

Our AFM and optical microscopy studies allow us to explain the observed colour variation with atomic crystal thickness. This behaviour can be understood as an interference
Figure 3.1: Optical microscope images of 2D atomic crystals. All scale bars are 20 microns. A) 13 nm thick crystal (dark cyan) B) 17 nm (dark blue) and 20 nm (light blue) thick crystals C) 42 nm thick crystal (bright green region) and 160 nm thick crystal (dark green region) D) Exfoliated crystal of varying height. The yellow and orange regions are both thicker than 100 nm.
Chapter 3. Magnetic excitations of Dy-BSCCO 2D atomic crystals

Figure 3.2: AFM image (left panel) and profile (right panel) of a 42 nm 2D atomic crystal. The red line in the image corresponds to the profile displayed in the right panel. An optical image of this same crystal is shown in figure 3.1 C).

effect. Specifically, contrast can be defined as the difference in reflected intensity from an exfoliated crystal and the bare substrate normalized to the substrate value. Using bulk optical constants from reference [34], a calculation of crystal contrast similar to reference [35] suggests that the thinner the crystal, the more blue it should appear. The results of this calculation are shown in figure 3.3 where we display the contrast as a function of crystal thickness and wavelength. The contrast for a 20 unit cell crystal peaks in the green. As the crystals become thinner, the peak contrast blue-shifts and decreases.

To confirm this calculation, visibility measurements were performed using a colour CCD camera coupled to an optical microscope. Figure 3.4 displays the measured (open circles) and calculated (curves) crystal visibilities for a variety of thicknesses. The calculated visibilities were determined by integrating the calculated contrast over the spectral response of a given CCD channel. These measurements show the results of the contrast calculation to be qualitatively correct. While this data suggests that these exfoliated pieces are indeed BSCCO, it is necessary to establish whether these exfoliated crystals remain BSCCO or form some other phase.
3.3 **Raman spectroscopy of Dy-BSCCO 2D atomic crystals**

Polarized Raman spectroscopy is a well established tool for identifying materials and has been widely applied to the cuprates\[36, 37\]. A Horiba Jobin Yvon LabRam Raman microscope with a 532 nm excitation source and 100x (0.8 NA) microscope objective was used to measure the Raman spectra of bulk and exfoliated samples. Measurements were performed in the backscattering geometry. The notation XY, for instance, refers to incident light polarized along the $a$ axis (along the Cu-O bond) with scattered light polarized along the $b$ axis; while $X'$ and $Y'$ refer to directions 45 degrees from $X$ and $Y$ respectively. Raman spectra contain components corresponding to the different symmetry projections of the material and these components can be distinguished by their different polarization dependences. BSCCO is known to be nearly tetragonal and so we take spectra in the $XX$, $X'X'$, $XY$, and $X'Y'$ polarization geometries. For tetragonal
Figure 3.4: CCD visibility measurements for red (top) and blue (bottom) channels. The solid curves represent the visibility expected from the calculation illustrated in figure 3.3 while open circles are the measured crystals visibilities.
(D\textsubscript{4h}) crystal symmetry, XX corresponds to B\textsubscript{1g} + A\textsubscript{1g}, X'X' to B\textsubscript{2g} + A\textsubscript{1g}, XY to B\textsubscript{2g} + A\textsubscript{2g}, and X'Y' to B\textsubscript{1g} + A\textsubscript{2g}.

At Raman shifts less than 1000 cm\textsuperscript{−1} exfoliated sample spectra are dominated by signal from the silicon substrate, making phonon peaks difficult to identify. Fortunately, bulk BSCCO has two features at higher energies: a collection of two-phonon peaks broadened into a single feature around 1250 cm\textsuperscript{−1} and a broad two-magnon feature centered between 2000-3000 cm\textsuperscript{−1} depending on doping (see references [36] and [37]). Since thin materials are easily damaged by laser radiation[29], we tried a variety of exposure times and excitation powers to maximize the signal to noise ratio while minimizing exposure to the Raman excitation source. Limiting the samples exposure to the laser to approximately ten seconds at 0.5 mW produced no observable changes in the Raman response. Finally, the measured spectra have been corrected for interference effects as described elsewhere[39]. Raman intensity units are arbitrary but consistent between plots.

The measured bulk spectra (figure 3.5 (a)) show both the two-phonon and the two-magnon features as expected from the literature. The two-phonon feature near 1300 cm\textsuperscript{−1} appears primarily in the fully symmetric A\textsubscript{1g} channel (XX and X'X'). In addition, a broad two-magnon feature appears in B\textsubscript{1g} (XX and X'Y') near 2500 cm\textsuperscript{−1}. For the most part, these two features are also visible in the exfoliated samples. Note that only data for x = 0.4 crystals is displayed, although the behaviour of x = 0.3 bulk and exfoliated crystals are qualitatively identical. The Raman features observed in typical exfoliated crystals (figure 3.5 (b)) generally retain the selection rules expected from bulk measurements and from the literature for an ab-face. This confirms that the cleavage plane is in fact the ab-plane. In both exfoliated and bulk samples, we find that the two-magnon feature is principally in the B\textsubscript{1g} symmetry channel while the two phonon excitation appears predominantly in A\textsubscript{1g}. This suggests that exfoliated samples retain the crystal symmetry of the bulk. The polarization dependence of the two-magnon feature in BSCCO also allows the identification of the crystal axes of an exfoliated sample, although it cannot
Figure 3.5: Polarized Raman spectra for a) bulk b) 42 nm exfoliated crystal c) degraded 30 nm exfoliated crystal d) XX and X′X′ spectra have been offset for clarity. The spectra in a) and b) show a marked polarization dependence compared with c).
distinguish between the $a$ and $b$ axes.

The polarization dependence of the Raman spectra also reveals information about degradation in the exfoliated crystals. Certain exfoliated sample spectra, particularly from older samples, do not exhibit the expected selection rules. As shown in figure 3.5 (c), spectra from such samples show only a slight polarization dependence and a weak two-magnon peak. This is attributed to sample degradation and is discussed in more detail later. There are, however, important differences between bulk and exfoliated spectra even when the expected selection rules are observed. Figure 3.6 (a) illustrates the evolution of the two-magnon line shape with thickness. Spectra from thin crystals ($< 50$ nm) show a large enhancement in the amplitude of the two-magnon peak, as well as an apparent blue shift in the peak positions of the two-magnon (from around 2500 cm$^{-1}$ to 2900 cm$^{-1}$). The shift is more clearly seen in figure 3.6 (b), which shows both bulk and 30 nm spectra. It should be noted that the bulk spectrum has been scaled to match the peak heights of the exfoliated 2D atomic crystal.

### 3.4 Discussion

There are several factors that could potentially cause significant change in the Raman spectra of the exfoliated samples. The first is the interference correction mentioned earlier. This correction is sensitive to the thickness of the SiO$_2$ layer, so any variation from the nominal value (280 nm) would produce a distortion of the Raman spectra. The thickness of the thermal oxide layers used in this work can vary by 5 percent, according to the manufacturer and confirmed by ellipsometry measurements. Figure 3.6 (c) shows the effect of this variation on the corrected spectra of a 10 unit cell exfoliated sample. The thickness of the oxide layer can affect the ratio of the two-phonon and two-magnon features as well as influence their lineshapes. However, this effect is insufficient to account for the observed blue shift and enhancement of the two-magnon. The Raman response
Figure 3.6:  a) Variation of XX spectra with thicknesses. b) XX spectra for bulk and a 10 unit cell exfoliated sample showing a shift in the two-magnon peak position. Data has been scaled to normalize peak height. c) Effect of oxide layer variation on interference corrected spectra.
therefore suggests a real change in the magnetism of the 2D atomic crystals with respect to bulk.

A change in doping level could account for the observed change in the exfoliated crystal magnetism. One possibility is environmental doping by charged impurities on the SiO$_2$ surface. This effect has previously been observed in graphene[40]. Typically holes are added to the graphene layer and we might expect a similar effect in exfoliated BSCCO. However, the two-magnon feature in hole-based cuprates is known to red-shift, weaken and broaden with doping[36, 37], while our spectra blue-shift and grow (see figures 3.6 (a) and 3.6 (b)). Another possibility is oxygen outdiffusion. This effect has been observed in BSCCO microwhiskers[41, 42]. Oxygen loss would be expected to reduce the number of holes in the exfoliated crystal and so is consistent with the observed change in the two-magnon. Indeed, the peak position of the two-magnon feature seen in the exfoliated crystals is consistent the peak location reported elsewhere for antiferromagnetic and insulating Bi-2212 [37]. Lastly, one might conjecture that a structural change in the exfoliated BSCCO sample could be responsible for shifting the two-magnon peak. As the energy and efficiency of the two-magnon process depends on the hopping integral $t$ and the exchange integral $J$[36, 43, 44], an increase in both of these parameters could explain the peak enhancement and shift observed in thin exfoliated crystals. Indeed, x-ray diffraction studies of BSCCO 2D atomic crystals have demonstrated a subtle modification in the lattice structure that might be expected to influence to Cu-O bond angle and therefore the hopping integral $t$[10].

Finally, BSCCO is known to degrade in atmosphere,[45] which would produce a corresponding change in the Raman spectra. Given the the thickness of these exfoliated samples, even thin surface degradation can be expected to have a pronounced effect on the measured Raman features. Indeed, the first work done on exfoliated BSCCO crystals found that even optimally doped exfoliated crystals were insulating[7] when deposited in air. We find that older samples tend to show less distinct symmetry, as evidenced
by the XX and X’X’ spectra shown in figure 3.5 (c). Specifically, the difference between
the XX and X’X’ geometries is less pronounced and the overall scattered intensity is
reduced. The particular sample shown in 3.5 (c) was exposed to air for tens of hours as
well as potentially damaged by over exposure to the Raman excitation laser. It should
be noted that the loss of selection rules suggests the crystals are becoming amorphous.
The two-phonon feature is also absent in 3.5 (c), consistent with a degradation of the
lattice structure. Polarized Raman spectroscopy therefore provides a powerful method
for identifying degradation in exfoliated samples. As we discuss in detail in chapter 4,
BSCCO 2D atomic crystals also evince a reduction in the optical conductivity $\sigma_1(\omega)$ due
to chemical changes near the sample surface.

3.5 Conclusions

The work described here suggests that exfoliated cuprate 2D atomic crystals can be
produced with dimensions suitable for device applications. FET devices would allow the
investigation of a number of important issues relating to cuprate physics, principally the
disentanglement of disorder and carrier density. Significant differences were observed
between the two-magnon Raman spectra of exfoliated and bulk BSCCO. However, when
properly handled, these samples demonstrate selection rules and energy scales similar
to bulk. This suggests that the 2D crystals remain sufficiently bulk-like to merit study.
Changes in the Raman spectra of these materials with time also indicate the importance
of minimizing sample exposure to atmosphere and to laser radiation. The two most
important directions for further research are transport measurements on exfoliated 2D
crystal devices (field effect and transport) as well as depositing BSCCO thin crystals on
other substrates. In particular, transport measurements could help elucidate the role of
disorder in the formation of the pseudogap and in normal state transport. A Raman-
inactive substrate (such as quartz) would allow study of the lower energy Bi-2212 phonon
modes and thus provide important insight into the structure of these cuprate thin crystals. Nonetheless, we have demonstrated the importance of AFM and Raman microscopy in establishing the quality of exfoliated samples for these applications.

3.6 Co-authorship

Chapter 3 is a reprint, with some modification, of ‘L.J. Sandilands, J.X. Shen, G.M. Chugunov, F. Zhao, S. Ono, Y. Ando, and K.S. Burch, “Stability of exfoliated Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ studied by Raman microscopy”, Physical Review B 82, 064503 (2010)’. The copyright is held by the American Physical Society and the material is reproduced with permission.

The thesis author was the primary investigator in this study, prepared the samples, performed the Raman and AFM measurements using existing instruments, and wrote the paper. The bulk BSCCO crystals used in this work were provided by Yoichi Ando and Shimpei Ono, then of CRIEPI in Japan. The AFM work was performed with assistance from Richard McAloney and Cynthia Goh at the University of Toronto.
Chapter 4

Carrier dynamics in BSCCO 2D atomic crystals

4.1 Introduction

Mechanical exfoliation of layered crystals has recently emerged as a new approach to producing unusual electronic materials, with the most prominent examples being graphene and single layer MoS$_2$. In pioneering work, Novoselov and collaborators showed that this method can be used to synthesize a wide array of ultra-thin films (termed ‘two-dimensional atomic crystals’), including single unit cell crystals of the high-$T_c$ cuprate superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (BSCCO)[7]. Besides enabling a variety of experiments[46], such as electrostatic gating[33, 47], these materials can have electronic properties that differ markedly from the bulk[8, 31]. Intriguingly, single-layer BSCCO was found to be insulating, in contrast to the metallic behavior observed in ultra-thin cuprate films grown by MBE or CVD[48, 49, 50], as well as to the expectation that the physics of the cuprates is intrinsically two-dimensional (i.e. a property of a single copper oxygen plane). To better understand this apparent contradiction, we have investigated the optical properties of two-dimensional BSCCO atomic crystals.
The electronic properties of the cuprates\cite{34, 51, 52, 53} and exfoliated materials\cite{31, 32} in general are often probed through optical methods. Indeed, optical spectroscopy is an ideal tool for studying exfoliated BSCCO, as it provides access to the carrier dynamics and electronic structure\cite{6}. This technique also has the advantage of not requiring nanofabrication (i.e. photoresists, solvents, and other chemicals) and is insensitive to contact resistance or extended defects that might be expected to influence DC measurements. In this work, we present the results of an optical study of exfoliated BSCCO of various thicknesses. Our measurements indicate pronounced changes in the optical properties with thickness, which we attribute to deoxygenation of the sample surface. Further analysis reveals an additional subtle modification of the electrodynamics of the underlying, pristine BSCCO. Specifically, the spectral function which describes the interaction between the conduction electrons and the system’s bosonic excitations is enhanced and blue-shifted. This can be understood as a consequence of a change in the distribution of bond angles within the CuO$_2$ plane that accompanies the suppression of the incommensurate superstructure recently observed by x-ray micro-diffraction\cite{10}.

The chapter is organized as follows: Section 4.1 details the exfoliated BSCCO samples and experimental methods used in our optical study. In section 4.2, we discuss how the optical constants of exfoliated BSCCO evolve as a function of thickness. Section 4.3 describes how the data can be understood using a simple effective medium approximation (EMA), which assumes that a region near the surface of the sample has become insulating. We then use this EMA to correct for the presence of the insulating layer and extract the optical constants of the underlying ‘intrinsic’ exfoliated BSCCO. In section 4.4, we demonstrate, through an extended Drude analysis of the carrier dynamics, that the electron-boson interaction in ‘intrinsic’ exfoliated BSCCO changes as a function of thickness. Finally, we present some final discussion and our conclusions in section 4.5.
4.2 Sample and experimental details

Two-dimensional atomic crystals of BSCCO were deposited, via the mechanical exfoliation technique\[7, 54, 55\], on 350 micron thick silicon substrates capped with 280 nm of silicon dioxide (Silicon Quest International). The optimally-doped bulk crystals used in the deposition were grown by the traveling floating zone method at Brookhaven National Laboratory and have typical transition temperatures of 90 K \[56\]. Prior to exfoliation, the substrates were prebaked at 425 K for 15 minutes in an effort to minimize the amount of adsorbed water at the BSCCO/SiO\(_2\) interface and the entire procedure (substrate baking and exfoliation) was performed in a dry atmosphere. Large (greater than 20 by 20 microns in area) samples were then identified through optical microscopy \[54\] and stored in vacuum prior to measurement at the Canadian Light Source. Film thickness was established with a Digital Instruments Nanoscope III atomic force microscope operating in contact mode. Sample thicknesses typically range from 10 to 200 nm.

It is worth noting at this point that our exfoliated BSCCO samples are well-defined single crystals that retain the symmetries of the bulk, with no evidence for structural granularity or any drastic changes in the lattice. First, TEM studies have demonstrated that BSCCO 2D atomic crystals are monocrystalline and have the same crystal structure as bulk\[7\]. This was further confirmed by Raman scattering and X-ray Laue microscopy experiments\[10, 57, 54\]. Raman scattering selection rules (i.e. whether an excitation can be observed or not) follow from the translational and point group symmetries of the lattice. Translational symmetry means that only \(q = 0\) processes can be observed, while point group symmetry impose certain polarization dependences. In a previous unpolarized Raman study of BSCCO 2D atomic crystals\[57\], Wang et al. studied scattering due to phonons as a function of thickness. They found that the number and frequency of these modes was unchanged with thickness, meaning that the lattice translational symmetry and dynamics are unperturbed in exfoliated BSCCO. As described in chapter 3, we have also studied the two-magnon feature in underdoped exfoliated BSCCO films us-
ing polarized Raman microscopy\cite{54}. While this feature was blue-shifted and enhanced compared to bulk, its polarization dependence was unaltered with thickness, meaning the pseudo-tetragonal symmetry of the BSCCO lattice is also unchanged. Finally, x-ray Laue micro-diffraction measurements show a diffraction pattern unchanged from bulk, save for subtle changes associated with the incommensurate superstructure, demonstrating unequivocally that our BSCCO films are single crystal with the $c$-axis oriented normal to the substrate surface\cite{10}.

Optical measurements of the BSCCO/SiO$_2$/Si/SiO$_2$ samples (shown schematically in the inset of figure 4.2 (c)) were performed at the Canadian Light Source Mid-IR beamline at room temperature with 16 cm$^{-1}$ resolution using a Bruker Hyperion infrared microscope equipped with a 15x (0.4 NA) objective, a Bruker Vertex 80v spectrometer and a liquid nitrogen-cooled HgCdTe detector. The spectra are referenced to nearby bare region of the substrate in order to minimize errors due to system drift or alignment. Given the orientation of our films as determined from Raman microscopy, this experimental geometry is sensitive to the $ab$-plane optical constants. Example reflectance and transmittance data for a 23 nm film are shown in figure 4.1. The minimum (maximum) in the reflectance (transmittance) is due to Fabry-Perot effects in the oxide layer, while the sharp feature near 1250 cm$^{-1}$ is a SiO$_2$ phonon. These measurements are reproducible to within 1.5 % and 0.5 % for transmittance and reflectance respectively. This reproducibility in turn determines the uncertainties in the measured optical constants.

Accurate knowledge of the substrate optical constants is needed to analyze the measurements of the multilayer structures described above. Similarly, the optical properties of our bulk BSCCO crystals need to be well-established if any changes with thickness are to be identified. We therefore measured the optical response of the ‘parent’ BSCCO crystals and of the oxidized silicon substrates. The optical properties of the substrate were determined using a combination of reflectance, transmittance and ellipsometric measurements, while the response of bulk BSCCO was extracted from broadband reflectivity data.
The reflectance and transmittance measurements were performed at room temperature using a Bruker Vertex 80v spectrometer with photon energies in the range of 80 to 11000 cm\(^{-1}\). For reflectance referencing, we used a gold mirror, and for the BSCCO a standard in situ gold overcoating technique was employed\cite{22}. Ellipsometric measurements of the substrates were performed using a Woolam VASE spectroscopic ellipsometer in the range 6000 to 36000 cm\(^{-1}\). The optical constants of BSCCO were determined by extending the measured reflectance to higher frequencies using previously published data\cite{34} and applying a Kramers-Kronig analysis. For the oxidized silicon substrates, the reflectance, transmittance and ellipsometric data were modeled using the Woolam VASE software. The optical constants of the Si and SiO\(_2\) layers were parameterized using an oscillator model which was then adjusted to match the experimental data. The results obtained in this way are consistent with reported measurements of BSCCO, silicon, and silicon dioxide\cite{34, 58, 59}.

To determine the optical constants of the BSCCO 2D atomic crystals from our microscopy data, we used a multilayer model implemented with the RefFIT software package\cite{60}. The model allows for multiple reflections in the BSCCO and SiO\(_2\) layers but not in the silicon substrate, as Fabry-Perot effects from the substrate are not visible at our experimental resolution of 16 cm\(^{-1}\). The thicknesses of the BSCCO layers were fixed to the values measured with AFM while the SiO\(_2\) thickness was set to 280 nm, according to the manufacturer’s specifications and confirmed by our ellipsometry measurements. To model the complex optical constants of the BSCCO samples, we used a Kramers-Kronig consistent variational dielectric function\cite{25}, which was then adjusted to reproduce the experimental data. Example fits for a 23 nm film are shown in figure 4.1 along with the corresponding data. The extracted BSCCO optical constants above 5200 cm\(^{-1}\) are sensitive to the thickness and optical constants of the oxide layer used in the multilayer model. In addition, SiO\(_2\) has several strong infrared-active phonons below 1400 cm\(^{-1}\). These features can lead to artifacts in the BSCCO optical constants and so
Figure 4.1: Top panel: Reflectivity data and model fit for a 23 nm exfoliated sample. The data is in black and the fit in red. Bottom Panel: Measured and model transmittance for the same sample. At low frequencies near 1250 cm\(^{-1}\), sharp features due to a SiO\(_2\) phonon are visible in both reflectance and transmittance. The broad reflectance minimum and transmittance maximum near 6000 cm\(^{-1}\) are due to interference effects in the SiO\(_2\) layer.
we limit our discussion to the frequency range 1400 to 5200 cm$^{-1}$.

### 4.3 Optical response of BSCCO 2D atomic crystals

The end result of the measurement and analysis procedure described above are the optical constants of exfoliated BSCCO. In considering the optical response of our samples, we focus on the real parts of the complex conductivity ($\sigma = \sigma_1 + i\sigma_2$) and the complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$). The real parts of these quantities are finite frequency generalizations of the DC conductivity and static dielectric constant respectively and reflect the carrier dynamics and electronic structure of the exfoliated BSCCO. The dielectric function ($\epsilon_1$) and optical conductivity ($\sigma_1$) of the exfoliated samples and of a bulk crystal are displayed in figures 4.2 (a) and 4.2 (b) respectively.

The optical functions $\sigma_1$ and $\epsilon_1$ of the 123 nm sample display Drude-like behavior that is the spectroscopic signature of metallic transport. This Drude mode manifests itself in the real part of the optical conductivity $\sigma_1$ as a zero frequency peak with a width given by the free carrier scattering rate $(1/\tau)$ and a spectral weight proportional to the squared plasma frequency $\omega_p^2 \propto (n/m_b)$, where $n$ is the carrier density and $m_b$ the optical mass [19]. This mode also leads to a negative $\epsilon_1$ that peaks at $\omega = 0$. Similar to $\sigma_1$, the finite frequency magnitude of the Drude mode in $\epsilon_1$ is strongly affected by the plasma frequency. As seen in figure 4.2 (a) and 4.2 (b), thinner exfoliated samples reveal a $\sigma_1$ that is systematically reduced and an $\epsilon_1$ that is increased. These results indicate a suppression of metallicity. The thinnest samples measured, 16 nm and 12 nm (not shown), reveal a flat, featureless $\sigma_1$ and a positive $\epsilon_1$ indicating fully insulating behavior. The loss of metallicity can be quantified through the integrated spectral weight[6]. Let us define $W = \int_{\omega_1}^{\omega_2} \sigma_1(\omega)d\omega$, where the integral is performed over the frequency range 1400 to 5200 cm$^{-1}$, and is shown for all samples in figure 4.2 (c). The thickest sample (123 nm) shows a weight of roughly $2 \times 10^6 \ \Omega^{-1}\text{cm}^{-2}$ only slightly suppressed from bulk,
Figure 4.2: Optical properties of exfoliated BSCCO 2D atomic crystals. (a) The real part of the dielectric function $\epsilon_1$. (b) The real part of the optical conductivity $\sigma_1$. The arrow indicates the trend of decreasing conductivity with decreased film thickness. (c) The spectral weight $W$ integrated from 1400 to 5200 cm$^{-1}$. Color coding is consistent between plots (a) and (b). A schematic of the measurement geometry is shown in the inset of (c). The overall decrease in $\sigma_1$ and increase in $\epsilon_1$ signals that the BSCCO 2D atomic crystals are becoming less metallic with decreasing thickness.
while the weight of the thinnest sample is depressed by an order of magnitude from the bulk value.

The observed changes are apparent in relatively thick (tens of nanometers) samples. Given the incoherent optical response\cite{51} and negligible electronic dispersion\cite{61} along the c-axis of BSCCO, we do not expect quantum size effects to be significant. On the other hand, several experiments have demonstrated oxygen depletion from BSCCO surfaces \cite{62, 63}, and so we attribute the reduced metallic behavior to a more prosaic effect, namely the escape of oxygen interstitials that causes a region near the surface to become insulating. This suggests that the insulating behavior observed in single unit cell BSCCO\cite{7} is an extrinsic effect.

4.4 Effective Medium Approximation

The scenario of a deoxygenated surface in our exfoliated films points to the interpretation of the optical data through an effective medium approximation (EMA) in which the measured response is a volume average of two different media (in this case an insulating surface and a relatively unperturbed core)\cite{64, 65}. For light with frequency $\omega = 2000$ cm$^{-1}$ and vacuum wavelength $\lambda_{\text{vac}} = 5$ µm, the optical constants of bulk BSCCO yield a refractive index $n \approx 5.8$, meaning the optical wavelength at this frequency is roughly $\lambda = \lambda_{\text{vac}}/n = 855$ nm inside the BSCCO. Similarly, the optical penetration depth is roughly 150 nm over the measured spectral range. Since this is an order of magnitude larger than the samples considered here (except for the thickest crystal), we can naively consider the samples as consisting of two conductors in parallel. Furthermore, the long wavelength of our probe photons means our measurements are also insensitive to short length-scale variations of the oxygen content, such as at the interface between conducting and insulating regions. The effective complex optical conductivity is then given by $\hat{\sigma}_{\text{EMA}} = f_b \hat{\sigma}_\text{int} + (1 - f_b) \hat{\sigma}_\text{surf}$. Here $\hat{\sigma}_\text{int}$ and $\hat{\sigma}_\text{surf}$ are the conductivities of metallic
BSCCO and the insulating layer, respectively; $f_b$ is the metallic volume fraction and is equal to $(t - d)/t$, where $t$ is the sample thickness as measured by AFM and $d$ is the thickness of the insulating layer.

To evaluate the validity of this approximation, we return to the spectral weight shown in 4.2 (c). Taking the real part of $\sigma_{EMA}$ and integrating yields $W_{EMA} = f_b W_{bulk} + (1 - f_b) W_{surf}$, where $W_{bulk}$ and $W_{surf}$ are the interior and surface spectral weights respectively. The change of the spectral weight with thickness shown in figure 4.2 (c) is well-described by this expression (plotted in solid red) assuming physically reasonable values for the insulating layer thickness ($d$), the insulating layer ($W_{surf}$) and bulk ($W_{bulk}$) spectral weights. Fitting these quantities to the data yields values $d = 14.6$ nm, $W_{surf} = 2 \times 10^5 \Omega^{-1} \text{cm}^{-2}$, and $W_{bulk} = 2.4 \times 10^6 \Omega^{-1} \text{cm}^{-2}$. The fitted parameters are in agreement with the measured bulk spectral weight, the measured insulating crystal spectral weight, and with the observed onset of insulating behaviour in the thinnest (less than 16 nm) samples. This agreement provides strong support for the presence of an insulating surface and for the applicability of the EMA.

Having established the validity of the EMA, we turn to the evolution of the intrinsic layer electrodynamics with thickness. We follow a previously established approach[64] to obtain the optical properties of the metallic BSCCO layer from the EMA. Briefly, we assume that the intrinsic layer optical constants are identical to bulk and that the insulating layer optical constants are equal to those of the 16 nm sample ($\sigma_1 \approx 50 \Omega^{-1} \text{cm}^{-1}$ and $\epsilon_1 \approx 3$). The measured optical constants are then fit using a single parameter, the volume fraction $f_b$. This value is then used to extract the optical properties of the ‘intrinsic’ layer by inverting the equation for $\hat{\sigma}_{EMA}$ given above. The thickness of the intrinsic layer is then computed by multiplying the fitted volume fraction by the total sample thickness measured in AFM. This procedure yields insulating layer thicknesses ranging from 5.5 to 15 nm, in rough agreement with the thickness inferred from the spectral weight. The $\sigma_1(\omega)$ and $\epsilon_1(\omega)$ of the intrinsic BSCCO that result from this procedure are shown in
Figure 4.3: Optical constants of the exfoliated, metallic BSCCO. (a) Optical conductivity $\sigma_1$. (b) Dielectric function $\epsilon_1$. (c) Optical scattering rate $1/\tau$. (d) Mass enhancement $m^*/m_b$. The effective thicknesses of these samples is listed in the legend. The pale cyan areas indicate the estimated uncertainty for the 9.5 nm exfoliated sample. As can be seen in panels (a) and (b), the optical properties of the BSCCO 2D atomic crystals differ from bulk, with a lower $\sigma_1$ and a slightly more negative $\epsilon_1$. This change is revealed in panels (c) and (d) to be due to a decrease in $1/\tau(\omega)$ and an increase in $m^*/m_b$. 
figures 4.3 (a) and 4.3 (b). The gross form of the spectra are consistent with a Drude feature and thus of delocalized, metallic states. Importantly, the variation in intrinsic layer optical functions from 44.5 nm to 5.5 nm shown in 4.3 (a) and 4.3 (b) is not systematic and is within our experimental uncertainty. While the conductivity behaves similarly to bulk in the 111 nm thick sample, it is suppressed and flattened with respect to bulk in the remaining exfoliated samples, particularly in the low frequency region. Finally, the agreement between optical constants of exfoliated samples of different thickness validates the above analysis. Fixing the dead layer thickness or allowing the dead layer optical constants to vary over a reasonable range does not qualitatively impact our results.

4.5 Extended Drude analysis and electron-boson coupling in exfoliated BSCCO

To gain further insight into the charge dynamics of exfoliated BSCCO, we employ the extended Drude analysis often applied to the cuprates and other correlated metals[6, 66, 67]. In this approach, the charge carriers are allowed to acquire a frequency-dependent scattering rate $1/\tau(\omega)$ and mass enhancement $m^*/m_b$. In the cuprates, the frequency dependent scattering rate and mass enhancement are typically attributed to coupling between the charge carriers and collective bosonic modes[68]. The scattering rate and the mass enhancement are related to the optical response by [34]:

$$\hat{\epsilon}(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2(m^*/m_b) + i\omega(1/\tau(\omega))}. \quad (4.1)$$

Here $\epsilon_\infty$ represents screening due to interband transitions. These two quantities are plotted in figure 4.3 (c) and (d) for various intrinsic thicknesses. We have used $\epsilon_\infty = 4.77$ and $\omega_p = 19364$ cm$^{-1}$, consistent with the literature[52] and our measurement of bulk BSCCO. The scattering rate of the exfoliated samples shows a quasi-linear increase at low
frequencies with a saturation around 3500 cm\(^{-1}\). The mass enhancement in the exfoliated samples decreases monotonically from a value of almost three at low frequency to a value approaching unity at 5000 cm\(^{-1}\). The mass enhancement should, by definition, approach 1 at high frequencies\(^5\). The fact that this behavior is observed in the intrinsic layer mass enhancements further validates our EMA analysis and suggests that the plasma frequency is unchanged in exfoliated BSCCO. Both \(1/\tau(\omega)\) and \(m^*/m_b\) differ significantly from the behaviour observed in bulk. Specifically, the spectra of the exfoliated samples have a similar shape to bulk but appear blue-shifted. Our results therefore indicate a change in the electron-boson interaction and, in particular, a redistribution of bosonic weight to higher frequencies.

To verify this scenario, we follow the procedure of reference \(^6\) and model the normal state optical conductivity of our bulk and exfoliated samples within the Allen approximation. In this approach, the electron-boson interaction is expressed through the spectral function \(\alpha^2 F(\omega)\), which accounts for both the strength of the coupling and the bosonic density of states. We start by parameterizing the electron-boson spectral function \(\alpha^2 F(\omega)\) as the sum of the imaginary part of a Lorentzian located at zero frequency and a Gaussian peak at finite frequency. However, the exact parameterization of \(\alpha^2 F(\omega)\) is unimportant and a variety of schemes have been shown to work. The electron-boson coupling is given in this case by

\[
\alpha^2 F(\Omega) = \frac{\Gamma \Omega}{\gamma^2 + \Omega^2} + Ae^{-\frac{(\Omega-\Omega_g)^2}{2\lambda^2}}
\]  

(4.2)

where \(\Omega\) is the frequency, \(\Gamma\) and \(\gamma\) are the Lorentzian parameters, and \(A\), \(\Omega_g\), \(\lambda\) are the Gaussian amplitude, center frequency, and width respectively. The optical scattering rate is then determined by the finite temperature Allen formula:

\[
1/\tau(\omega) = \frac{1}{\omega} \int_0^{\omega_c} d\Omega \alpha^2 F(\Omega)[2\omega \coth(\frac{\Omega}{2T})-\omega-\Omega]\coth(\frac{\Omega+\omega}{2T})+\omega-\Omega]\coth(\frac{\Omega-\omega}{2T})] + \Gamma_i,
\]  

(4.3)

where \(\omega_c\) is a high-energy cutoff, \(\Omega\) is the energy of a bosonic scatterer, \(T\) is the tem-
Figure 4.4: Model and experimental optical constants for bulk and exfoliated BSCCO. (a) Scattering rate $1/\tau(\omega)$. (b) Mass enhancement $m^*/m_b$. (c) Electron-boson spectral functions used to generate model curves in (a) and (b). The good agreement between the model curves and the measured $1/\tau(\omega)$ and $m^*/m_b$ suggest that $\alpha^2 F(\omega)$ blue-shifts and is enhanced in BSCCO 2D atomic crystals.
temperature and $\Gamma_i$ is the scattering rate due to impurities. For our calculations, we have employed a high-frequency cutoff $\omega_c$ of 3000 cm$^{-1}$, consistent with previous work[69].

The scattering rate and the mass enhancement are Kramers-Kronig related as they are in the most general sense a parameterization of the complex polarizability $\hat{\epsilon}(\omega)$, a linear response function. The mass enhancement $m^*/m_b$ can therefore be computed from the scattering rate by a Kramers-Kronig transform[70]. We have attempted to reproduce the measured optical response of our bulk and exfoliated samples by varying the parameters in equation 4.2 and thereby varying the electron-boson spectral function. The parameters resulting from this procedure for each spectral function are displayed in table 5.1. A shift in weight to higher frequencies can be seen in the increase of the Gaussian component. Note that these parameters are not the result of a fit. The two spectral functions are merely to demonstrate that a shift of bosonic weight to higher frequencies can explain the optical data.

The results of our calculations of $1/\tau(\omega)$ and $m^*/m_b$ are shown in figure 4.4, for the three example spectral functions plotted in 4.4 (c). These functions were chosen to capture the behavior observed in our bulk and exfoliated samples, as well as to illustrate the effect of red-shifting the bulk spectrum. The bulk $\alpha^2 F(\omega)$ is similar to previous reports [69, 71]. Importantly, the bulk and exfoliated spectral functions differ in that the spectrum of the two-dimensional atomic crystal has significantly more weight at higher frequencies and less at low frequencies. This is consistent with the shift of the scattering rate and mass enhancement spectra seen in figures 4.3 (c) and (d).

Let us now consider alternative explanations of this behavior, including possible changes in $\omega_p$ or $\epsilon_{\infty}$, uncertainties in the insulating layer optical constants, or other
rearrangements of $\alpha^2 F(\omega)$. Given the suspected decrease in oxygen content, it is tempting to attribute the decrease in the scattering rate to a decrease in $\omega_p$. However, a decrease in $\omega_p$ would also reduce $m^*/m_b$, which we do not observe experimentally. The change cannot be explained by a reduction in impurity scattering either. Our bulk data is well described by $\Gamma_i = 375$ cm$^{-1}$. Reducing this quantity, even to zero, is therefore insufficient to explain the experimental scattering rates of exfoliated BSCCO, which are typically reduced from the bulk value by 500 cm$^{-1}$. Naively, the increased $m^*/m_b$ observed in BSCCO 2D atomic crystals could be explained by a increase in $\omega_p$. However, an increased plasma frequency would require an even greater decrease in impurity scattering. Additionally, the measured mass enhancement of the exfoliated samples is not related to the bulk mass enhancement by a simple multiplicative factor, as can be seen in figure 4.3 (d). These changes are also not due to errors in the measured insulating layer optical constants. If this were the case, we would expect a significant difference between spectra from the thicker (44.5 nm) and thinner (5.0 nm) samples. We note that other possible changes in the spectral function cannot explain the key aspects of the data (namely the reduced scattering and enhanced mass). An overall reduction (increase) in $\alpha^2 F(\omega)$ causes a reduction (increase) in both scattering and the mass enhancement. Finally, a movement of weight to lower frequencies leads to an increase in both the scattering rate and a decrease in mass enhancement, as shown in figure 4.4. Thus, a redistribution of weight to higher frequencies is the only scenario that properly accounts for the behavior we observe.

We would also like to emphasize that we make no claim regarding the precise functional form of the spectral function. While there is a theoretical motivation for an overdamped Lorentzian lineshape$^{[69]}$, a histogram representation of $\alpha^2 F(\omega)$ has also been shown to describe the measured optical conductivities of a variety of cuprates$^{[72]}$, as has a sum of Lorentzian terms$^{[73]}$. A more definite determination of the spectral function requires data extending over a larger frequency range than do our measurements, as well
as a more sophisticated inversion technique[71, 73]. Our analysis is only intended to illustrate the redistribution of weight in $\alpha^2 F(\omega)$.

4.6 Discussion and Conclusions

Our measurements signify a change in the intrinsic carrier dynamics of BSCCO 2D atomic crystals due to a pronounced hardening of $\alpha^2 F(\omega)$ without significant change in carrier density. This hardening in turn implies a change in either the bosonic density of states or the electron-boson coupling strength. We suspect that the observed changes arise from a subtle modification of the crystal lattice. Indeed, X-ray micro-diffraction experiments show a change of the incommensurate superstructure in samples of comparable thickness to those discussed here[10]. The modification of the superstructure, which is known to periodically modulate bond angles in the copper oxygen plane[74], could in turn lead to an overall straightening of the Cu-O-Cu bond. As the exchange constant $J$ is highly sensitive to the Cu-O-Cu bond angle[75, 76], we hypothesize that the suppression of the superstructure causes an increase in the magnitude and spatial homogeneity of $J$ and therefore the observed hardening and narrowing of $\alpha^2 F(\omega)$ and the two-magnon Raman feature[54]. While a change in the lattice structure might also be expected to modify the phonon frequencies, we stress that no such change is observed in Raman scattering[57].

Our study has led to two conclusions regarding exfoliated BSCCO. Based on the trend in spectral weight with thickness, the surface of exfoliated BSCCO has a tendency to become insulating. This suggests that the insulating behavior previously observed in 2D atomic crystals of BSCCO is an extrinsic effect[7] and that exfoliated BSCCO devices would likely require steps to prevent or compensate for surface degradation. Possibilities include oxygen annealing or employing a gold capping layer. We have also found that the electron-boson spectral function is modified in exfoliated BSCCO thinner than about 50 nm, possibly due to an overall straightening of the typical Cu-O-Cu bond angle. To cor-
robort this scenario, an additional measurement of the electron-boson spectral function, such as inelastic tunneling[77], as well as more detailed crystallography (in particular a measurement of the lattice constants), are desirable. Low-temperature inelastic tunneling would also provide insight into how this modified electron-boson coupling impacts the superconductivity.

4.7 Co-authorship

Sections 4.2 to 4.4 of chapter 4 have been published as ‘L.J. Sandilands, A.A. Reijnders, A.H. Su, V. Baydina, Z. Xu, A. Yang, G. Gu, T. Pedersen, F. Borondics, and K.S. Burch “Origin of the insulating state in exfoliated high-\(T_c\) two-dimensional atomic crystals”, Physical Review B 90, 081402(R) (2014)’. The copyright is held by the American Physical Society and the material is reproduced with permission. The thesis author was the primary investigator for this work, prepared the samples, collected the microscopy data using an existing instrument at the CLS, performed the data analysis, and wrote the manuscript. The bulk BSCCO crystals used in this study were provided by the research group of Genda Gu at Brookhaven National Laboratory. The microscopy work at CLS was done with the assistance of beamline staff Tor Pedersen and Ferenc Borondics. The AFM work was performed with assistance from Richard McAloney, Alon Eisenstein, and Cynthia Goh at the University of Toronto.
Chapter 5

Doping-dependent charge dynamics in Cu$_x$Bi$_2$Se$_3$

5.1 Introduction

The concept of topology in condensed matter physics has attracted renewed interest in recent years due to the discovery of topological insulators, materials where the non-trivial topology of the electronic band structure leads to conducting surface states[78, 79, 80]. The principle of band topology soon led to the realization that superconductors can similarly be classified according to the topology of the Bogoliubov-De Gennes Hamiltonian and that topological superconductors could manifest isolated Majorana fermions[79]. In this context, the discovery of superconductivity in Cu intercalated Bi$_2$Se$_3$, a prototype topological insulator, was notable and this material has attracted significant experimental and theoretical effort [11, 13, 81, 82]. ARPES measurements have demonstrated the persistance of the topologically-protected surface states in superconducting Cu$_x$Bi$_2$Se$_3$[12, 83], while tunneling and thermodynamic measurements have hinted at an unconventional superconducting state[14, 15, 84, 85]. Doping dependent studies revealed an unusual increase in the residual resistivity ($\rho_o$) and a suppression of the superfluid
density ($\rho_s$). The increase in $\rho_o$ was interpreted as an increase in disorder and these two findings therefore suggest unconventional superconductivity in Cu$_x$Bi$_2$Se$_3$[15]. In contrast, the superconducting critical temperature ($T_c$) depends only weakly on doping and the carrier density ($n$) is completely independent of Cu content[15, 83]. These findings hint at the complex effects of introducing Cu to Bi$_2$Se$_3$. However, the detailed effect of Cu doping on the electronic structure and disorder level remains poorly understood. Indeed, a combined ARPES and quantum oscillation study has revealed an open Fermi surface at higher carrier densities[86].

To understand the effect of Cu doping on the electronic structure, we have measured the optical response of Cu$_x$Bi$_2$Se$_3$ as function of Cu content $x$. Optical spectroscopy is a well-established tool for investigating the electronic structure of solids[6, 19] and optical techniques have been widely applied to topological insulator materials[87, 88, 89], and to Bi$_2$Se$_3$ in particular[90, 91, 92, 93, 94, 95]. However, a systematic study of intra- and interband excitations, as well as disorder levels, as a function of Cu content has not been reported. With this in mind, we have performed reflectance and ellipsometric measurements on a series of Cu$_x$Bi$_2$Se$_3$ samples ($x$=0.15, 0.22, 0.32, and 0.42). We observe that the mid-infrared plasma minimum, which is related to the free carrier dynamics, progressively red-shifts with Cu doping. This result indicates a reduction in $n$ and/or enhancement in the effective mass ($m_b$) of the carriers with Cu doping. However, the energy of interband transitions from the valence band to the Fermi level $E_f$ does not show a concurrent shift. Taken together these results indicate the carrier density $n$ is indeed nearly insensitive to Cu doping for $x \geq 0.15$, while the effective mass $m_b$ of the carriers is increased. This result explains the unusual doping dependent evolution of the superfluid density $\rho_s$ and emphasizes the non-trivial effect of the Cu doping.
5.2 Experimental Details

Single crystal Cu$_x$Bi$_2$Se$_3$ samples were prepared at Osaka University via the electrochemical intercalation technique described in reference [96] with $x = 0.15, 0.22, 0.32,$ and $0.42$. The superconducting properties were investigated through magnetization measurements. The superconducting critical temperatures ($T_c$) were found to be 3.6, 3.5, 3.3, and 3.1 K respectively, while the shielding fraction ranged from roughly 20 to 40%, consistent with previous reports[13, 15, 96]. The Cu content was determined by carefully weighing the samples before and after intercalation.

We carried out reflectance and ellipsometric measurements at 295 K in order to obtain the optical constants of Cu$_x$Bi$_2$Se$_3$. Reflectance measurements were performed at near-normal incidence using a modified Bruker 80v FTIR spectrometer with a series of sources and detectors, as detailed in reference [97]. Prior to measurement, each sample was freshly cleaved using adhesive tape, meaning our measurements probe charge dynamics in the $ab$-plane. In the case of the $x=0.42$ sample, the poor sample morphology made cleaving difficult. We therefore prepared a fresh sample surface using a micro-tome. For $x=0.15, 0.32$ and 0.42, we measured the reflectance from 100 meV to 805 meV. This range was extended to 5 meV to 1.24 eV in the case of the $x=0.22$ sample. We used an in situ gold overcoating technique to provide an absolute intensity reference for our measurements[22]. The dielectric function $\hat{\epsilon}(\omega)$ of all four samples was then measured directly for the range 0.75 eV to 5 eV using a Woolam VASE ellipsometer. Importantly, the reflectance computed from the ellipsometric data is in good agreement with the measured reflectance in the frequency region where the two data sets overlap. We also checked the quality of the micro-tomed $x=0.42$ surface by varying the polarization of incident light in our reflectance measurement and the angle of incidence in ellipsometry. Neither variation produced a meaningful change in the data, validating our surface preparation technique.

To extract the dielectric function $\hat{\epsilon}(\omega)$ from the optical data, we employ a variational dielectric function implemented in the RefFIT software package[25, 60]. We simultane-
ousely fit the reflectance and ellipsometric data in order to constrain the phase of $\hat{\varepsilon}(\omega)$ at high energies\cite{24, 97}. In considering the optical response of our sample, we focus on the imaginary part of the dielectric function $\varepsilon_2(\omega)$, which represents charge excitations in a solid\cite{21}. Finally, to make connections between the optical response and transport measurements, $\varepsilon_2(\omega)$ can also be recast in terms of the real part of the optical conductivity $\sigma_1(\omega) = \omega \varepsilon_2(\omega)/4\pi$ (CGS units), the finite frequency generalization of the DC conductivity.

5.3 Broad band optical response

$\text{Cu}_x\text{Bi}_2\text{Se}_3$ exhibits the optical response characteristic of a heavily-doped metallic semiconductor. Before discussing the data in detail it is therefore worthwhile to review the semiclassical Drude model, the common starting point for understanding the charge dynamics of a metal\cite{19, 21}. Within the Drude model, the dielectric function $\hat{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ is given by:

$$
\hat{\varepsilon}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega(1/\tau)}.
$$

(5.1)

Here $1/\tau$ is the free carrier scattering rate, $\varepsilon_\infty$ represents screening due to interband transitions located at higher energies, and $\omega_p$ is the plasma frequency and is proportional to $(n/m_b)^{1/2}$, where $n$ is the carrier density and $m_b$ is the optical band mass. A Drude analysis therefore allows access to parameters characterizing both the electronic structure ($\omega_p$ and $\varepsilon_\infty$) and disorder level $(1/\tau)$.

It is also informative to consider the low and high frequency limits of this model dielectric function. At low frequencies, $\varepsilon_1$ is large and negative. Accordingly, the reflectance in a metal is high at low frequencies. For $\omega_p \gg 1/\tau$, the real part of the dielectric function $\varepsilon_1$ has a zero crossing at the screened plasma frequency $\tilde{\omega}_p = \omega_p/\sqrt{\varepsilon_\infty}$. This leads to a characteristic dip in the reflectance known as the plasma minimum whose line shape is
determined by $1/\tau$. The location and width of the plasma minimum therefore provide insight into the free carrier dynamics.

In the top panel of figure 5.1 we display the broadband optical response of Cu$_{0.22}$Bi$_2$Se$_3$ at 295K. Several features merit mention. At low frequencies, the reflectance is dominated by a Drude line shape with a well-defined plasma minimum near 0.2 eV. This is in rough agreement with previous optical studies of Cu$_x$Bi$_2$Se$_3$ which reported plasma minima between 70 and 200 meV depending on Cu content\cite{95, 92}. The slight kink below 0.01 eV is the $\alpha$ phonon typically observed in Bi$_2$Se$_3$\cite{90}, which we do not discuss further. The slope of the reflectance also shows a weak maximum near 2 eV due to interband transitions\cite{90}.

These various features are more readily discerned from the optical conductivity $\sigma_1(\omega)$ shown in the bottom panel of figure 5.1. A strong, narrow peak due to the $\alpha$ phonon can be seen on top of a broad Drude contribution due to the free carriers. At 0.35 eV, $\sigma_1$ rises sharply as excitations from the valence band to the conduction band become energetically allowed. The low energy dynamics are well-described by a single Drude lineshape and therefore with a single species of carriers. In contrast, a previous optical study of Cu$_{0.07}$Bi$_2$Se$_3$\cite{95} identified a peak at finite (25 meV) energy, indicating the presence of an impurity band, as well as a Drude component. Furthermore, Dordevic et al.\cite{98} interpreted the free carrier contribution to $\hat{\epsilon}(\omega)$ in a variety of topological insulator materials in terms of carrier density inhomogeneity. Our observation of a single Drude mode suggests such inhomogeneities are small in our samples. The interband transitions are similar to those observed in pristine Bi$_2$Se$_3$, albeit with a Moss-Burstein shifted direct gap\cite{90, 99, 100}. 
Figure 5.1: Optical properties of Cu$_{0.22}$Bi$_2$Se$_3$ at 300 K. Top panel: Reflectance. Bottom panel: Optical conductivity $\sigma_1(\omega)$. Both spectra are compatible with a heavily-doped, metallic semiconductor.
5.4 Doping dependence of the plasma minimum and interband transitions

In the top panel of figure 5.2, we show the mid-infrared \(ab\)-plane reflectance for samples with different doping levels. The location of the plasma minimum (\(\tilde{\omega}_p\)) red-shifts with doping and implies a change of the in-plane carrier dynamics. To quantitatively study the evolution of the carrier dynamics, we fit our reflectance data near the plasma minimum (111 meV to 600 meV) to a Drude model. In figure 5.2 (b) and (c) we show the \(\omega_p^2 \propto n/m_b\) and \(1/\tau\) values derived from this procedure. As expected from the reflectance data, \(\omega_p^2\) red-shifts by 40% over the measured doping range. \(1/\tau\) is relatively constant before sharply increasing by 20% for the \(x=0.4\) sample. For comparison, we note that previous optical spectroscopy measurements of pristine Bi\(_2\)Se\(_3\) found a room temperature \(1/\tau\) ranging from 1 to 8 meV, significantly lower than our values\[90, 101\]. These works also reported \(\omega_p\) values between 47 and 197 meV, also much lower than ours. This indicates that both \(n\) and disorder are increased relative to the pristine compound. The shift of \(\omega_p\) in our data with doping signifies a change in the quantity \(n/m_b\), where \(m_b\) is the \(ab\)-plane optical band mass. Hall effect\[15\] and ARPES\[83\] measurements have shown that \(n\) is effectively constant over the measured doping range, and so our data indicates an increase in \(m_b\) with Cu doping.

In order to confirm a constant \(n\) in our samples, we now consider the interband transitions present in Cu\(_x\)Bi\(_2\)Se\(_3\). In a doped semiconductor, the onset of interband transitions is increased from the bare band gap \(E_g\) by the Fermi level \(E_f\), an effect known as the Moss-Burstein shift\[99, 100\]. In the simplifying case of a direct gap semiconductor with parabolic bands, the Moss-Burstein edge \(\omega_{mb}\) is expected to vary as \(\omega_{mb} = E_g + (1 + m_c/m_v)(E_f - 4k_BT)\), where \(E_g\) is the optical gap of pristine Bi\(_2\)Se\(_3\), \(m_c\) (\(m_v\)) is the conduction (valence) band mass, and \(E_f\) is the Fermi level measured from the bottom of the conduction band\[99\]. The onset of interband transitions \(\omega_{mb}\) therefore provides a
Figure 5.2:  Doping dependence of the free carrier dynamics in Cu$_x$Bi$_2$Se$_3$. a) Mid-infrared reflectance b) Squared plasma frequency $\omega^2_p$. c) Scattering rate $1/\tau$. The error bars in $\omega_p$ are smaller than the symbols used in b). The reflectance minimum $\tilde{\omega}_p$ is seen in panel a) to red-shift with doping, suggesting a change in carrier dynamics. This is borne out by the fitted values of $\omega^2_p$, which red-shifts by roughly 40%. In contrast, $1/\tau$ shows only a slight increase at high doping. The change in $\omega_p$ is due to an increase in the band mass $m_b$. 

\[ \omega^2_p \]
measure of $E_f$. As can be seen in the bottom panel of figure 5.1, interband transitions become important above 0.35 eV. For $x=0.15-0.32$, these features are consistent with 0.6 eV excitations from the valence band to $E_f$ that are broadened by disorder. In figure 5.3 (a), we plot the quantity $(\epsilon_2\omega^2)^2$ for $x = 0.32$ which shows a linear variation in energy between 0.7 and 0.85 eV. This is a signature of the onset of direct optical transitions between parabolic bands and the intercept with the energy axis gives the value of the gap\cite{21}. The large blue-shift of the direct gap with respect to the 115-150 meV optical gap of pristine Bi$_2$Se$_3$\cite{91, 94} at 295K is due to the the Moss-Burnstein effect\cite{99, 100}. This interpretation is consistent with photoemission. Specifically, ARPES suggest that the lowest energy direct optical transition from the valence band to $E_f$ should occur at roughly 0.6-0.7 eV\cite{12, 83}.

Interband transitions are also sensitive to disorder. Indeed, below below the gap (roughly 0.6 eV), the absorption $\alpha(\omega)$ in Cu$_x$Bi$_2$Se$_3$ follows an exponential form as can be seen in figure 5.3 (b) for $x=0.3$. This in-gap ‘Urbach tail’ is a well-known phenomenon in semiconductors and is caused by structural and thermal disorder\cite{102, 103}. The ab-
Figure 5.4: Doping dependent charge dynamics in Cu$_x$Bi$_2$Se$_3$. a) Optical resistivity $\rho_{opt}$. b) Moss-Burstein edge $\omega_{mb}$. c) Band mass $m_b$ from optical ($m_{opt}$) and quantum oscillation ($m_{qo}$) measurements. d) Superfluid density $\rho_s = \lambda^{-2}$ versus inverse bandmass $m_b^{-1}$. $\rho_{opt}$ shows an increase with doping, consistent with the behavior of the residual resistivity observed in DC transport[15]. $\omega_{mb}$ and therefore $n$, does not vary systematically with doping, while $m_b$ can be seen to increase. $\rho_s$ and $1/m_b$ show a linear relationship, indicating that the doping dependence of $\rho_s$ is due to the increased $m_b$, rather than disorder. The error bars in $\omega_p$ are smaller than the symbols used in a).
sorption in this regime is typically parameterized as \( \ln(\alpha(\omega)) \propto -(E - \omega_{mb})/\sigma_o \) where \( \omega_{mb} \) is energy of the transition and \( \sigma_o \) is the Urbach parameter that determines the width of the exponential region and is related to the disorder. The \( x=0.15, 0.22, \) and \( 0.32 \) samples show Urbach tail behavior. For \( x=0.42 \), we observe significant in-gap weight that does not follow the Urbach tail form.

5.5 Discussion

In table 5.1 we summarize the parameters characterizing the electronic structure of \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) for \( x=0.15-0.4 \). \( \omega_{mb} \) and \( \sigma_o \) are obtained from fits to the direct gap and Urbach expressions described previously. \( \sigma_o \) in fact decreases by 10\%, suggesting that the level of disorder is roughly constant. The gap itself shows only a minimal doping dependence that is almost within our experimental error. Importantly, this suggest that \( n \) does not vary systematically in our samples and is relatively constant, consistent with Hall[15] and ARPES[83] measurements in other crystals. Indeed, taking \( E_g = 0.15 \text{ eV}[91] \) and \( m_c/m_v = 1[94] \) yields an \( E_f \) of 326-356 meV for our samples, in good agreement with photoemission experiments which suggest values between 290 and 350 meV[83, 86]. With reference to figure 5.4 (b), we also observe that the maximum allowed decrease in \( E_f \) is \( \delta E_f = 32 \text{ meV} \). Using this fact, we can estimate the largest possible decrease in \( n \) allowed by our data. Given that \( E_f \propto n^{2/3}, \delta n/n \approx 3\delta E_f/2E_f \approx3(30 \text{ meV})/2(326 \text{ meV}) = 0.15 \).

The observed behaviour of \( E_f \) and \( n \) is in stark contrast to the decrease of \( \omega_p \) with doping. In particular, a 15\% decrease in \( n \) is insufficient to explain the observed decrease in \( \omega_p^2 (\propto n/m_b) \), which decreases by 40\%. Our results therefore demonstrate a change in the band mass \( m_b \) with increased Cu content, rather than a simple change in \( n \). In figure 5.4 (c), we show the \( m_b \) implied by our data. We assumed a free carrier density of \( 1.5 \pm 0.4 \times 10^{20} \text{ cm}^{-3} \) after reference [15], which results in the relatively large error bars. Our results are in good agreement with other \( m_b \) values reported in the literature and
we have included for comparison in figure 5.4 (c) the masses deduced by other groups [95, 104, 105] from quantum oscillation measurements.

Our measurements show that the band mass progressively increases with Cu content, reaching a value roughly twice that of pristine Bi$_2$Se$_3$ at $x=0.42$. We also note that Lahoud et al.[86] reported quantum oscillation measurements suggesting a $m_b = 0.25m_e$ for heavily-doped Cu$_x$Bi$_2$Se$_3$, although they do not specify the Cu content $x$. Finally, an $m_b$ of 0.25$m_e$ has also been identified though previous optical measurements in heavily-doped Cu$_x$Bi$_2$Se$_3$ and interpreted in terms of band non-parabolicity[92]. While this value is in good agreement with our results, our work has revealed that mass enhancement can occur without significant change in $n$.

A recent study of Cu$_x$Bi$_2$Se$_3$ identified an unusual doping dependence of the residual resistivity $\rho_o$ measured by DC transport[15]. The variation in $m_b$ that we observe naturally explains this effect. In figure 5.4 (a), we show the DC resistivity $\rho_{opt}$ implied by our data. This quantity increases by roughly a factor of two over the measured doping range, similar to $\rho_o$[15]. Given that $m_b$ increases by a comparable factor while $1/\tau$ is relatively unchanged, we can attribute the increased $\rho_{opt}$ and $\rho_o$ to the increased $m_b$, rather than an increase in disorder.

The variation in bandmass also accounts for the anomalous evolution of the superfluid density with doping without invoking disorder and unconventional pairing[15]. The superfluid density $\rho_s$ can be defined as $1/\lambda^2 \propto m_b^{-1}$, where $\lambda$ is the superconducting penetration depth[5]. In 5.4 (d), we plot $\rho_s$ (reproduced from Kriener et al.[15]) versus our measured $m_b^{-1}$, demonstrating a clear linear relationship. Heuristically, the Cooper pairs are becoming heavier and so the condensate is less effective in screening an applied magnetic field leading to an increased $\lambda$. More generally, this trend is a manifestation of the Homes’ superfluid scaling relation, which states that $\rho_s \propto \sigma_1(0)T_c$ [106]. Since $\sigma_1(0) \propto m_b^{-1}$, an increase in $m_b$ reduces the low energy spectral weight available to the condensate and so decreases $\rho_s$. We also note that Cu$_x$Bi$_2$Se$_3$ is firmly in the dirty limit.
in the doping range studied, with $1/\tau \sim 30$ meV much larger than the superconducting gap $\Delta \sim 0.6$ meV estimated from $T_c[12]$. Although our measurements of $1/\tau$ were performed at 295 K, $\rho(4 K)/\rho(295 K) \sim 0.5$ in our samples [96] and so we do not expect $1/\tau$ to change by more than a factor of 2 at low temperature.

The origin of the increased $m_b$ is not clear. One possibility is that Cu intercalation distorts the host Bi$_2$Se$_3$ lattice and reduces the effective in-plane bandwidth. Indeed, Cu intercalation is known to increase the $c$-axis lattice constant[11, 95] and so would naively be expected to alter the electronic dispersion in this direction. Any effective in-plane hoppings which involve intermediate steps between layers would therefore be similarly reduced, leading to an increased in-plane mass.

The mass enhancement could also be a many-body effect, specifically band gap renormalization[107, 108, 109]. Accounting for many body effects, the zero temperature measured optical band gap $\omega_{opt}$ of a doped semiconductor is given by $\omega_{opt} = E_g - \Delta_{RN} + (1 + m_c/m_v)E_f$, where $\Delta_{RN}$ is the band gap reduction due to many-body effects[110] and $(1 + m_c/m_v)E_f$ is the Moss-Burstein shift. This band-gap reduction would also be expected to influence the conduction band mass, such as predicted by $k \cdot p$ theory[21]. A possible explanation of our data is therefore that the band gap renormalization nearly cancels the Moss-Burstein shift, resulting in an almost constant optical band gap, and also leads to an increased effective mass.

Our results also point to the complex nature of Cu doping. Previous work in this direction has emphasized the ambipolar nature of the Cu dopant[11, 111]. In particular, Cu atoms are thought to enter the Bi$_2$Se$_3$ lattice in two principle ways: in the van der Waals gap, where each dopant atom donates a single electron, and substitutionally on a Bi site, where the dopant instead decreases the free electron concentration[111]. In this context, one would naively expect two possibilities upon progressive Cu doping. If the dopant atoms continue to enter the van der Waals gap, then $n$ should increase monotonically, in contrast to experiment. On the other hand, if at high concentrations
some fraction of the dopants begin occupying Bi sites such that \( n \) remains constant, then we would expect a drastic increase in the in-plane scattering rate \( 1/\tau \). However, as can be seen in table 5.1 both \( 1/\tau \) and \( \sigma_o \), two measures of disorder, are effectively constant. This suggests that Cu atoms do not substitute for Bi in large numbers. Indeed, our optical spectroscopy reveal that beyond simply adding carriers or introducing disorder, Cu doping impacts the electronic dispersion, as evinced by the increased \( m_b \). Further work is therefore required to elucidate in detail the effect of Cu doping at high concentrations. For instance, channeling experiments, such as have been performed on (Ga,Mn)As\[112\], would be helpful in determining the precise location of the Cu atoms within the Bi\(_2\)Se\(_3\) lattice. Scanning tunnelling microscopy and \textit{ab initio} calculations have recently been used to identify a variety of dopant positions in Cu\(_x\)Bi\(_2\)Se\(_3\)[113] and would also be useful to investigate any local changes in electronic structure associated with these various dopant locations.

Finally, the fact that \( m_b \) is only modestly increased by Cu doping up to \( m_b \sim 0.3m_e \) at \( x =0.42 \) is in apparent contradiction with the mass \( m_{sh} = 2.6m_e \) inferred from the electronic specific heat\[13\]. However, the specific heat data was interpreted under the assumption that the density of states at \( E_f \) is given by the free electron model. Recent ARPES experiments have demonstrated that spin-plasmon excitations cause a giant surface state mass enhancement in Cu\(_x\)Bi\(_2\)Se\(_3\)[114]. This means that the free electron model is possibly inadequate for describing the density of states at \( E_f \) and so the \( m_{sh} \) derived from such a treatment should be interpreted with caution.

### 5.6 Conclusions

In summary, we have studied the doping dependent charge dynamics of the candidate topological superconductor Cu\(_x\)Bi\(_2\)Se\(_3\) using optical spectroscopy. We observe a pronounced decrease in \( \omega_p \). Taken together with our analysis of the interband transitions
Table 5.1: Parameters characterizing the electrodynamics of Cu$_x$Bi$_2$Se$_3$. The parameters are the plasma frequency $\omega_p$, the free carrier scattering rate $1/\tau$, the Moss-Burnstein edge $\omega_{mb}$, and the Urbach parameter $\sigma_0$. $\omega_{mb}$ does not vary systematically, within our experimental accuracy, implying a constant carrier density $n$. Taken together with the decrease in plasma frequency $\omega_p$, this indicates an increase in the band mass with Cu doping $x$.

<table>
<thead>
<tr>
<th>x</th>
<th>$\omega_p$ (meV)</th>
<th>$1/\tau$ (meV)</th>
<th>$\omega_{mb}$ (meV)</th>
<th>$\sigma_0$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>1023±5</td>
<td>30.5 ±0.6</td>
<td>601±15</td>
<td>175±1</td>
</tr>
<tr>
<td>0.22</td>
<td>907±8</td>
<td>28.0±1.4</td>
<td>666±11</td>
<td>169±1</td>
</tr>
<tr>
<td>0.32</td>
<td>845±6</td>
<td>27.2±1.0</td>
<td>661±67</td>
<td>159±1</td>
</tr>
<tr>
<td>0.42</td>
<td>804±5</td>
<td>34.5±4.2</td>
<td>639±87</td>
<td>—</td>
</tr>
</tbody>
</table>

that show that $n$ is essentially constant, this suggests an increase in the optical band mass $m_b$ while the free carrier scattering rate $1/\tau$ remains relatively unchanged. The increased $m_b$ accounts for the apparent suppression of $\rho_s$ and the increase in $\rho_o$ with doping. Our results highlight the non-trivial nature of Cu doping in Bi$_2$Se$_3$.

5.7 Co-authorship

Chapter 5 is a reprint, with some modification, of a ‘L.J Sandilands, A.A. Reijnders, M. Kriener, K. Segawa, S. Sasaki, Y. Ando, and K.S. Burch, “Doping-dependent charge dynamics in Cu$_x$Bi$_2$Se$_3”$, in press, Physical Review B (2014)’. The copyright is held by the American Physical Society and the material is reproduced with permission. The thesis author was the primary investigator for this work, collected the data using existing instruments, wrote the manuscript, and helped conceive of the project. The Cu$_x$Bi$_2$Se$_3$ crystals used in this study were prepared at Osaka University in the group of Yoichi Ando. The microtome sample preparation was performed with the assistance of Peter Brodersen at Surface Interface Ontario at the University of Toronto.
Chapter 6

Relativistic electronic structure of RuCl$_3$

6.1 Introduction

A variety of novel electronic phases are predicted to emerge in the solid state when the spin-orbit coupling $\lambda$ becomes comparable to or stronger than to the electron-electron interaction strength $U$ and the hopping $t$\cite{16, 115}. A prominent example is the suggestion that the honeycomb iridates, a class of strongly spin-orbit coupled Mott insulators, could realize the Heisenberg-Kitaev model\cite{116, 17, 18}. In this scenario, the combined action of spin-orbit coupling and orbital degeneracy leads to the formation of $j_{\text{eff}} = 1/2$ pseudospins. The spatial anisotropy inherent to these pseudospins leads to bond-dependent exchange interactions that can be mapped onto the Kitaev model\cite{17}, which in turn hosts a quantum spin liquid ground state\cite{116, 117}. Indeed, inelastic x-ray and neutron scattering experiments have provided evidence for Kitaev-type interactions in the prototype honeycomb iridate Na$_2$IrO$_3$\cite{118, 119}. However, Na$_2$IrO$_3$ possesses significant structural non-idealities \cite{120, 121, 122} and the existence of localized $j_{\text{eff}}$ moments in these materials has been questioned\cite{123, 124, 125}. The identification of other spin-orbit
coupled Mott insulators, especially on the honeycomb lattice, is therefore an experimental priority[126].

In this context, some of us have recently argued that α-RuCl₃ (hereafter RuCl₃) is a promising alternative for investigating the physics of the spin-orbit coupled Mott insulator on the honeycomb lattice[127]. RuCl₃ crystallizes in a layered structure (space group $P\overline{3}12$) consisting of planes of edge-sharing RuCl₆ octahedra arranged on a honeycomb lattice[128], as shown in figure 6.1. It is thought to be a Mott insulator due to the observation of insulating behaviour in DC transport and Curie-Weiss behavior at high temperatures[129, 130, 131]. An important structural detail is that the Ru $d^5$ ion sits in an almost perfect Cl octahedron[128, 131]. The expectation is therefore that non-cubic crystal fields are small and that the modest $\lambda \approx 100$ meV of the Ru 3+ ion is sufficient to induce a $j_{\text{eff}}$ state[132]. \textit{Ab initio} band structure calculations find a highly two-dimensional electronic structure with Ru $d$ states dominant near the Fermi level $\epsilon_F$. Importantly, spin-orbit coupling was demonstrated to play a central role in the electronic structure of this material. In figure 6.1 (b), we show the calculated density of states (DOS) reproduced from reference [127]. Here the $t_{2g}$ states can be seen to split into an unoccupied conduction band and an occupied valence band. Indeed, both $U$ and $\lambda$ are required in density functional theory to reproduce the small gap of 0.15 eV measured in optical spectroscopy, and spin-orbit coupling is also needed explain the line shapes observed in x-ray absorption at the Ru L₂ and L₃ edges[127].

Existing experimental studies of the electronic structure of RuCl₃ are limited. ARPES measurements found an almost dispersionless feature near $\epsilon_F$ which was attributed to localized bands originating from Ru $d$ states[133, 134]. Meanwhile, DC transport has revealed activated behaviour and a Hall mobility that increases at low temperature, suggesting band-like transport with an energy gap of 0.1 to 0.4 eV[129]. Previous optical absorption and reflectivity measurements have identified a series of peaks in the range 0.1 to 10 eV[135, 136, 137]. Of particular interest are three features found between 0.1
Chapter 6. Relativistic electronic structure of RuCl$_3$

and 1 eV, which we label $\alpha_1 - \alpha_3$. These features have been interpreted as localized, even parity $d-d$ excitations of the Ru 3+ ion$^{135, 136}$. Overall, experimental studies of the RuCl$_3$ electronic structure have been hampered by a lack of supporting band structure calculations, which are now available$^{127}$.

Despite these studies, the role of spin-orbit coupling in determining the low energy electronic structure in RuCl$_3$ remains poorly understood and controversy exists as to the identity of the low lying electronic transitions$^{129}$. We have therefore investigated in detail the temperature dependent electronic excitations in this material using infrared and electronic Raman scattering spectroscopies. Infrared spectroscopy has been widely applied to the study of electronic excitations in strongly correlated insulators$^{6, 138, 139}$ and has provided key insight into the spin-orbit coupled electronic structure of various iridate materials$^{140, 141, 124, 142, 143, 144, 145, 146}$. Raman scattering also probes electronic excitations$^{147}$ and has been successfully applied to a variety of correlated electron systems$^{148}$. The distinct selection rules for optical and Raman processes provide can be used to unambiguously determine the symmetry of a given excitation and allow us to obtain a comprehensive picture of the electronic excitations in RuCl$_3$$^{149}$. In the case of RuCl$_3$, these selection rules allow us to discriminate between inter- and intrasite excitations.

Our combined infrared and Raman study has resolved the long-standing issue regarding the nature of the low-lying $\alpha$ excitations in $\sigma_1(\omega)$ of RuCl$_3$, which we interpret at transitions between $t_{2g}$-like bands. These features are anomalously narrow and weak, pointing to extremely flat electronic bands in the vicinity of $\epsilon_F$. This is a combined effect of spin-orbit coupling and the edge-sharing hopping topology of RuCl$_3$, which conspire to suppress the intersite hopping $t$. We also observe a Raman active excitation near the onset of the optically-active electron-hole continuum. Taken together, our results provide further support for the existence of the relativistic Mott insulating state in RuCl$_3$. 
Figure 6.1: Lattice and electronic structure of RuCl$_3$

(a) Layered crystal structure of a single honeycomb plane in RuCl$_3$. Ruthenium atoms are indicated in blue, while Cl atoms are shown in red. The crystallographic $c$ axis is perpendicular to the $ab$ plane.

(b) Theoretical electronic density of states reproduced from reference [127]. Importantly, both SOC and U are needed in density functional theory to split the $t_{2g}$ states while reproducing the small (0.1-0.2 eV) gap in $\sigma_1(\omega)$. 


6.2 Experimental Details

The $\alpha$-RuCl$_3$ crystals used in this study were grown by vacuum sublimation of pre-reacted RuCl$_3$ powder, as described in reference [127]. The optical conductivity $\hat{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ of RuCl$_3$ was measured from 0.1 to 6 eV. For the range 0.9 to 6 eV, $\hat{\sigma}(\omega)$ was determined for an $ab$ crystal face using a Woolam VASE ellipsometer. For 0.1 to 1.2 eV, we measured the transmittance through a thin RuCl$_3$ sample using a modified Bruker 80v FTIR spectrometer described in reference [97], with light polarized in the crystallographic $ab$ plane. The optical conductivity $\hat{\sigma}(\omega)$ was then extracted from the data using a standard model for the transmittance of a plate sample which accounts for interference effects. $\hat{\sigma}(\omega)$ was parameterized using a variational dielectric function and the phase of $\hat{\sigma}(\omega)$ was constrained with the $\hat{\sigma}(\omega)$ obtained from ellipsometry[24].

Raman scattering measurements were performed in the quasi-back-scattering geometry in both collinear (XX) and crossed (XY) polarizations using a Horiba Jobin Yvon spectrometer equipped with an Andor CCD. The light polarized in the $ab$ plane. Exciting light from a 532 nm laser was focussed down to a $\sim$10 $\mu$m spot and the power at the sample is estimated to be 500 $\mu$W. A pair of holographic notch filters (Ondax) were used to reject light from the fundamental, leading to a lower cutoff of 4 meV. The resolution of our Raman spectrometer is estimated to be 0.6 meV.

6.3 Experimental Results

The real part of the optical conductivity $\sigma_1(\omega)$ at 295 K is shown in figure 6.2. The spectra consist three narrow peaks below 1 eV ($\alpha_1 - \alpha_3$), another three peaks between 1 and 4 eV ($\beta_1 - \beta_3$), and a strong feature ($\delta$) at 5 eV. We note that the data is in good agreement with previous reports[135, 136, 137]. The narrow bandwidths and large number of peaks are unusual for a Mott insulator (see for example reference [150]).
Chapter 6. Relativistic electronic structure of RuCl$_3$

Figure 6.2: Optical conductivity $\sigma_1(\omega)$ of RuCl$_3$. a) Low energy (0.1-0.95 eV) region. b) High-energy (1-5.5 eV) regime. Note the different conductivity scales of (a) and (b). Features identified through a dispersion analysis are shown with broken lines. The low energy regime (a) exhibits weak and narrow $t_{2g}^5t_{2g}^5 \rightarrow t_{2g}^4t_{2g}^6$ transitions, while the high energy region (b) is dominated by $t_{2g}^5t_{2g}^5 \rightarrow t_{2g}^4(t_{2g}^5e_g)$ and charge transfer excitations ($\delta$). The low intensity, narrow widths, and number of the $t_{2g} \rightarrow t_{2g}$(UHB) transitions are due to spin-orbit coupling and the edge-sharing hopping topology of RuCl$_3$. 
identify any changes in electronic structure with temperature, and in particular to verify
the insulating ground state, we turn to the temperature dependence of $\sigma_1(\omega)$. In figure
6.3 (a), we show $\sigma_1(\omega)$ below 1 eV at 10 K and 295 K. The intensity in this region peaks
decreases smoothly and $\sigma_1(\omega)$ retains a clear gap of 0.15 eV at 10 K.

To quantify the temperature dependent optical response of RuCl$_3$, we fit $\sigma_1(\omega)$ to a
Lorentz oscillator model\[23\], where $\sigma_1(\omega) = \sum_n S_n \Gamma_n \omega^2/((\omega^2 - \omega_n^2)^2 + \omega^2 \Gamma_n^2)$. Here $S_n$, $\Gamma_n$, and $\omega_n$ are the oscillator strength, the line width, and the energy of the $n$th oscillator.

Two Lorentzians were required to fit features $\alpha_1$ and $\alpha_2$, while the remaining features
are well-described by single oscillators. This is not surprising, given the number of bands
near $\epsilon_F$ suggested by DFT\[127\]. The results of this fitting procedure are shown in figure
6.2 (a) for the 295 K case. Importantly, the fitting reveals that the loss of spectral weight
in the 0-1 eV region occurs almost entirely due to the narrowing of $\beta_1$ and a loss of
intensity in $\alpha_1$. This can be seen explicitly in figure 6.3 (b), where we plot the total
oscillator strength $S$ associated with each $\alpha$ feature versus temperature. $\alpha_1$ decreases by
roughly 50 % in intensity, while $\alpha_2$ and $\alpha_3$ are relatively constant. We also obtain similar
results by directly integrating the spectral weight of each feature.

Before continuing in our discussion of the optical data, we first present our comple-
mentary Raman results. In figure 6.4 (a), we show the Raman susceptibility $\text{Im} \chi(\omega)$ for
two polarization geometries at 5 K. Below 50 meV, the spectra show sharp features due
to optical phonon modes, which we will discuss elsewhere. Instead, we focus on the high
energy region of our data shown in 6.4 (a), where a sharp feature is present near 144
meV. This feature is observed exclusively in the XY polarization channel and so has $A_{2g}$
symmetry. The energy of the 144 meV mode is large compared to both the Curie-Weiss
temperature $\Theta_{CW}$ (2-3.5 meV)\[131, 151\] and the phonon energies, meaning this mode
is not a magnetic or two-phonon excitation. Instead, the energy and pure $A_{2g}$ (chiral)
character of this mode are suggestive of an electronic excitation\[152, 153\].

The origin of the chiral excitation is not clear. As can be seen in figure 6.4 (b), the
Figure 6.3: Temperature dependent $\sigma_1(\omega)$ in RuCl$_3$. a) $\sigma_1(\omega)$ at 10 and 295 K. b) Oscillator strengths $S_n$ for $\alpha_1$, $\alpha_2$, and $\alpha_3$. The majority of the change in spectral weight occurs in $\alpha_1$. This is due to the importance of indirect transitions near the band gap. Furthermore, the fact that $\alpha_1$ and $\alpha_2$ do not significantly change with temperature indicates that these features are not vibronically-activated, $d - d$ transitions.
energy of this feature corresponds closely with the onset of the $\alpha_1$ transition (e.g. the electron-hole continuum) observed in $\sigma_1(\omega)$. We note that a similar feature has been observed in the RIXS spectra of a variety of iridates\cite{120, 154} and is thought to arise from a coupling between the delocalized electron-hole continuum and a localized orbital excitation between SOC split $j_{\text{eff}} = 1/2$ and $j_{\text{eff}} = 3/2$ states\cite{155}. The presence of this excitation in our data is therefore suggestive of the importance of SOC in RuCl$_3$.

The comparison of $\sigma_1(\omega)$ and Im $\chi(\omega)$ also allows us to determine the parity of the electronic excitations. RuCl$_3$ consists of weekly bound layers with symmetry $D_{3d}$. While the full space group $P3_112$ does not contain inversion symmetry, the $D_{3d}$ point group of the individual RuCl$_3$ layers does. As such, we expect that the electronic states of RuCl$_3$ retain an effective inversion symmetry and can thus be classified according to their parity. This has important consequences for our measurements. In the presence of inversion symmetry, Raman scattering exclusively probes even parity excitations, while $\sigma_1(\omega)$ will reflect odd parity excitations (i.e. excitations that carry a dipole moment)\cite{149}. Indeed, as shown in figure 6.4 (b), no trace of the chiral excitation can be seen in $\sigma_1(\omega)$. Similarly, the tail of $\alpha_1$ does not appear in the Raman spectrum. This reveals that the electronic excitations that we observe have well-defined parity. Specifically, the chiral excitation is even parity while $\alpha_1$ is necessarily odd.

6.4 Discussion

The intensity and band widths of the $\alpha$ features in $\sigma_1(\omega)$ are remarkably small compared to typical interband excitations in Mott insulators (see for example reference [150]). As we shall explain later, this is a consequence of the spin-orbit coupled electronic structure of RuCl$_3$. With reference to the calculated DOS shown in figure 6.1 (b), we interpret the $\sigma_1(\omega)$ spectra in a local picture as follows. We assign the $\alpha$ and $\beta$ peaks to the inter site process $|t_{2g}^5 t_{2g}^5\rangle \rightarrow |t_{2g}^4 t_{2g}^6\rangle$ and the $\beta$ peaks to $|t_{2g}^5 t_{2g}^5\rangle \rightarrow |t_{2g}^4 (t_{2g}^5 e_g)\rangle$ excitations. The $\delta$
peak is then a charge transfer excitation involving the states with a strong Cl $p$ character \( |t_{2g}\rangle \rightarrow |t'_{2g}L\rangle \) (\( L \) denotes a ligand hole). In this notation, the initial and excited states are specified in terms of the orbital population of a pair of Ru atoms. For instance, the $\beta$ transitions involve exciting an electron from the \( t_{2g} \) orbital of one Ru atom to the $e_g$ orbital of its neighbour. Importantly, these excitations carry a dipole-moment and are therefore odd parity, in agreement with our combined $\sigma_1(\omega)$ and Im $\chi(\omega)$ data. This assignment is consistent with the \textit{ab initio} band structure in figure 6.1, which suggests that \( |t'_{2g}t'_{2g}\rangle \rightarrow |t^4_{2g}t^6_{2g}\rangle \) processes should be important below 1 eV, \( |t^5_{2g}t^5_{2g}\rangle \rightarrow |t^4_{2g}(t^3_{2g}e_g)\rangle \) transitions dominant between 1 and 4 eV, and \( |t_{2g}\rangle \rightarrow |t'_{2g}L\rangle \) transitions contributing allowed above 4 eV. The $\alpha$ and $\beta$ transitions are indicated in the theoretical DOS shown in 6.1 (b).

Our interpretation also means that the onset in $\sigma_1(\omega)$ visible near 0.15 eV at 10 K in figure 6.3 (a) corresponds to the true optical gap (e.g. the energy cost for creating an electron-hole pair). We regard this value to be in fair in agreement with DC transport studies that find a gap between 0.1 and 0.4 eV[129, 156]. The discrepancy is due to either extended defects in the samples used in the transport studies or excitonic effects that reduce the optical gap from the true single particle value. Intersite excitations are also expected to contribute to the photoconductivity, and so this assignment is also consistent with the observation of a peak structure near the energy of $\alpha_3$ in low-temperature photoconductivity experiments[136].

The calculated band structure provides a natural explanation of the temperature dependence of the $\alpha_1$ peak spectral weight. Specifically, the band structure shown in figure 3 of reference [127] suggests that the lowest lying optical excitations correspond to indirect transitions originating at the L point in the valence band and terminating at the $\Gamma$ point of the conduction band. The energy of these transitions is predicted to be roughly 0.18 eV, in good agreement with our experimental value of 0.15 eV. Indirect optical transitions require the involvement of either acoustic or optical phonons to conserve
crystal momentum. These transitions acquire a characteristic temperature dependence that reflects the number of relevant phonons present[21, 157]. We therefore conclude that α_1 contains a significant indirect character, leading to the smooth decrease in oscillator strength shown in figure 6.3 (b).

The narrow widths (∼ 0.1 eV) and low intensity of the α features reflect the importance of spin-orbit coupling, which tends to promote the formation of flat electronic bands[146, 142, 158]. Indeed, for the ideal case of a 90 degree bond angle, the hopping t between nearest neighbour j_{eff} = 1/2 states in an edge sharing geometry is zero[17]. The optical conductivity associated with this hopping process scales as t^2 and so an intersite excitation between j_{eff} = 1/2 states is therefore expected to be weak[155, 159]. Transitions between states with strong j_{eff} = 1/2 character in Na_2IrO_3 indeed evince very low intensities[124]. Similarly, the small t leads to almost dispersionless bands and therefore to the very narrow features in \sigma_1(\omega) and weakly dispersing peaks in ARPES[133]. This is corroborated by the \textit{ab initio} DOS shown in figure 6.1 (b), where narrow peaks are observed near the Fermi level[127].

Spin-orbit coupling also provides a natural explanation for the three α peaks. Orbital degeneracy is known to produce additional structure in the σ_1(ω) of Mott insulators due to final state multiplet effects, even in 4d and 5d materials[138, 155, 160]. We therefore expect that the α transitions will show structure due to spin-orbit splitting of the |t_4^4\ell_2^6⟩ final state. In the limit of large 10Dq, the lowest energy t_2^4 state will be in a 3T₁ configuration. Under the action of SOC, this term is expected to split into into three states with energies −2\lambda, −\lambda and \lambda, yielding splittings of \lambda and 2\lambda[161]. Heuristically, this is due to the different ways of populating the j_{eff} = 1/2 states (e.g. two electrons, one electron, or no electrons). Assuming the Ru d^4 free ion value of \lambda ≈ 115 meV (ζ = 172 meV) [132], this produces splittings of 115 and 230 meV, in reasonable agreement with the 200-230 meV splittings between α peaks observed in figure 6.2 (a). This picture is also consistent with the \textit{ab initio} band structure, where the inclusion of SOC induces
Figure 6.4: Chiral excitation in RuCl$_3$. a) Raman susceptibility Im $\chi(\omega)$ for $E_g + A_{1g}(XX)$ and $E_g + A_{2g}(XY)$ channels at 10 K. b) Im $\chi(\omega)$ and $\sigma_1(\omega)$ at 10 K. The chiral excitation is visible near 143 meV. This excitation has a well-defined $A_{2g}$ symmetry as it appears exclusively in the XY scattering geometry. Similarly, the onset of the $\alpha_1$ feature in $\sigma_1(\omega)$ does not appear in Im $\chi(\omega)$, meaning it is a true odd-parity excitation.

The $\alpha$ transitions that we discuss here have previously been interpreted as intrasite $d-d$ excitations of the Ru $3^+$ ion$^{[136, 135]}$. Specifically, the low-lying $\alpha$ features have been attributed to $^2T_1 \rightarrow ^6A_1$, $^2T_1 \rightarrow ^4A_1$ and $^2T_1 \rightarrow ^4T_2$ spin-forbidden $d-d$ transitions. These excitations are even parity and so require the participation of an odd parity phonon (i.e. a vibronic absorption mechanism) to become optically-active, leading to a characteristic temperature dependence$^{[161]}$. However, the oscillator strength, detailed temperature dependence and symmetry of these excitations make make an intrasite $d-d$ assignment difficult.

First, the intensity of the $\alpha$ features in RuCl$_3$ is in fact anomalously large for $d-d$ transitions. The Ru site symmetry in RuCl$_3$ is very close to $O_h^{[128, 131]}$. In this situation, we expect that intrasite $d-d$ excitations should be dipole-forbidden, but
could become infrared active due to a vibronic absorption mechanism which involves the simultaneous absorption or emission of an odd-parity optical phonon[161]. In this situation, spin-allowed (i.e. spin-conserving) $d - d$ transitions typically display spectral weights one or two orders of magnitude lower than the transitions in RuCl$_3$. For example, a recent optical study of KCuF$_3$ revealed a series of $d - d$ transitions with a spectral weight $SW = \int_{0.6 \text{ eV}}^{1.9 \text{ eV}} \sigma_1(\omega) d\omega \approx 0.08 \Omega^{-1} \text{cm}^{-1} \text{ eV}$ at 8 K[162]. In contrast, our measurements show that the spectral weight $SW = \int_{0.1 \text{ eV}}^{0.87 \text{ eV}} \sigma_1(\omega) d\omega$ of the $\alpha$ features in RuCl$_3$ is $2 \Omega^{-1} \text{cm}^{-1} \text{ eV}$, more than an order of magnitude larger. Additionally, the low spin state of the Ru $d^5$ ion dictates that the low lying $d - d$ transitions are spin-forbidden (i.e. do not conserve the spin of the Ru ion) and would therefore expected to be orders of magnitude less than the spin-allowed transitions observed in KCuF$_3$[161], although SOC would relax this constraint to some degree. Finally, we note that assigning these features to the $^2T_1 \rightarrow ^6A_1$, $^2T_1 \rightarrow ^4T_1$ and $^2T_1 \rightarrow ^4T_2$ transitions and employing the Tanabe-Sugano diagram for a low-spin $d^5$ ion requires $10Dq \approx 1.5 \text{ eV}$[133], in contradiction with the value of 2.3 eV measured in x-ray absorption spectroscopy and suggested by DFT[127].

This reasoning is corroborated by the details of the temperature dependence. As can be seen in figure 6.3 (b), the majority of the spectral weight loss occurs almost entirely in $\alpha_1$, while $\alpha_2$ and $\alpha_3$ do not show significant temperature dependence. This is again at odds with the scenario of vibronic intrasite absorption mechanism, which would be expected to reduce features $\alpha_2$ and $\alpha_3$ as well, and points to an intersite excitation[161]. It is important to distinguish between the indirect absorption mechanism discussed here and the vibronic mechanism mentioned earlier in relation to possible localized $d - d$ transitions. Indirect transitions involve either acoustic or optical phonons providing the crystal momentum necessary for optical transitions between Bloch states located at different points in the Brillouin zone. In contrast, vibronic absorption refers to a process where an odd parity optical phonon enables transitions between localized, even parity electronic states. The comparison of $\sigma_1(\omega)$ and $\text{Im } \chi(\omega)$ also supports an intersite interpretation.
In the scenario of the $\alpha$ peaks being intrasite $d - d$ exceptions[136], we would expect these excitations to be Raman active due to their even parity, in contradiction with our measurements.

In summary, we have studied the electronic structure of RuCl$_3$ using optical and Raman spectroscopy. Our results are broadly suggestive of the importance of spin-orbit coupling in determining the electronic structure of RuCl$_3$. In particular, the small oscillator strength, narrow band widths, and number of features present in $\sigma_1(\omega)$, as well as the chiral excitation observed in Raman scattering, can all be understood by accounting for spin-orbit coupling. RuCl$_3$ is therefore an excellent candidate material for investigating the physics of the Heisenberg-Kitaev model in the solid state.

### 6.5 Co-authorship

This chapter is reproduced from a manuscript currently in preparation for publication. The manuscript is ‘L.J. Sandilands, A.A. Reijnders, Y. Tian, K.W. Plumb, V.V. Shankar, H.Y. Kee, Y.J. Kim, and K.S. Burch,“Relativistic electronic structure of RuCl$_3$ from optical and Raman spectroscopy”’. The thesis author was the primary investigator for this work, collected the data using existing instruments, prepared the manuscript, and helped conceive of the project. The RuCl$_3$ crystals were prepared by Kemp Plumb and Young-June Kim at the University of Toronto. The density functional theory calculations were performed by Vijay Shankar Venkataraman and Hae-Young Kee, also at the University of Toronto.
Chapter 7

Magnetic excitations and spin-phonon coupling in RuCl$_3$

7.1 Introduction

A key feature of magnets with competing or frustrated interactions is the presence of a large ground state degeneracy\cite{163}. This degeneracy obstructs long-range order and instead allows for a variety of unusual ground states, including quantum spin liquids. While these states have been extensively studied theoretically, the experimental picture is more limited due to the small number of candidate material systems\cite{164}. In this context, it was recently suggested\cite{17, 18} that the honeycomb iridates, a class of Mott insulators characterized by strong spin-orbit coupling, could manifest a quantum spin liquid ground state. The combination of strong spin-orbit coupling and orbital degeneracy leads to the formation of $j_{\text{eff}} = 1/2$ 'pseudospins' whose bond-dependent exchange interactions map onto the Kitaev model\cite{116}. Because of the bond-dependent interactions, this model is intrinsically frustrated and possesses an exotic, spin-disordered ground state. While there is indeed evidence for Kitaev-type interactions in the honeycomb iridates\cite{118, 119}, the experimental situation is complicated by non-cubic structural distortions \cite{120, 121, 122}.
and the existence of localized $j_{\text{eff}}$ moments has also been questioned[123].

As described in chapter 6, $\alpha$-RuCl$_3$ (hereafter RuCl$_3$) is a spin-orbit assisted Mott insulator and therefore a promising system in which to investigate Kitaev physics[127]. Similar to the honeycomb iridates, RuCl$_3$ crystallizes in a layered structure with planes of edge-sharing RuCl$_6$ octahedra arranged in a honeycomb lattice, as shown in figure 7.1 (d). These layers are weakly coupled and stack to form a CrCl$_3$-type structure with space group $P3_112$($\#151$)[128]. Crucially, the Ru atoms are in a low spin $d^5$ configuration and sit in an almost perfect Cl octahedron[131]. As the Ru $d$ states are less extended than in iridates, the effects of electron itineracy and non-cubic fields should be minimized. The resulting degeneracy of the $t_{2g}$ states is therefore expected to favour the formation of $j_{\text{eff}}$ states. Indeed, it was found that both spin-orbit coupling and electron-electron interactions are needed in density functional theory to reproduce the optical gap, meaning RuCl$_3$ should be considered a spin-orbit assisted Mott insulator, similar to Sr$_2$IrO$_4$[142]. The spin-orbit coupled character of the unoccupied Ru $d$ states was also directly verified by x-ray absorption spectroscopy at the Ru L$_2$ and L$_3$ edges[127]. These considerations combine to make RuCl$_3$ an excellent candidate Kitaev system.

The magnetism in RuCl$_3$ has been subject to a number of previous studies[128, 130, 131, 134]. Magnetic susceptibility measurements have identified a cusp near $T_N = 13$-16 K that was attributed to antiferromagnetic ordering[130, 131]. Above 100 K, the susceptibility shows Curie-Weiss behavior with an effective moment $\mu_{\text{eff}} = 2.25 \mu_B$ and a Curie temperature $\Theta_{\text{CW}} \approx 23$-40 K (2-3.5 meV)[131, 130]. Kobayashi et al. concluded that the intraplane (interplane) interactions are ferromagnetic (antiferromagnetic) and that ferromagnetic correlations develop within the plane at 100 K[131]. Intriguingly, powder neutron diffraction suggested that either the ordered moment is small ($< 0.5 \mu_{\text{eff}}$) or else that the moment lies parallel to the c-axis (perpendicular to the honeycomb plane)[130].

Despite these measurements, detailed spectroscopic information on the magnetic and
lattice excitations of RuCl$_3$ is lacking. Moreover, Raman scattering measurements on both quantum spin liquids and relativistic Mott insulator materials are limited\[165, 166, 167\]. We have therefore investigated the Raman response of this compound in the temperature range 5 to 300K. Raman spectroscopy is an excellent tool for the study of low-dimensional magnets, as it can simultaneously probe magnetic, lattice and electronic excitations\[147, 148, 168\]. Indeed, our measurements reveal two types of magnetic scattering: a quasi-elastic (QES) component at low energies and a broad continuum extending up to 20 meV. Both features display significant temperature dependence, with the QES component losing intensity as temperature decreases while the continuum progressively gains spectral weight below 120 K. Finally, the asymmetric (Fano) line shape and temperature dependence of two low energy phonon modes reveal coupling between (pseudo)spin and lattice degrees of freedom. Our results provide evidence for unusual magnetic excitations in RuCl$_3$.

7.2 Experimental Details

The $\alpha$-RuCl$_3$ crystals used in this study were grown by vacuum sublimation of pre-reacted RuCl$_3$ powder, as described in reference [127]. The Raman scattered intensity was measured in the quasi-back-scattering geometry in both collinear (XX) and crossed (XY) polarizations, with light polarized in the basal (cleavage) plane. The measured scattering intensity $I(\omega)$ can be related to the Raman susceptibility $\text{Im} \chi(\omega)$ through $I(\omega) \propto (n(\omega) + 1) \text{Im} \chi(\omega)[26]$, where $n(\omega)$ is the thermal Bose factor. Exciting light from a 532 nm laser was focussed down to a 10 $\mu$m spot and the power at the sample is estimated to be 500 $\mu$W. A pair of holographic notch filters (Ondax) were used to reject light from the fundamental, leading to a lower cutoff of 4 meV. The resolution of our spectrometer is estimated to be 0.6 meV. Halving the power and doubling the integration time produced no noticeable change in the spectra recorded at 5 K, suggesting negligible
Chapter 7. Magnetic excitations and spin-phonon coupling in RuCl$_3$

7.3 Experimental Results

The polarized Raman intensity of $\alpha$-RuCl$_3$ is shown in figure 7.1 for two representative temperatures, 5 and 295 K. The 5 K spectrum in figure 7.1 (b) consists of a series of sharp phonon modes superimposed on a weak, magnetic continuum that extends up to roughly 20 meV. The continuum is shown in more detail in figure 7.1 (c). Strong and
sharp phonon modes are resolved at 14, 20, 34, 37, and 38 meV, with weaker modes detected at 27 and 42 meV.

The number and symmetry of the phonons modes α-RuCl₃ can be understood in terms of an isolated RuCl₃ layer of symmetry $D_{3d}$, rather than the full space group. In this case, group theory predicts a total of six (4$E_g$ and 2$A_{1g}$) Raman-active modes[169]. The 4$E_g$ modes are expected to be visible in both polarization channels while the 2$A_g$ modes vanish in the crossed geometry. Indeed, the modes at 38 and 42 meV are suppressed in the crossed (XY) geometry and so can be assigned $A_{1g}$ symmetry. The remaining five modes as well as the continuum are present in both polarization channels and therefore have $E_g$ symmetry, meaning RuCl₃ exhibits one more $E_g$ phonon mode than expected from group theory for a single $D_{3d}$ layer. We therefore suspect that the mode at 27 meV is in fact either defect activated or due to interlayer interactions, as it is the lowest intensity peak in the $E_g$ channel. Given that the spectra show only weak deviations from the ideal $D_{3d}$ symmetry of a single layer, we conclude that interlayer lattice interactions are weak in this compound. Although all observed phonon modes broaden in going from 5 to 295 K, the number of modes does not change, meaning the $D_{3d}$ symmetry of the individual RuCl₃ layers is unperturbed.

We also note that the two lowest energy $E_g$ phonons at 14 and 20 meV show asymmetric (Fano) line shapes[170, 171]. This effect arises generically when a narrow resonance couples to broad continuum and in the case of RuCl₃ demonstrates that the continuum is indeed real (i.e. is not due to spurious experimental background) and that it extends up to at least 20 meV, given the asymmetric line shape of the phonon at this energy.

### 7.4 Discussion

RuCl₃ is electrically insulating with an optical gap of at 0.15 eV and a transport gap between 0.1 and 0.4 eV, which rules out an electronic origin for the continuum[127, 129].
We therefore attribute the continuum to magnetic scattering.

The broad line shape, lack of obvious peak, and energy scale of the magnetic scattering are unusual. Two possible explanations for this feature are scattering from either spinons (the excitations of a quantum spin liquid) or from heavily-damped two-magnon excitations. Spinon scattering continua have been identified in other 2D systems such as the candidate quantum spin liquid herbertsmithite \((\text{ZnCu}_3(\text{OH})_6\text{Cl}_2)\)[165] and in the paramagnetic state of the related material clinoatacamite \((\text{Cu}_2(\text{OH})_3\text{Cl})\)[172]. Given the possibility of Kitaev interactions in RuCl\(_3\), a broad spinon continuum might also be anticipated on theoretical grounds[173].

Indeed, the energy scale of the continuum scattering is high for conventional magnetic scattering given the Curie-Weiss temperature \(\Theta_{\text{CW}}\) inferred from the in-plane susceptibility is at most 3.5 meV (40 K) [131]. The mean field result for the exchange interaction \(J = 3k_B\Theta_{\text{CW}}/2zS(S + 1)\) yields \(J \approx 2.5\) meV for spin \(S = 1/2\) and three nearest neighbours \(z\). In the Ising limit, this would imply a two-magnon energy of roughly \(E_{2M} \approx 2J = 5\) meV. In contrast, identifying \(J\) with the Kitaev interaction \(J_K = J_x = J_y = J_z\) would yield a spinon bandwidth of \(6J_K\)[116]. Scattering from two spinon-antispinon pairs, which is expected to contribute to the Raman scattered intensity in a quantum spin liquid[174], would then extend up to roughly \(12J_K = 30\) meV, in fair agreement with our experimental estimate of 20 meV.

Although an explanation in terms of spinon scattering is appealing, the possibility of strongly damped two-magnon scattering also exists. Spin-phonon coupling is known to lead to anomalously broad two-magnon line shapes in both the cuprates and the layered honeycomb magnet \(\text{NiPS}_3\) [175]. Indeed, the Fano line shapes evinced by the lowest lying phonons in RuCl\(_3\) are indicative of some coupling between lattice and magnetic degrees of freedom. As described later, the continuum line shape in RuCl\(_3\) does not vary significantly with temperature. This fact is seemingly at odds with magnon decay into phonons, which would naively be expected to decrease with reduced temperature. How-
ever, discriminating the two possible scenarios (spinon or spin-phonon coupling) would likely require a detailed theory of spin-phonon coupling in RuCl$_3$ or a more detailed spectroscopic measurement of the magnetic excitations, namely inelastic neutron scattering.

A comparison of the spectra collected at 295 K shown in figure 7.1 (a) to the 5 K data in 7.1 (b) reveals another source of scattering. Specifically, a quasielastic scattering (QES) component of $A_{1g}$ symmetry (i.e. only visible in the XX channel) peaked at low energies emerges at high temperatures, while the continuum is suppressed. Similar to the continuum scattering, the low energy of the QES is suggestive of a magnetic origin. Indeed, QES has been observed in a variety of low dimensional spin systems[168], including the candidate quantum spin liquid herbertsmithite[165], and is usually attributed to scattering from fluctuations in magnetic energy density[176].

Having identified the various excitations present, we now consider the details of the temperature dependence of the spectra. In figure 7.2 (a) and (b), we plot the imaginary part of the Raman response function $\text{Im} \chi(\omega)$ for the XX channel at several representative temperatures. The temperature dependence of the Raman intensity $I(\omega)$ is dominated, especially at low energies, by the thermal Bose factor $n(\omega)$ and so we focus on $\text{Im} \chi(\omega)$ in order to identify subtler spectral changes. As can be seen in figure 7.2 (a), at energies below 10 meV $\text{Im} \chi(\omega)$ decreases as temperature is lowered from 295 K to 170 K. This change reflects the loss of intensity from the QES feature, which is no longer visible below 170 K. At temperatures below 100 K, the magnetic continuum gains intensity. Accordingly, $\text{Im} \chi(\omega)$ increases in a region extending to roughly 20 meV as temperature is further lowered, as can be seen in figure 7.2 (b).

This temperature dependence can be more readily appreciated by considering the integrated spectral weight $SW = \int_{\omega_l}^{\omega_h} \text{Im} \chi(\omega)$ where the cut-offs $\omega_l$ and $\omega_h$ are 4 and 5.5 meV respectively. These cutoffs are selected to include both QES and continuum contributions. We show this quantity for the XX channel in figure 7.2 (c). As anticipated from figures 7.2 (a) and (b), the spectral weight first decreases, reflecting the loss of
QES intensity, before sharply increasing below 100 K as the magnetic continuum gains weight. This is in contrast to the XY spectral weight shown in 7.2 (d). Since the QES is not present in this polarization channel, the XY spectral weight is flat at high temperatures before showing a similar continuum related increase below $T^* \sim 120$ K. The persistence of magnetic scattering far above $T_N$ also hints at an extended fluctuation regime, consistent with highly two-dimensional magnetism and/or frustration. Kobayashi et al.[131] attributed deviations from paramagnetic behaviour in the susceptibility near 100 K to the build-up of in-plane spin correlations.

While it gains intensity, the continuum scattering line shape does not vary strongly with temperature, even below the ordering temperature $T_N \approx 15$ K. Typically, the broad magnetic continuum will evolve into well-defined peaks due to scattering from one or two magnon excitations associated with long range order[177, 178, 179]. In contrast, the magnetic scattering in RuCl$_3$ displays no obvious peaks or changes upon ordering, as can be seen by comparing the 5 and 15 K data in figure 7.2 (b). A possible explanation is that well-defined magnon modes exist below our experimental cutoff of 4 meV or else the the magnetic excitations participating the Raman scattering are strongly-damped. In any case, the persistence of the broad magnetic continuum in our data indicate that the magnetic excitations remain strongly damped even in the ordered phase.

The smooth reduction in QES with temperature suggests a similarly smooth evolution of the low energy spin dynamics. In particular, the spectra do not show evidence for a well-defined gap, as this would produce an exponential drop in QES intensity with temperature[176]. The QES is only visible in our measurement down to 170 K and so our data does not rule out the development of a gap at still lower temperatures.

The Raman spectra also reveal signatures of coupling between the continuum and lattice degrees of freedom in RuCl$_3$, as evinced by the Fano line shapes of the two lowest lying $E_g$ phonons shown in figure 7.3 (a). The Fano effect can occur when a well-defined excitation, in this case an optical phonon, overlaps and also interacts with broad continuum
Figure 7.2: Magnetic scattering in RuCl₃. a) Im \(\chi(\omega)\) in \(E_g\) and \(A_{1g}\) (XX). b) Im \(\chi(\omega)\) in \(E_g\) and \(A_{1g}\) (XY). c) \(E_g\) and \(A_{1g}\) (XX) low energy spectral weight (SW) vs. temperature. d) \(E_g\) and \(A_{2g}\) (XY) low energy spectral weight (SW) vs. temperature. As shown in (a), the quasi-elastic scattering (QES) decreases in intensity as temperature is reduced. In contrast, the intensity of the continuum increases as temperature is reduced, as can be seen in (b). This is more clearly resolved in (c), where the \(E_g\) and \(A_{1g}\) SW initially decreases, reflecting the suppression of QES, before increasing below \(T^* \approx 120\) K as the continuum gains weight. Since the QES has \(A_{1g}\) symmetry, it does not contribute to the \(E_g\) and \(A_{2g}\) SW shown in d). The \(E_g\) and \(A_{2g}\) is therefore constant at high temperatures before rising below \(T^* \approx 120\) K due to the continuum contribution.
of typically electronic or magnetic origin. These two excitations can interfere, leading to an asymmetric (Fano) resonance\[180\]. Indeed, Fano lineshapes have been observed in the phonon spectra of several low-dimensional magnets\[165, 181\]. The scattering profile of this resonance as a function of frequency $\omega$ is\[182\]:

$$f(\omega) = \frac{I_s}{q^2 - 1} \frac{(q + \epsilon^2)}{1 + \epsilon^2}.$$  \hspace{1cm} (7.1)

Here $I_s$ is the integrated intensity, $q$ is the Fano asymmetry parameter, and $\epsilon = \frac{2(\omega - \omega_o)}{\Gamma}$ is a reduced frequency determined by the phonon frequency $\omega_o$ and width $\Gamma$. The factor of $q^2 - 1$ in the denominator is a normalization factor chosen such that the integrated intensity is independent of $q$.

We find that the spectral region depicted in 7.3 (a) is well-fit at all temperatures and both polarization geometries by a function consisting of the sum of two Fano line shapes (equation 7.1) and a constant background term. A fit to a sum of three Lorentzians (one for the continuum and two for the phonons) was also tried, but yielded a consistently worse fit (e.g. the reduced $\chi^2$ was a factor of three larger than that of the Fano parameterization at low temperatures). The observation of Fano line shapes firmly establishes the existence of the continuum.

The temperature dependence of the line shape parameters $\Gamma$ and $q$ mirrors the onset of continuum scattering that we observe directly in the data, as expected for spin-phonon coupling. In figure 7.3 (b)-(d) we show the line width $\Gamma$, asymmetry $1/q$, and mode frequency $\omega_o$ for the 20 meV phonon. The 14 meV phonon shows qualitatively similar behavior. The line width $\Gamma$ displays a non-monotonic temperature dependence. It decreases almost linearly with decreased temperature from 300 K down to 120 K. At this point, the width begins to grow slowly before plateauing at low temperature. The phonon frequency $\omega_o$ also changes with temperature, blue-shifting monotonically with decreasing temperature by 1.7%. Finally, the asymmetry of the mode, given by $1/q$, shows an onset near 120 K. We have also included the $E_g + A_{2g}$ (XY) spectral weight in
7.3 (c) for comparison. This quantity can be seen to closely track \(1/q\).

The non-monotonic temperature dependence of \(\Gamma\) implies an unconventional contribution to the phonon relaxation, distinct from the typical anharmonic behavior. To illustrate this, we first review the expected impact of anharmonicity on phonon line widths. Decay into a pair of acoustic modes of opposite momenta yields the following expressions for the phonon line width and frequency\[183\]:

\[
\Gamma(T) = \Gamma_o + A[1 + 2n(\omega_o/2)], \quad (7.2)
\]
\[
\omega(T) = \omega_o - B[1 + 2n(\omega_o/2)], \quad (7.3)
\]

where \(\omega_o\) is the bare phonon frequency, \(\Gamma_o\) is the zero-temperature line width, \(A\) and \(B\) are constants, and \(n(\omega_o/2)\) is the Bose factor for a phonon of energy \(\omega_o/2\). Importantly, equations 7.2 and 7.3 are monotonic functions of temperature, varying quasi-linearly for temperatures greater than \(\omega_o\) while changing slowly at temperatures less than \(\omega_o\). In general, other combinations of acoustic and optical phonons that satisfy energy and momentum conservation can also contribute\[184\]. However, these processes lead to a similar monotonic temperature dependence that is almost constant at low temperatures and quasi-linear at high-temperatures. In contrast to the expectations of this simple theory, the experimental \(\Gamma\) reveals a non-monotonic temperature dependence and cannot be fit to equation 7.2 over the full temperature range. To demonstrate this, we have included in figure 7.3 (b) a plot of equation 7.2. Here \(\Gamma_o\) and \(A\) were chosen from a fit to the high temperature linear regime between 160 K and 300 K, while \(\omega_o\) was chosen from the 5 K value derived from the Fano fits. Clearly, the data and the fit diverge near 120 K, implying an additional relaxation mechanism.

We conclude that there are two principle contributions to the low-lying \(E_g\) phonon self-energies: an anharmonic term which is present at all temperatures and a component due to spin-phonon coupling which increases sharply at low \(T^* \sim 120 K\) temperature,
causing an increase in both $\Gamma$ and $1/q$. As can be seen in figure 7.3, the temperature dependence of these two quantities parallels the change in spectral weight of the magnetic continuum, meaning that (pseudo)spin and lattice degrees of freedom are linked in RuCl$_3$.

### 7.5 Conclusions

To conclude, we have studied the elementary excitations of the relativistic Mott insulator $\alpha$-RuCl$_3$ using polarized Raman scattering. Our measurements reveal a magnetic quasielastic scattering component and a broad continuum that couples to the two lowest energy phonons. The temperature dependence of the continuum reveals an onset near $T^* \sim 120 \text{ K}$, a temperature scale that we identify with the development of in-plane spin correlations. This temperature scale is also manifest in the line widths of certain phonons, pointing to coupling between the pseudospin and lattice degrees of freedom in RuCl$_3$. Our results demonstrate that RuCl$_3$ hosts unusual magnetic excitations. Finally, our findings motivate further experiments to elucidate the unusual magnetism and local electronic structure in this material, in particular neutron and x-ray scattering spectroscopies.

### 7.6 Co-authorship

This chapter is reproduced from a manuscript currently in preparation for publication. The manuscript is ‘L.J. Sandilands, Y. Tian, K.W. Plumb, Y.J. Kim, and K.S. Burch, “Magnetic Raman scattering in the honeycomb lattice relativistic Mott insulator $\alpha$–RuCl$_3$”’. The thesis author was the primary investigator for this work, collected the data using an existing instrument, prepared the manuscript and conceived the work. The RuCl$_3$ crystals studied were grown by Kemp Plumb and Young-June Kim at the University of Toronto.
Figure 7.3: Temperature dependence of the $E_g$ Fano resonances. a) Data and Fano fit to the low energy scattering. b)-d) Energy $\omega_0$, asymmetry $1/q$, and line width $\Gamma$ of the high intensity phonon. e) Magnetic contribution to the phonon line width. The low-energy data is well-described by the Fano form and indicates a coupling between the continuum and the lattice. This coupling is also manifest in the temperature dependence of $1/q$ and $\Gamma$, which show anomalies near $T^* \sim 120$ K. Indeed, $1/q$ closely tracks the XY spectral weight which is also shown in c).
Chapter 8

Conclusions

In the course of this thesis, a number of van der Waals solids were studied using optical and Raman spectoscopies. We summarize our findings below and also suggest possible avenues for furthering the understanding of these compounds.

8.1 Electrodynamics of BSCCO 2DACS

In chapters 3 and 4, we presented Raman and infrared spectromicroscopy data from ultra-thin BSCCO 2D atomic crystals. We also detailed how these samples can be produced and identified by their appearance under an optical microscope. Our microscopies revealed several changes in the electrodynamics of these samples with respect to their bulk properties. Most prominently, the evolution of $\sigma_1(\omega)$ with thickness in the optimally-doped samples suggests the presence of an insulating surface layer. This explains the previous observation of insulating behaviour in these samples as an extrinsic effect. Secondly, our studies have demonstrated a modification of the bosonic excitations in these compounds. After correcting for the presence of an insulating layer, we employed an extended Drude analysis of $\sigma_1(\omega)$ to demonstrate a change in carrier dynamics. This was interpreted as a blue-shift of the electron-boson spectral function $\alpha^2 F(\omega)$ in our samples and therefore of the characteristic energy scale of the bosons that couple to the free carriers. A clue
to the origin of this effect was obtained in our Raman scattering study of Dy-BSCCO 2D atomic crystals. Specifically, we observed pronounced hardening of the two-magnon Raman feature, suggesting $J$ increases from roughly 115 to 135 meV. This is consistent with the behaviour of $\alpha^2 F(\omega)$ if we identify the bosons that couple to charge carriers as magnetic excitations. Taken together with x-ray Laue microscopy performed by our collaborators, we interpret our results as due to a straightening of the average Cu-O bond angle that accompanies the modification of the incommensurate superstructure in BSCCO 2D atomic crystals.

Our results suggest that any devices (i.e. for electrostatic gating experiments) based on exfoliated BSCCO would likely require steps to prevent or compensate for surface degradation. In particular, the insulating surface layer would be expected to lead to high contact resistance in a transport measurement. Possibilities include oxygen annealing, employing a gold capping layer, or performing the sample preparation and measurement in an inert atmosphere. It would also helpful to identify the precise cause of the surface degradation. The application of surface analysis techniques, such as x-ray photoelectron spectroscopy or secondary ion mass spectroscopy, is desirable in this regard.

Several measurements would be useful to solidify the finding of modified magnetic dynamics in these samples. First, the change in $\alpha^2 F(\omega)$ should be verified by other techniques, specifically inelastic tunnelling or photoemission. A central technical challenge for these probes would be the preparation of a suitable surface on a BSCCO 2D atomic crystal. Second, a measurement of the two-magnon Raman feature in the optimally-doped 2D atomic crystals is needed. The two-magnon tends to red-shift and lose intensity with doping and so we were not able to observe it in our samples. However, a recent study has revealed that this effect is principally due to a modification of the charge transfer excitations (e.g. a change in the resonance condition) rather than the two-magnon excitation itself[185]. Therefore a Raman study using a lower excitation frequency could potentially detect the two-magnon in optimally-doped BSCCO 2D atomic crystals.
The change in the spectrum of magnetic excitations in BSCCO 2D atomic crystals also presents a novel opportunity to study the role of magnetism in driving the high-temperature superconductivity. An infrared microscopy study at lower temperatures and photon energies would be helpful in this regard, as this would provide access to both the superfluid density ($\rho_s$) and the energy gap ($\Delta$). Based on existing studies of bulk crystals, an infrared study of the superconductivity would require extending the measurements below 100 meV[34]. The SiO$_2$ phonons of the Si substrates used in this study make measurements below 175 meV difficult. A solution would therefore be to exfoliate the BSCCO samples onto a more convenient substrate, such as bare silicon (which has no infrared active phonons). In our experience, it also difficult to obtain reliable data below 125 meV with the spectromicroscopy setup used in this work. This cutoff is a combined result of the MCT detector and the beam line design. Switching to a silicon bolometer and a beam line optimized for the spectral region below 100 meV would therefore be an ideal approach in this respect.

8.2 Doping dependent charge dynamics in Cu$_x$Bi$_2$Se$_3$

In chapter 5, we considered the charge dynamics of superconducting Cu$_x$Bi$_2$Se$_3$ for varying Cu content $x$. We observed a decrease in the plasma frequency ($\omega_p$) with increasing $x$. Through an analysis of the interband transitions, we demonstrated that the carrier density $n$ is not significantly affected. The disorder level, parameterized by the free carrier scattering rate ($1/\tau$) and the Urbach parameter ($\sigma_o$), is also relatively constant. Taken together, these findings indicate that the primary effect of Cu doping is to increase the conduction band mass ($m_b$), rather than to increase carrier density or disorder. Importantly, this means that the evolution of the superfluid density ($\rho_s$) with doping is primarily a band structure effect, rather than due to disorder, and so does not provide evidence for unconventional superconductivity[15]. Furthermore, this result emphasizes
the non-trivial effect of Cu doping in this compound.

Given the complex nature of Cu doping, further work is needed to elucidate the behaviour of the Cu dopant atoms at high concentrations. Possible experiments would include channeling experiments to determine the locations of the dopant atoms in the host lattice as well as scanning tunnelling microscopy to investigate any local changes in electronic structure driven by the dopant atoms. Another intriguing experiment would be to investigate the $c$-axis optical conductivity ($\sigma_c(\omega)$) of $\text{Cu}_x\text{Bi}_2\text{Se}_3$. Photoemission and quantum oscillation measurements have detected a quasi two-dimensional Fermi surface at high doping levels. This effect suggests a very large $c$-axis dynamical mass. It would be helpful to establish the connection between this behaviour, the possible many-body origin of the $ab$-plane mass increase, and the emergence of superconductivity. Indeed, iron-based and cuprate superconductors show highly unusual charge dynamics perpendicular to the CuO$_2$ and FeSe planes[186].

### 8.3 Electronic and magnetic excitations of $\alpha$-RuCl$_3$

In chapters 6, we presented an optical and Raman spectroscopy study of the electronic excitations of the honeycomb lattice Mott insulator RuCl$_3$. We observed a small optical gap of 0.15 eV and a Raman-active exciton at similar energy. Furthermore, the low intensity and narrow line widths of the excitations across the Mott gap in $\sigma_1(\omega)$ below 1 eV are consistent with the expectation of suppressed hopping between $j_{\text{eff}} = 1/2$ states on the honeycomb lattice. The number of peaks in $\sigma_1(\omega)$ are due to spin-orbit splitting of the optically excited state. Our results demonstrate the importance of spin-orbit coupling in determining the electronic structure of this compound.

In chapter 7, we investigated the low energy lattice and magnetic excitations of RuCl$_3$ through Raman scattering. Our main finding is a broad magnetic continuum extending up to roughly 20 meV. This indicates that RuCl$_3$ hosts unusual magnetic excitations,
which is consistent with theoretical expectations for the spin-orbit coupled Mott insulator on the honeycomb lattice. RuCl$_3$ also evinces a quasielastic scattering component that is suppressed at low temperatures, while the magnetic continuum gains in intensity below a temperature $T^* \sim 120 \, K$, which we identify with the development of short-ranged spin correlations. The line shapes of the two low energy phonons show anomalies due to spin-phonon coupling at the same temperature.

Our results motivate several further experiments. Determining the details of the ordered magnetic structure and the magnetic excitation spectrum through neutron or x-ray techniques is highly desirable. A measurement of the $c$-axis $\hat{\sigma}(\omega)$ would be helpful to validate our assignment of the low-lying transitions to inter site excitations, as these are expected to be suppressed in this geometry[150]. Finally, a measurement of much thicker crystals could potentially detect weak optical excitations related to the spinons (if present), as have been seen in a number of candidate spin liquid systems[187, 188]. The proposed optical and neutron scattering experiments would both require larger single crystal samples than are currently available.
Bibliography


[74] Y. He, S. Graser, P. J. Hirschfeld, and H.-P. Cheng, “Supermodulation in the atomic structure of the superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ from ab initio calculations,” *Phys. Rev. B*, vol. 77, p. 220507, Jun 2008.


dependence of Raman active modes in CuGeO$_3$, ” Solid State Communications,


[183] Y. J. Um, J. T. Park, B. H. Min, Y. J. Song, Y. S. Kwon, B. Keimer, and
M. Le Tacon, “Raman scattering study of the lattice dynamics of superconducting

scattering by phonons in Si, Ge, and $\alpha$-Sn: Anharmonic effects,” Phys. Rev. B,

[185] Y. Li, M. Le Tacon, Y. Matiks, A. V. Boris, T. Loew, C. T. Lin, L. Chen,
M. K. Chan, C. Dorow, L. Ji, N. Barišić, X. Zhao, M. Greven, and B. Keimer,
“Doping-dependent photon scattering resonance in the model high-temperature
superconductor HgBa$_2$CuO$_{4+\delta}$ revealed by Raman scattering and optical ellipsom-

G. D. Gu, and D. N. Basov, “Incoherent c-axis interplane response of the iron
chalcogenide FeTe$_{0.55}$Se$_{0.45}$ superconductor from infrared spectroscopy,” Phys. Rev.

Y. S. Lee, and N. Gedik, “Spin-induced optical conductivity in the spin liquid