INFRARED AND OPTICAL STUDIES OF TOPOLOGICAL INSULATORS

$\text{Bi}_2\text{Te}_3$, $\text{Bi}_2\text{Se}_3$ AND $\text{Sb}_2\text{Te}_3$

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INFRARED AND OPTICAL STUDIES OF TOPOLOGICAL INSULATORS

$\text{BI}_2\text{TE}_3$, $\text{BI}_2\text{SE}_3$ AND $\text{SB}_2\text{TE}_3$

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Thesis

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ABSTRACT

Topological insulators are currently a main focus of condensed matter research. They have a unique property in which the bulk of the material acts as an insulator, while the surface states display metallic behavior. Using infrared, optical and magneto-optical spectroscopy, we have studied 3D topological insulators Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$_3$ to understand their optical properties. The measurements were carried out using a Fourier Transform Infrared Spectrometer (FTIR) and an ultraviolet - visible spectrometer at varying temperatures ranging from 5 Kelvin to 300 Kelvin and at varying magnetic fields up to 18 Tesla.

We use the Drude - Lorentz model to replicate the experimental data of the samples allowing to gain an understanding of the physical phenomena happening in the infrared, visible and ultraviolet regions of radiation. This understanding gives us insight on the optical properties of the materials such as charge dynamics. Results show that the temperature and magnetic field have an effect on the charge carriers especially near the plasma frequency.
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CHAPTER I

INTRODUCTION

Infrared and optical spectroscopy are prime experimental techniques in determining the physical phenomena of a solid’s response to electromagnetic radiation. Optical frequencies refer to visible and ultraviolet light pertaining $12500 \text{ - } 50000 \text{ cm}^{-1}$. The interaction of these frequencies with a solid leads to energy excitations of outer shell electrons giving insight on electron inter-band transitions and plasma oscillations. While, the infrared frequencies are lower in frequency compared to optical having $30 \text{ - } 12500 \text{ cm}^{-1}$. In this region the solid can absorb the energy which can lead to lattice vibrations, electron intra-band transitions and also plasma oscillations. Thus this broad frequency range, $30 \text{ - } 50000 \text{ cm}^{-1}$, allows for understanding of charge dynamics, low-energy excitations and electronic band structure [1, 2, 3].

Within the past several years a newly discovered ‘state of matter’ called topological insulators has emerged with unique physical properties. Although the name is deceiving they behave as an insulator in the bulk, but have edge (2D case) or surface (3D case) states that allows for the motion of free electrons [4, 5]. The actual skin depth of conducting edges/surfaces is unknown. Their band structure follows from the conventional insulator, meaning there is an energy gap between the valance band and the conduction band, but on the boundary there are these gapless edges or
surface states that are protected by time reversal symmetry. [4, 5, 6, 7, 8].

Since topological insulators are relatively new materials, knowledge and understanding of their physical properties are limited. At the current time there has been no other research published using infrared and optical spectroscopy. Thus being ideal to gain insight on their optical properties.
CHAPTER II

TOPOLOGICAL INSULATORS

This chapter discusses some of the basic physical properties known of the materials.

2.1 Bi$_2$Te$_3$, Sb$_2$Te$_3$, Bi$_2$Se$_3$

The first 2D topological insulators were predicted in 2006 in HgTe/CdTe quantum wells then experimentally observed in 2007. This was then generalized to 3D where the first 3D topological insulator predicted was Bi$_{1-x}$Sb$_x$ alloy within a certain range of doping $x$ [4]. The surface structure of Bi$_{1-x}$Sb$_x$ was found to be rather complex which lead to the search for other 3D topological insulators. Then emerged the “second generation” 3D topological insulators [5], Bi$_2$Te$_3$, Sb$_2$Te$_3$, Bi$_2$Se$_3$, which are the samples experimented on in this paper.

The crystal structure of Bi$_2$Te$_3$, Sb$_2$Te$_3$, Bi$_2$Se$_3$ are classified as a rhombohedral lattice in space group D$_{3d}^5$ [4]. An example of Bi$_2$Se$_3$ is given in figure 2.1. The crystal structure consists of five-atom layers stacked in the $z$ direction, called quintuple layers, and each individual layer forms a triangular lattice. The primitive lattice vectors $\vec{t}_{1,2,3}$ and the rhombohedral primitive unit cells are shown in figure 2.1.

Bismuth is a non insulating pentavalent semimetal found in the post-transition metals on the periodic table. Although being classified as a metal its electrical resis-
Figure 2.1: (a) Crystal structure of Bi$_2$Se$_3$ with three primitive vectors labeled $\vec{t}_{1,2,3}$. The red box indicates the quintuple layer with Se1-Bi1-Se2-Bi1'-Se1'. (b) Top view along the z-direction showing one quintuple layer. Each layer is a triangular lattice with inequivalent positions labeled by A, B and C. (c) Side view of the quintuple layer structure. Along the z direction, Se and Bi atomic layers are stacked in the sequence: C(Se1')-A(Se1)-B(Bi1)-C(Se2)-A(Bi1')-B(Se1')-C(Se1). From reference [4].

tance is very high and its thermal conductivity is very low being very close to that of an insulator. Antimony is in the same group as bismuth and is also considered a non insulating pentavalent semimetal. Antimony also has similar properties to bismuth such as high resistivity and low thermal conductivity. Tellurium is classified as a semimetal displaying both metal and non-metal properties.

The surface state of a 3D topological insulator consists of a single 2D massless Dirac fermion. The theoretically calculated dispersion forms the so-called Dirac cone shown in figure 2.2 for Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Se$_3$ [4]. The figure displays the band structure on the [111] surface and it is seen that the bulk conduction band (top red region) is separated from the bulk valance band (bottom red region) by the energy
gap (blue region). The two red lines connecting the conduction and valance bands are the gapless surface states. For Bi$_2$Se$_3$ these two lines meet at Γ (origin) and zero energy forming the Dirac tip of the cones (top and bottom). This point is also the inversion point and is protected by time reversal symmetry [4, 6, 7, 8, 9, 11]. These surface states (Dirac cone) happen due to the band inversion of the orbitals of opposite parity closest to the Fermi level, which is due to the spin-orbit coupling of Bi and Se [4, 6, 7, 8, 9, 11]. Thus the difference between a typical insulator and a topological insulator is the protected edges or surface states caused by the spin-orbit coupling. Where a typical insulator dispersion is shown for Sb$_2$Se$_3$. 
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CHAPTER III
THEORY

3.1 Infrared and Optical Spectroscopy

Both infrared and optical spectroscopy allow for the analysis of a solid’s response to an electromagnetic (EM) wave. The prime response functions to an EM wave of a solid are given by the complex dielectric function \( \tilde{\epsilon}(\omega) \) and the complex optical conductivity \( \tilde{\sigma}(\omega) \) [12]. These two response functions describe the electric polarization and current induced response to an applied electric field. They cannot be determined directly through experiment, but reflectance measurements yield the percent reflectance \( R(\omega) \) and through a transformation the functions can be determined. This section also briefly discusses the theory behind the optical conductivity and the dielectric function and following with the theory of the Fourier transform infrared spectroscopy.

3.1.1 Optical definitions

By beginning with Maxwell’s equations and finding the wave equations in terms of the electric and magnetic field, one can obtain the spatial and time dependent electric and magnetic field vectors as a propagating plane wave given by

\[
\vec{E} = E_0 e^{i(k \cdot \vec{r} - \omega t)} \quad \text{and} \quad \vec{B} = B_0 e^{i(k \cdot \vec{r} - \omega t)}
\]  

(3.1)
where \( \vec{k} \) is the wave vector and \( \omega \) is the frequency. In an absorbing medium, the wave vector \( \vec{k} \) is directly proportional to the complex refractive index \( \tilde{n}(\omega) \).

\[
k = \tilde{n}(\omega) \frac{\omega}{c}
\]

(3.2)

where \( c \) is the speed of light and

\[
\tilde{n} = n(\omega) + i\kappa(\omega)
\]

(3.3)

\( n(\omega) \) is known as the refractive index and is the real part of the complex refractive index, while \( \kappa(\omega) \) is the extinction coefficient and is the imaginary part of the complex refractive index [13]. The refractive index \( n(\omega) \) is the ratio of the speed of light in vacuum to that of the speed of light in the medium. The extinction coefficient is directly related to the absorption coefficient of the material. The absorption coefficient tells us about the attenuation of the beam incident upon the medium.

From the wave equations, the relation of the complex index of refraction of a medium to the complex dielectric function \( \tilde{\varepsilon}(\omega) \) of the medium can be found as (at optical frequencies the magnetic permeability \( \mu = 1 \)) [13]

\[
\tilde{n}(\omega) = \sqrt{\tilde{\varepsilon}}
\]

(3.4)

Where the the complex dielectric function and complex optical conductivity are defined as
\[ \tilde{\epsilon} = \epsilon_1 + i\epsilon_2 \quad \tilde{\sigma} = \sigma_1 + i\sigma_2 \] (3.5)

and combing equations (3.3) and (3.5) into (3.4), the real and imaginary parts of \( \tilde{n} \) and \( \tilde{\epsilon} \) are related by

\[ \epsilon_1 = n^2 - \kappa^2 \quad \epsilon_2 = 2n\kappa \] (3.6)

or inversely,

\[ n = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2 + \epsilon_1}}{2}} \quad \kappa = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2 - \epsilon_1}}{2}} \] (3.7)

The complex dielectric function is related to the optical conductivity by

\[ \tilde{\epsilon}(\omega) = 1 + \frac{4\pi i\tilde{\sigma}(\omega)}{\omega} \] (3.8)

and in real and imaginary parts

\[ 4\pi\sigma_1 = \omega\epsilon_2 \quad 4\pi\sigma_2 = \omega(\epsilon_1 - 1) \] (3.9)

The complex reflectivity coefficient \( \tilde{r}(\omega) \) is defined as the ratio of the reflected electric field to the incident electric field

\[ \frac{E(\text{refl})}{E(\text{inc})} = \tilde{r}(\omega) = \rho(\omega)e^{i\theta(\omega)} = \frac{\tilde{n} - 1}{\tilde{n} + 1} \] (3.10)
where $\rho(\omega)$ is known as the amplitude and $\theta(\omega)$ is the phase [14]. The reflectance $R(\omega)$ is the real measured quantity (dimensionless) and is given by the ratio of the intensity of the reflected field to the intensity of the incident field and is related to the dielectric function as

\[ R = \tilde{r}\tilde{r}^* = \rho^2 = \left| \frac{\tilde{n} - 1}{\tilde{n} + 1} \right|^2 = \left| \frac{\sqrt{\tilde{\epsilon}} - 1}{\sqrt{\tilde{\epsilon}} + 1} \right|^2 \] (3.11)

$R$ can also be written in terms of $n$ and $\kappa$

\[ R = \frac{(n - 1)^2 + \kappa^2}{(n + 1)^2 + \kappa^2} \] (3.12)

The relation of the reflectance $R(\omega)$ to the dielectric function in equation (3.11) is of importance. This equation allows for the modeling of the reflectance curves once the dielectric function is known.

### 3.1.2 Kramer-Kronig Transformations

Since the measured quantity is the reflectance $R(\omega)$ (real part of $\tilde{r}(\omega)$), one must also know the phase $\theta(\omega)$ (imaginary part of $\tilde{r}(\omega)$) in order to calculate the prime response functions $\tilde{\epsilon}(\omega)$ and $\tilde{\sigma}(\omega)$ [12]. Using the Kramers-Kronig relations, the phase of the response function $\tilde{r}(\omega)$ can be found from the real part and vice-versa. Rewriting the complex reflectivity coefficient as $\ln \tilde{r}(\omega) = \ln \sqrt{R(\omega)} + i\theta(\omega)$ one can find the relationship between the phase and reflectivity as [12, 14]

\[ \theta(\omega) = \frac{\omega}{\pi} \int_0^\infty \frac{\ln \left[ R(\omega')/R(\omega) \right]}{\omega^2 - \omega'^2} d\omega' \] (3.13)
This equation has the limits from 0 to ∞. In real experiments this is not attainable. Thus data must be extrapolated from both the high and low frequency for a complete spectrum. At high frequencies, the frequency is assumed to drop off as ω−s where s can vary between 2 and 4. At low frequencies, the method of extrapolation depends on the material. For conductors the Hagen-Rubens relation is

\[ R = 1 - \sqrt{\frac{8\varepsilon_0\omega}{\sigma_{DC}}} \]  

(3.14)

where \( \sigma_{DC} \) is the DC conductivity [14]. For insulators the extrapolated data is usually constant.

3.2 Drude-Lorentz Model

The Drude-Lorentz model is a classical model used to understand the response of a dielectric material incident upon an EM wave. There are several types of oscillations that can occur when an EM wave is incident upon a medium. There are bound electron oscillators, free electron oscillators and vibrational oscillators also known as phonons [13]. The bound electron oscillators are held in a stable orbit around the nucleus. Their attachment to the nucleus is represented by a spring that has a restoring force for small displacements [13]. Each electron will have its own natural frequency \( \omega_0 \) that is determined by the spring constant and the reduced mass of the system. Since the mass of the nucleus is much larger than that of the electron the
reduced mass can be approximated to that of the electron. This is known as the Lorentz model (dipole oscillator) and the equation of motion for the electron is:

\[ m_e \frac{d^2 \vec{r}}{dt^2} + m_e \gamma \frac{d\vec{r}}{dt} + m_e \omega_0^2 \vec{r} = -e \vec{E} \]  

(3.15)

where \( m_e \) is the mass of the electron, \( e \) is the electronic charge, \( \gamma \) is the damping rate or scattering rate, \( \omega_0 \) is the natural frequency and \( \vec{E} \) is the applied electric field. The first term \( m_e \frac{d^2 \vec{r}}{dt^2} \) is the acceleration of the electron. The term \( m_e \gamma \frac{d\vec{r}}{dt} \) is known as the damping term and is a frictional force. The term \( m_e \omega_0^2 \vec{r} \) is the restoring force of Hooke’s law. The term of the right side is the driving force of the oscillation due to an alternating electromagnetic field. In this case the magnetic field is neglected.

Most materials will have multiple electrons attached to the nucleus. In this case each electron \( j \) will have its own resonance frequency \( \omega_{0j} \). Along with substitution of a periodic time-dependent electric field given by (3.1) into equation (3.15) one can find the optical conductivity for multiple bound electron oscillators as:

\[ \sigma(\omega)_{\text{Bound}} = \sum_j \frac{\omega_{pj}^2}{4\pi} \frac{i\omega}{\omega^2 - \omega_{0j}^2 + i\gamma_j \omega} \]  

(3.16)

and substitution of (3.16) into (3.8) the dielectric function can be found as

\[ \epsilon(\omega)_{\text{Bound}} = \epsilon_\infty + \sum_j \frac{\omega_{pj}^2}{4\pi} \frac{1}{\omega_{0j}^2 - \omega^2 - i\gamma_j \omega} \]  

(3.17)

with
\[ \omega_{pj} = \sqrt{\frac{4\pi Ne^2}{m}} \] (3.18)

where \( \omega_{oj} \) is the resonance frequency of the oscillator, \( \omega_{pj} \) the plasma frequency, \( \gamma_j \) the scattering rate, \( N \) the density of electrons with frequency \( \omega_{oj} \) and \( \epsilon_\infty \) is the high frequency dielectric constant that represents the high frequency oscillators.[14].

The previous section discussed bound electrons, but in metals and doped semiconductors there are a considerable amount of free electrons. These electrons are not bound to any atom or nucleus present in the material. Since these free electron oscillators are not bound to the nucleus they can move away from the parent nucleus. This approach is called the Drude model and is similar to that of the Lorentzian model except there is no restoring force on the electrons [13]. Thus in this model when an electric field is applied the free electrons are able to accelerate away from their parent nucleus. Equation (3.15) can be used to examine the motion of the oscillators by setting \( \omega_0 = 0 \) and re-writing it as:

\[ m_e \frac{d\vec{v}}{dt} + m_e \frac{\vec{v}}{\tau} = -e\vec{E} \] (3.19)

where \( \gamma = 1/\tau \) and \( \tau \) is known as the scattering time or average time between collisions [13]. This is now a first order differential equation and one can find the optical conductivity as:

\[ \sigma(\omega)_{Free} = \sigma_1 + i\sigma_2 = \sigma_{DC} \frac{\omega^2}{1 - i\omega\tau} = \frac{1}{4\pi} \frac{\omega_{pj}^2\tau}{1 - i\omega\tau} \] (3.20)
and the dielectric function can be written as

$$\epsilon(\omega)_{\text{Free}} = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$  \hspace{1cm} (3.21)

where $\omega_p^2 = 4\pi Ne^2/m$ and is still the plasma frequency [13]. Also, $\sigma_{DC} = Ne^2\tau/m_e$ is the DC conductivity found from a DC electric field. The complete Drude-Lorentz model for optical conductivity is written as the contribution of free electrons that represent the intraband transitions and the bound electrons that represent the interband transitions [14]:

$$\sigma(\omega) = \sigma(\omega)_{\text{Free}} + \sigma(\omega)_{\text{Bound}} \quad \epsilon(\omega) = \epsilon(\omega)_{\text{Free}} + \epsilon(\omega)_{\text{Bound}}$$  \hspace{1cm} (3.22)

$$\sigma(\omega) = \frac{1}{4\pi} \frac{\omega_p^2\tau}{1 - i\omega\tau} + \sum_j \frac{\omega_{pj}^2}{4\pi} \frac{i\omega}{\omega^2 - \omega_{0j}^2 - i\gamma_j\omega}$$  \hspace{1cm} (3.23)

and the complete dielectric function is written as:

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} + \sum_j \frac{\omega_{pj}^2}{4\pi} \frac{1}{\omega_{0j}^2 - \omega^2 - i\gamma_j\omega}$$  \hspace{1cm} (3.24)

Notice that for both (3.23) and (3.24) the free electron part comes from the bound electron part by setting $\omega_{0j} = 0$. Although the equation (3.24) was solved from the equation of motion for electrons this can also be used to describe phonons.
The plasma frequency, $\omega_p$, is estimated from a sum rule. This sum rule originates from the conservation of charge [2, 15]. By integrating the real part of the optical conductivity $\sigma(\omega)_1$ for all frequencies to account for all possible electrons [2, 15]

$$\int_0^\infty \sigma(\omega)_1 d\omega = \frac{\omega_p^2}{8} = \frac{\pi N e^2}{2 m_e} \quad (3.25)$$

where $m_e$ is the free electron mass and $N$ is the total number of carriers. This equation shows that the plasma frequency $\omega_p$ is proportional to the total number of charge carriers over the mass of the carriers $N/m$. Due to experimental limitations, the integration limit to infinity is not possible, thus effective spectral weight is defined as [2, 15]:

$$N_{eff}(\omega) = \int_0^\omega \sigma(\omega)_1 d\omega \quad (3.26)$$

and if $\omega \to \infty$ then the sum rule is defined by equation (3.25). $N_{eff}$ represents the effective number of carriers that contribute to the optical absorption. Finally to describe the shift in the spectral weight we use the spectral loss function define as

$$\Im \left[ \frac{1}{\epsilon(\omega)} \right] = \frac{\epsilon_2(\omega)}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} \quad (3.27)$$
3.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy is a technique used to measure the intensity of light as a function of frequency. In order to obtain a spectrum an interferometer, shown in figure 3.1, produces and controls the interference pattern created by combination of two light beams [16]. This pattern is called an interferogram, which is the intensity versus the optical path difference between the two beams. To obtain a spectrum from the path difference domain, a Fourier transformation is used to convert to the frequency domain. From the spectrum, one is able to determine the reflectance, transmission or absorption as a function of frequency.

![Figure 3.1: A simple schematic view of a Michelson interferometer. From reference [18]](image)

The interferometer used in these experiments is the Michelson Interferometer. The essential parts for the interferometer are the source, the beamsplitter, a fixed mirror and a movable mirror. A source creates a collimated beam towards the
beamsplitter and splits the beam. The beamsplitter is a material that reflects roughly 50% and transmits 50% of the incident beam. One beam is reflected from a fixed mirror and returns back to the beamsplitter. The other beam reflects off of a movable mirror and returns back to the beamsplitter where the beams re-combine before hitting the detector resulting in an interferogram.

An interferogram as function of the optical path difference $x$ for a monochromatic light is found as

$$I(x) = I(\nu)[1 + \cos(2\pi \nu x)]$$

where $I(\nu)$ is the intensity as a function of the wavenumber $\nu$ which has units of cm$^{-1}$ [18]. Wavenumbers are also referred to as frequency and is simply the inverse of wavelength. In spectroscopy wavenumber is commonly used instead of wavelength since wavenumber is proportional to energy.

Since the process to obtain an interferogram for monochromatic light would take a sufficient amount of time. Allowing only one frequency at a time. A polychromatic source allows for multiple frequencies at once for more convenient. The Fourier transform allows for multiple frequencies at once and thus for a polychromatic source an interferogram is given by [18]:

$$I(x) = \int_0^{\nu_{\text{max}}} I(\nu)[1 + \cos(2\pi \nu x)]d\nu$$
where the integration limits allows for frequencies $0 \rightarrow \nu_{\text{max}}$. The desired quantity is $I(\nu)$ and so a Fourier transform is used to obtain the spectrum.

$$I(\nu) = \int_{0}^{\infty} I(x)[1 + \cos(2\pi\nu x)]dx$$

(3.30)

The sample is now integrated from 0 to $\infty$ [18]. This allows for each position of the moveable mirror to be sampled. In practice this is impractical and the limits must be finite. So at some point the interferogram is truncated. This truncation leads to sidelobes. To eliminate the sidelobes, the interferogram is multiplied by a function called the apodisation [18]. The effect of this improvement can reduce the resolution. All Fourier transforms and truncations are performed by the computer.
CHAPTER IV
EXPERIMENTAL

The infrared and optical frequencies range from 30 - 50000 cm\(^{-1}\). In order to analysis this range two different spectrometers are used. A Fourier Transform Infrared (FTIR) Spectrometer covers the far-, mid- and near-infrared. A ultraviolet- visible (UV-Vis) spectrometer overlaps some of the near-infrared and covers the visible and a portion of the UV spectrum. The measured quantity for each spectrometer was either the reflectance \(R(\omega)\) or the transmittance \(T(\omega)\). This section discusses the set-up and technique used for the FTIR, UV-Vis and magneto-optical measurements.

4.1 Fourier Transform Infrared Spectroscopy Experimental Set-up

The FTIR spectrometer used was a Bruker IFS 66v/S. The main part of the spectrometer is shown in figure 4.1. To obtain the regions of far-infrared up to the mid-infrared region (50 - 4000 cm\(^{-1}\)) a globar source is used as a light source. A globar source is a silicon carbide rod that is an electronically heated to about 1500 Kelvin. The globar source is located in the upper right hand corner of region I. Following the arrows, the beam travels to region II, the interferometer, where it splits and recombines heading towards region III. Region III has precisely placed mirrors to properly align the beam to reflect onto and off the sample. The sample and the reference mirror are located
in the cryostat directly below region III. The beam is then sent into Region IV where the detectors are located.

There are two different detectors depending upon which infrared spectrum is being detected. The detector for the mid infrared, red container, is mercury cadmium telluride (MCT) while the far infrared detector, gold, is a bolometer as shown in figure 4.2. Liquid nitrogen is poured into the detectors before sampling to cool the detectors for better signal. This is to reduce thermal fluctuations from the signal.

The cryostat is shown in figure 4.3 and is mounted at the front of the FTIR. At the bottom of the cryostat is the sample chamber. The FTIR and sample chamber are separated by a metal divider with a circular hole. The hole is sealed with a bromine lens for the light to pass through. The divider is placed there due to the pressure difference between the sample chamber and the FTIR. The tube connected
to the sample chamber leads to a roughing pump and a turbo molecular pump that brings the pressure down to $10^{-3}$ mbar and $10^{-6}$ mbar, respectively, while the FTIR pressure is brought to 1-2 mbar.

The hole on the left side of figure 4.3 is filled in with an evaporator. The evaporator, shown in figure 4.4, consists of a tungsten filament with five strips of gold wrapped around the filament. Once the sample is measure against a known reference mirror, a current is sent through the evaporator to evaporate the gold strips, which deposits a thin layer onto the sample. The sample with gold coating is then re-measured against the mirror reference as will be explained in section 4.1.2.
The sample set-up is shown in figure 4.5. The sample is glued perpendicular
to the tip of a cone to ensure the incident beam reflects properly. A cone is used to
reflect away light that does not hit the sample. The back of the cone has a small strip
of copper wire soldered on to help with the thermal conductivity especially at low
Figure 4.5: A sample coated with gold on the cryostat holder.

temperatures. The cone is then mounted onto the sample holder of the cryostat. From figure 4.5 another hole is actually 90 degrees above the sample (not seen in picture). This hole is the reference mirror and is set-up the same as the sample. The cryostat is then placed inside the cryostat chamber.

At the top of the cryostat, figure 4.3, a transfer line is placed inside leading to a dewer filled with liquid helium. The liquid helium (helium 4) is always being pumped into the cryostat. The flow of the helium is controlled by the flow valves (not shown). The temperature near the sample is regulated by a control box that sends the appropriate current for the desired temperature. Thus allowing for any temperature above 5 Kelvin up to room temperature to be sampled.

4.1.1 FTIR Procedure

Single crystals of Bi$_2$Te$_3$, Sb$_2$Te$_3$ and Bi$_2$Se$_3$ were grown by the flux method [19, 20]. X-ray diffraction (XRD) spectra were taken with Cu K$_\alpha$ radiation ($\lambda = 0.15418$ nm)
using a Rigaku Miniflex X-ray machine. Unit cell refinement obtained by fitting the XRD spectra using the Rietica software showed that samples were single phase and with lattice parameters consistent with previous results [21].

The samples Bi$_2$Te$_3$, Sb$_2$Te$_3$ and Bi$_2$Se$_3$ were placed, as shown above, onto the cryostat holder and placed into the cryostat. When the evaporator was placed into its hole the resistance was checked to ensure there was no unwanted contact inside the chamber. Then FTIR and the cryostat are pumped to 1-2 mbar and 10$^{-6}$ mbar, respectively. The temperature of the cryostat is then dropped to 5 Kelvin. There are two different temperature sensors. One sensor is placed right next to the sample to determine the sample’s temperature. The other sensor is placed in the vicinity of the sample to determine the surrounding temperature. Measurements of the reflectance are taken when the two temperatures become stable.

The first measurements are always that of the reference mirror. Once the reference mirror is scanned then the cryostat was rotated 90 degrees to scan the sample. The samples were measured 3 times. For each measurement the sample was scanned 200 times. Meaning the moveable mirror moved back and forth 200 times. Then cryostat was rotated back to the mirror for another set of measurements. This process would be repeated about 10 more times giving about 6000 scans per sample at a given temperature. When compiling the final curves the data was averaged over all the scans.

Once all the scans for each temperature are complete for the sample, gold was then evaporated onto the sample. This was done by applying a voltage to the two
metal rods of the evaporator, shown in figure 4.4. The voltage was slowly increased to 18 volts over a 1 minute period. Then the voltage was increased to 20 volts and 1 minute was waited to ensure all the gold was evaporated. After 1 minute the voltage was decreased to zero and the battery was disconnected.

Once the gold was onto the sample the same procedure given above is done for the sample. The purpose of the gold evaporation allows ultimately for the cancelation of the mirror reference and gives the reflectance ratio of the plain sample over the gold coated sample. This can be seen by the double ratio of the sample reflectance $R_{\text{sample}}$ to the reflectance of the reference mirror $R_{\text{mirror}}$ to the ratio of the reflectance of sample coated with gold $R_{\text{gold}}$ to the reflectance of the reference mirror $R_{\text{mirror}}$

$$\frac{R_{\text{sample}}}{R_{\text{mirror}}} = \frac{R_{\text{sample}}}{R_{\text{gold}}}$$  \hspace{0.5cm} (4.1)

Where the reflectance for $R_{\text{gold}}$ is nearly 100%. Thus giving the reflectance of the sample $R_{\text{sample}}$. The purpose of gold, as just stated, is due to the very high reflectivity of infrared red light, nearly 100% in the infrared region.

### 4.2 Ultraviolet-Visable Experimental Set-Up

The UV-Vis spectrometer used was a Cary 300 Scan. A schematic of the spectrometer is given in figure 4.6. There are 5 regions that the light beam travels through. The path of the beam is indicated by the red lines and begins in Region I where the source is located. Also in this region the beam hits its first grating isolating a region of the
desired frequency. As the beam passes to region II it goes through an entrance slit limiting its size. In region II the beam hits another grating allowing for the dispersion of more precise wavelengths. Now as the beam passes into region III it passes through another slit that filters the undesired wavelengths. In region III the single beam is then split into two beams by a chopper (beamsplitter). Each beam then passes into region IV where one beam hits the sample/reference mirror and the other beam simply passes through the region. Then both continue to region V where another chopper re-combines the beam and finally hitting the detector. Before measuring the sample the reference mirror is first measured. Then the mirror is replaced with the sample and measured.

4.3 Magneto-Optical Spectroscopy

FTIR measurements were also taken at the National High Magnetic Field Lab with the samples placed inside a superconducting magnet. The FTIR process is the same as section 4.1 except the temperature is always at 4.2 Kelvin, and the magnetic fields on the samples were changed. The magnetic was able to produce fields up to 18 Tesla. A schematic of a typical superconducting magnetic is shown in figure 4.7. The magnet is placed inside a container. The actual height of the container is about 16 feet. The samples are placed at the end of an 8 foot long rod. The rod fits inside the center of the container, where the samples are nearly placed in the middle of the magnet so ensure the most uniform field. The sample holder fits three samples and a reference mirror as shown in figure 4.8. Since the placement of the rod inside the
magnet is such that the magnetic field produced is parallel to the rod. From figure 4.7, the samples are flat when placed inside the holder and therefore the magnetic field will be perpendicular to the samples.

Since the magnet is superconducting, liquid helium is always inside the container. This made the process of placing the rod into and out of the container time consuming. The rod was at room temperature and had to be slowly placed into the magnetic to reduce the amount of liquid helium lost. Thus taking about 3 hours to
completely place the rod inside. A similar process was done to take the rod out. This did not have to be done slowly, but since the rod was completely frozen it was best to let thaw. To increase the speed of taking the rod out a heat gun was applied. The total time to take out the container was about two hours.

The magnetic fields were automatically controlled by a computer. Unlike a DC resistive magnetic where the time to increase and decrease the magnetic field is seconds, while a superconducting magnetic is not so instantaneous. The current to increase the magnetic has to slowly increase and decrease at a specified rate due to quenching. If a small piece of the superconducting magnet is not superconducting then the current passing through this piece will produce large heat dissipation.
Figure 4.8: Picture of the sample holder that fits inside the superconducting magnetic.

The final set-up of the experiment is shown in figure 4.9. The tan instrument in the background in the middle of the picture is the FTIR. The path of the beam leaves the FTIR traveling through to the top pipe sending it into the magnetic, located at the bottom of the picture. The beam hits the sample then proceeds to the detector which is located in the magnet. Also, the samples were measured against a reference mirror, but no gold was evaporated onto the samples.
Figure 4.9: Picture of the complete set-up of the magneto-optics experiment. The picture also includes from left to right: Dr. Sasa Dordevic (advisor), Dr. Nenad Stojilovic (previous advisor and group member) and Michael Wolf (author).
CHAPTER V
RESULTS AND DISCUSSION

The following sections will present the results for the infrared/optical and magneto-optical measurements of FTIR and UV-Vis for Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$ and Bi$_{0.985}$Sb$_{0.015}$. After all the scans from both FTIR and UV-Vis the final results are the average of all the collected measurements. The data was obtained as a spectrum with the low frequency cut off at 30 cm$^{-1}$. The Hagan-Rubens relation was used to extrapolate to lower frequencies by adjusting the $\sigma_{DC}$ for the best possible fit to the reflectance curve. This allows for the Kramers-Kronig transformation to calculate the optical functions. This process was completed for each sample at each temperature.

5.1 Reflectance Results

The reflectance curves for Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ for the temperatures 5, 77, 200 and 300 Kelvin are shown in figure 5.1. The figure displays the reflectance versus a log plot of wavenumbers [cm$^{-1}$] on the bottom axis. A wavenumber is inverse wavelength with units cm$^{-1}$. The reflectance curve for Bi$_{0.985}$Sb$_{0.015}$ is shown in figure 5.2 which displays the reflectance versus wavenumber.
Figure 5.1: Reflectance of Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ at the temperatures of 5, 77, 200 and 300 Kelvin.
Figure 5.2: Reflectance of Bi$_{0.985}$Sb$_{0.015}$ at the temperatures of 5, 77, 200 and 300 Kelvin.

For Bi$_2$Se$_3$ there are three characteristic features seen on the graph. The large drop in reflectance at 200 cm$^{-1}$ is known as plasma edge. This specific frequency is the plasma frequency given by equation (3.18) and (3.27) which shows no temperature dependence. The plasma frequency for conventional metals does not shift. These results clearly show that the plasma frequency is temperature dependent and does not follow conventional metals. The position of the plasma frequency, 200 cm$^{-1}$, is also very low in frequency compared to conventional metals which usually are in the UV region or shorter wavelengths of the visible spectrum.

Lower in frequency, there are two absorption dips at 135 cm$^{-1}$ and 50 cm$^{-1}$.
The first absorption at 50 cm\(^{-1}\) is seen to exist at all four temperatures and begins to shift to lower frequencies at lower temperatures. At first thought this would be considered a phonon, but in the next section the magneto-optical results show it is not a phonon or at least a conventional phonon. The absorption at 135 cm\(^{-1}\) is a phonon and as the temperature decreases this becomes more defined. Around the plasma edge the reflectance has the most temperature dependence. Approaching the plasma edge from lower frequencies, the reflectance increases as the temperature decreases. While approaching from higher frequencies, the reflectance decreases with decreasing temperature.

To clearly see the shift in the plasma edge as a function of temperature figure 5.3 displays the spectral loss function versus frequency, \(\Im\left[\frac{1}{\epsilon}\right]\). The shifting in the plasma edge is an interesting feature since, as mentioned above, the plasma edge for conventional metals is independent of temperature. This graph shows as the temperature decreases, the spectral weight shifts to lower frequencies. This indicates a shift in the interband transitions. The charge carriers are participating in the optical conductivity at lower frequencies.

The reflectance for Bi\(_{0.985}\)Sb\(_{0.015}\) clearly shows that the plasma edge is effected by temperature. The temperatures 5, 77, and 200 Kelvin appear to be the same with the plasma frequency being at about 100 cm\(^{-1}\). Only at 300 Kelvin is the reflectance curve effected with the plasma edge being at about 200 cm\(^{-1}\). Thus as temperature decreases the plasma edge shifts towards lower frequencies. This shift towards lower frequencies indicates a shift in the onset of interband transitions to lower frequencies.
Figure 5.3: Spectral loss function for Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ at the temperatures 5, 77, 200 and 300 Kelvin.
For Bi$_2$Te$_3$ the plasma edge occurs in the mid-infrared range at about 700 cm$^{-1}$. The graphs show an apparent temperature dependence in the reflectance specifically around the plasma edge. The frequencies below the plasma edge show reflectance going to approximately 1 as the frequency goes to 0. At the plasma frequency, as the temperature increases the edge clearly begins to shift towards higher frequencies and the drop becomes steeper. This is also seen in the spectral loss function also indicating the onset of interband transitions is shifting to higher frequencies.

For Sb$_2$Te$_3$ below the plasma edge, the reflectance approximately goes to 1 as the frequency goes to 0. Clearly from the reflectance graph the plasma edge shifts to higher frequencies as the temperature decreases. At 300 Kelvin the plasma edge is at 1000 cm$^{-1}$, while at 10, 77 and 200 Kelvin the plasma edge is around 1150 cm$^{-1}$. This is more clearly indicated in figure 5.3 showing that the onset of interband transitions begins at higher frequencies at lower temperatures. Also at 300 Kelvin, the spectral function is more broad and as the temperature lowers the function becomes narrower.

5.2 Magneto-Optical Results

The magneto-optical results for Bi$_2$Te$_3$ are shown in figure 5.4 with the reflectance curve at 4 Kelvin plotted on top on the graph. The graph displays the reflectance ratios of a given magnetic field to zero magnetic field. The ratios are indicated by the color bar to the right of the graph. The frequency range is around the plasma frequency as seen from the reflectance curve.
Magnetic fields lower than 8 Tesla seem to have little dependence on the charge carriers. While as the magnetic field is increased beyond 8 Tesla there is clear indication that the magnetic field has an effect on the reflectance around 700 cm$^{-1}$. The effect shows that the reflectance is increasing.

The magneto-optical results for Sb$_2$Te$_3$ are shown in figure 5.5 along with its reflectance curve at 4 Kelvin. The frequency range is centered around the plasma frequency as seen from the curve. Clearly the reflectance is effected by the presence of the magnetic field near the plasma frequency. Although there needs to be fields beyond 10 Tesla just to show over a 5% change in the reflectance ratio. Even at fields
higher than 10 Tesla only the reflectance near the plasma edge is effected.

The results for Bi$_2$Se$_3$ are shown in figure 5.6 with the reflectance curve at 4 Kelvin. Figure 5.7 can also be used to visualize the reflectance ratios at a given magnetic field to zero magnetic field. This helps emphasize the color difference in figure 5.6.

The frequency range covers the plasma frequency and the absorption dips in the reflectance. The charge carriers at 210 cm$^{-1}$ (plasma edge) and 50 cm$^{-1}$ appear to be very dependent on magnetic field. In conventional metals phonons are not effected by an external magnetic field. Thus the absorption dip at 50 cm$^{-1}$ is believed not to
Figure 5.6: This graph displays the reflectance ratio of Bi\textsubscript{2}Se\textsubscript{3} at a given magnetic field to zero magnetic field. The color bar on the right indicates the ratio.

be a phonon. Although the absorption dip at 130 cm\textsuperscript{-1} is not present when compared to the curve which is expected indicating this is indeed a phonon.

Fields lower than 4 Tesla do not seem to effect the charge carriers significantly at 210 cm\textsuperscript{-1} and 50 cm\textsuperscript{-1}. Beyond 4 Tesla the charge carriers are strongly effected seeing at least a 10% change in reflectance. Comparing to both Bi\textsubscript{2}Te\textsubscript{3} and Sb\textsubscript{2}Te\textsubscript{3}, the magnetic dependence on the charge carriers for Bi\textsubscript{2}Se\textsubscript{3} are stronger near the plasma edge. The ratio 1.1 begins to occur at about 5 Tesla in both features for Bi\textsubscript{2}Se\textsubscript{3}, while in both Bi\textsubscript{2}Te\textsubscript{3} and Sb\textsubscript{2}Te\textsubscript{3} the ratio 1.1 is only reached at about 16 Tesla.
Figure 5.7: This graph displays the reflectance ratio of $\text{Bi}_2\text{Se}_3$ at a given magnetic field to zero magnetic field.

The results for $\text{Bi}_{0.985}\text{Sb}_{0.015}$ are shown in figure 5.8 along with the reflectance curve at 4 Kelvin. This graph is the absolute reflectance versus frequency unlike the previous graphs which were ratios. Below the plasma edge and at zero magnetic field the reflectance is nearly 100%. As the magnetic field increases the reflectance is suppressed especially at high magnetic fields. Which is seen to drop by almost 20%. Below the plasma edge and at low magnetic fields the reflectance is about 55%. As the magnetic field is increased the reflectance increases by almost 5%.
5.3 Drude-Lorentz Fits

Using the commercially available program RefFIT provided by [22], the reflectance data can be modeled by the Drude-Lorentz model as shown in figure 5.7. From the figure a reflectance curve (blue line) is being modeled (red line) by the equation (3.11) with the dielectric function from equation (3.24). Each term is a Lorentzian and has 3 parameters that can change: transverse frequency $\omega_0$, plasma frequency $W_p$ and the scattering rate $G$ as indicated in the program. When the transverse frequency $\omega_0$ is zero this is a Drude as mentioned in section 3.1.3. This fit allows for
the determination of the transverse frequency $\omega_0$, the plasma frequency $\omega_p$, and the scattering rate $\gamma$ for each Lorentzian.

Figure 5.9 shows an example of a reflectance curve being fit with 1 Drude and 3 Lorentzians. The parameters are easily changeable in the parameter control menu. There is also setting that will fit the data curve using a best fit curve. Although this is not alway beneficial since sometimes the parameters will be negative which cannot be true. Once the curve is modeled the program can create the corresponding optical conductivity and dielectric function curves by using a Kramers-Kronig transformation as shown at the bottom of figure 5.9. The units used by the program for the the three parameters are cm$^{-1}$.

![Figure 5.9: This picture displays a window of the program RefFIT used to model the reflectance curves.](image-url)

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The fit lines for each temperature for Bi$_2$Te$_3$ is shown in figure 5.10. For each model only one Drude and one Lorentzian are needed to fit the curve. The physical meaning of one Drude term indicates there are free electrons present. The Lorentzians indicate inter-band transitions since each Lorentzian is in the near-infrared region and beyond the plasma edge. This is all that is needed to describe the range provided in the plots (around the plasma frequency). What this does not indicate is if there are more inter-band transitions in the spectra at higher frequencies. The complete information for each fit are given in the following tables and the parameters are summarized after the tables.

For frequencies below the plasma edge the model fits well with with the actual data at all temperatures. Even at the plasma edge the model still fits well. After the plasma edge, the dip, the model has the characteristic shape, but does not fit very well. The measured reflectance has a broader dip, while the models have more of a peak shape. This becomes apparent at low temperatures. Beyond the dip, the model fits the shape of the reflectance up to a frequency and begins to fail as seen near the edge of the graphs. This is only due to the amount of Lorentzians used since we were only interested in the frequencies near the plasma edge. As a whole the model fit displays the key characteristics of the data rather well.
Table 5.1: Fitting parameters for Bi$_2$Te$_3$ at 5 Kelvin with $\epsilon_\infty = 1$

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$\omega_0$</th>
<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>5978.7</td>
<td>25.02</td>
</tr>
<tr>
<td>Lorentzian 1</td>
<td>9128.4</td>
<td>69417</td>
<td>13296</td>
</tr>
</tbody>
</table>

Table 5.2: Fitting parameters for Bi$_2$Te$_3$ at 77 Kelvin with $\epsilon_\infty = 1$

<table>
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<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>5978.7</td>
<td>25.02</td>
</tr>
<tr>
<td>Lorentzian 1</td>
<td>9128.4</td>
<td>69417</td>
<td>13296</td>
</tr>
</tbody>
</table>

Table 5.3: Fitting parameters for Bi$_2$Te$_3$ at 200 Kelvin with $\epsilon_\infty = 1$

<table>
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</tr>
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<td>Lorentzian 1</td>
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<td>69417</td>
<td>7586.4</td>
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</table>

Table 5.4: Fitting parameters for Bi$_2$Te$_3$ at 300 Kelvin with $\epsilon_\infty = 1$

<table>
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<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>5651.5</td>
<td>111.86</td>
</tr>
<tr>
<td>Lorentzian 1</td>
<td>8386.6</td>
<td>66024</td>
<td>10260</td>
</tr>
</tbody>
</table>
Figure 5.10: These graphs show the actual reflectance (red) and the modeled reflectance (blue) for each temperature for Bi$_2$Te$_3$.

The fits for all four temperatures are very similar. For Lorentzian 1, $\omega_0$ and $\omega_p$ are the same for temperatures 5, 77 and 200 Kelvin and for 300 Kelvin they decrease by 741.8 cm$^{-1}$ and 3393 cm$^{-1}$, respectively. The scattering rate $\gamma$ is the same for 5 and 77 Kelvin but decreases for 200 Kelvin by 5709.6 cm$^{-1}$ and decreases by 3036 cm$^{-1}$ for 300 Kelvin. For the Drude term, $\omega_p$ is the same for 5 and 77 Kelvin but decreases by about 360 cm$^{-1}$ and 330 cm$^{-1}$ at 200 and 300 Kelvin, respectively. Also for the Drude term, $\gamma$ is the same for 5 and 77 K but increases at higher temperatures.
The fits for Sb$_2$Te$_3$ are shown in figure 5.11. Due to the simplicity of the reflectance curve only one Drude is needed to model the curve. Meaning that only free electron oscillators are present in describing the reflectance at the frequencies in the plots. The tables below show the complete information for the fits.

Below the plasma frequency the model fits very well at all temperatures. The model also fits well at the plasma edge. Not until after the plasma edge, the dip, does the model fail. The actual reflectance is less than the model for all temperatures at the dip. After the dip the model fits the data well. Although as the temperature decreases the fit becomes better. At 300 Kelvin the difference in reflectance from the model to the actual data is about 10% while for 5 Kelvin the difference is about 5%. Overall the model fits the data well.

Table 5.5: Fitting parameters for Sb$_2$Te$_3$ at 5 Kelvin with $\epsilon_\infty = 54.9$

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$\omega_0$</th>
<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>8203.3</td>
<td>65.669</td>
</tr>
</tbody>
</table>

Table 5.6: Fitting parameters for Sb$_2$Te$_3$ at 77 Kelvin with $\epsilon_\infty = 54.9$

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$\omega_0$</th>
<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>8244.8</td>
<td>72.236</td>
</tr>
</tbody>
</table>
Table 5.7: Fitting parameters for Sb$_2$Te$_3$ at 200 Kelvin with $\epsilon_\infty = 54.8$

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$\omega_0$</th>
<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>8057.6</td>
<td>89.577</td>
</tr>
</tbody>
</table>

Table 5.8: Fitting parameters for Sb$_2$Te$_3$ at 300 Kelvin with $\epsilon_\infty = 51$

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$\omega_0$</th>
<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>6906.7</td>
<td>183.69</td>
</tr>
</tbody>
</table>

Since only a Drude is needed to describe the reflectance curves only the plasma frequency and scattering rate are changing. The plasma frequency for 5 and 77 Kelvin are very similar to each, but as the temperature increases $\omega_p$ shifts towards lower frequencies. For 200 Kelvin the shift is only by 200 cm$^{-1}$ but for 300 Kelvin the shift is about 1300 cm$^{-1}$. For the scattering rate $\gamma$, as the temperature increases so does $\gamma$. The difference from the 5 Kelvin to 300 Kelvin being about 118 cm$^{-1}$.

The fits for Bi$_2$Se$_3$ are shown in figure 5.12. Since the reflectance curves for Bi$_2$Se$_3$ have two extra features besides the plasma edge then there must be two extra Lorentzians per fit making a total of 1 Drude and 3 Lorentzians. As mentioned in the section 3.2 the equation (3.24) can also describe phonons or phonon like features such at the two dips in the reflectance. The first Lorentzian is centered on the first dip in the reflectance and its physical meaning is not understood at the current time. The second Lorentzian is centered on the second dip which is a phonon indicating the
Figure 5.11: These graphs show the actual reflectance (red) and the modeled reflectance (blue) for each temperature for Sb$_2$Te$_3$.

Lorentzian describes the phonon. The third Lorentzian is an inter-band transition. Even though it is at low frequencies it is still beyond the plasma edge. The Drude term is still the free electron contribution. The fitting parameters for each temperature are given in the following tables and are summarized after the tables.

Beginning at low frequency, the model does not fit the first absorption dip very well, but manages to have the general shape. For the second absorption dip, the fit follows the curve very well at all temperatures. The model on the plasma
edge fits rather well for all temperatures also. Beyond the plasma edge, at the dip, the model fails at all temperatures up to 300 cm\(^{-1}\) and becomes increasingly worse at lower temperatures. Beyond 300 cm\(^{-1}\), the model fits well again. Overall the key characteristics of the curves can be modeled, but model fails for an accurate description.

Table 5.9: Fitting parameters for Bi\(_2\)Se\(_3\) at 5 Kelvin with \(\epsilon_\infty = 3\)

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>(\omega_0)</th>
<th>(\omega_p)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>830.43</td>
<td>1.22</td>
</tr>
<tr>
<td>Lorentzian 1</td>
<td>60.43</td>
<td>685</td>
<td>8.45</td>
</tr>
<tr>
<td>Lorentzian 2</td>
<td>133.9</td>
<td>83.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Lorentzian 3</td>
<td>3565</td>
<td>19159</td>
<td>6015.8</td>
</tr>
</tbody>
</table>

Table 5.10: Fitting parameters for Bi\(_2\)Se\(_3\) at 77 Kelvin with \(\epsilon_\infty = 3\)

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>(\omega_0)</th>
<th>(\omega_p)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>860.43</td>
<td>1.22</td>
</tr>
<tr>
<td>Lorentzian 1</td>
<td>60.42</td>
<td>685</td>
<td>8.45</td>
</tr>
<tr>
<td>Lorentzian 2</td>
<td>133.9</td>
<td>83.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Lorentzian 3</td>
<td>3565</td>
<td>19159</td>
<td>6015.8</td>
</tr>
</tbody>
</table>
Table 5.11: Fitting parameters for Bi$_2$Se$_3$ at 200 Kelvin with $\epsilon_\infty = 1$

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$\omega_0$</th>
<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>768.16</td>
<td>3.85</td>
</tr>
<tr>
<td>Lorentzian 1</td>
<td>64</td>
<td>778.3</td>
<td>9.1</td>
</tr>
<tr>
<td>Lorentzian 2</td>
<td>130.75</td>
<td>112</td>
<td>10</td>
</tr>
<tr>
<td>Lorentzian 3</td>
<td>2187.6</td>
<td>11790</td>
<td>3920.5</td>
</tr>
</tbody>
</table>

Table 5.12: Fitting parameters for Bi$_2$Se$_3$ at 300 Kelvin with $\epsilon_\infty = 1$

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$\omega_0$</th>
<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>908.66</td>
<td>7.43</td>
</tr>
<tr>
<td>Lorentzian 1</td>
<td>63.03</td>
<td>675.9</td>
<td>17.5</td>
</tr>
<tr>
<td>Lorentzian 2</td>
<td>126.94</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>Lorentzian 3</td>
<td>2029.5</td>
<td>11249</td>
<td>3920.5</td>
</tr>
</tbody>
</table>

The fitting parameters for 5 Kelvin and 77 Kelvin are identical for the Drude and all 3 Lorentzians except for the $\omega_p$ in the Drude term, which differs by 30 cm$^{-1}$. Most of the parameters change slightly between the 77 Kelvin to 300 Kelvin. The most notable changes are in the Lorentzian 3 parameters. For Lorentzian 3 the parameters $\omega_0$, $\omega_p$ and $\gamma$ decrease as the temperature changes from 5 Kelvin to 300 Kelvin by 1535.5 cm$^{-1}$, 7910 cm$^{-1}$ and 2095.3 cm$^{-1}$ respectively.
Figure 5.12: These graphs show the actual reflectance (red) and the modeled reflectance (blue) for each temperature for Bi$_2$Se$_3$.

The Drude-Lorentz fits for Bi$_{0.985}$Sb$_{0.015}$ are shown in figure 5.13. Each fit uses 2 Drudes and no Lorentzians. The physical meaning of two Drude terms, naively saying, is the contribution of free electrons and holes contributing to the reflectance. The fitting parameters are given in the tables below along with a summary.

Below and at the plasma edge the model follows the curve very accurately for all four temperatures. Examining the 300 K curve, the model is only slightly raised around the dip at 300 cm$^{-1}$. Afterwards the model matches the curve again. Now
the 77 K and 200 K curves show that the model very slightly detours at about 200 cm\(^{-1}\), but picks up the curve again at about 350 cm\(^{-1}\). The 5 K model fits well until about 320 cm\(^{-1}\) where model is slightly raised and does not quite come back to the curve. Overall the model describes the insulator very well.

Table 5.13: Fitting parameters for Bi\(_{0.985}\)Sb\(_{0.015}\) at 5 Kelvin with \(\epsilon_\infty = 96\)

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>(\omega_0)</th>
<th>(\omega_p)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude 1</td>
<td>0</td>
<td>1125</td>
<td>8.1</td>
</tr>
<tr>
<td>Drude 2</td>
<td>0</td>
<td>1350.4</td>
<td>273.75</td>
</tr>
</tbody>
</table>

Table 5.14: Fitting parameters for Bi\(_{0.985}\)Sb\(_{0.015}\) at 77 Kelvin with \(\epsilon_\infty = 90\)

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>(\omega_0)</th>
<th>(\omega_p)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude 1</td>
<td>0</td>
<td>1063.6</td>
<td>8.435</td>
</tr>
<tr>
<td>Drude 2</td>
<td>0</td>
<td>1406.1</td>
<td>308.4</td>
</tr>
</tbody>
</table>

Table 5.15: Fitting parameters for Bi\(_{0.985}\)Sb\(_{0.015}\) at 200 Kelvin with \(\epsilon_\infty = 90\)

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>(\omega_0)</th>
<th>(\omega_p)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude 1</td>
<td>0</td>
<td>1084.3</td>
<td>12.34</td>
</tr>
<tr>
<td>Drude 2</td>
<td>0</td>
<td>1369.1</td>
<td>300.84</td>
</tr>
</tbody>
</table>
Table 5.16: Fitting parameters for Bi$_{0.985}$Sb$_{0.015}$ at 300 Kelvin with $\epsilon_\infty = 99$

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$\omega_0$</th>
<th>$\omega_p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude 1</td>
<td>0</td>
<td>1873.9</td>
<td>31.848</td>
</tr>
<tr>
<td>Drude 2</td>
<td>0</td>
<td>1790.8</td>
<td>243.36</td>
</tr>
</tbody>
</table>

Since the reflectance curves for 5, 77 and 200 Kelvin are almost identical the fitting parameters for each model are almost the same. There are some slight differences, but not too significant. As for 300 Kelvin, since the plasma edge shifts by about 100 cm$^{-1}$ the parameters change more significantly. The plasma frequency $\omega_p$ shifts to higher frequency for both Drude 1 and Drude 2 by 789 cm$^{-1}$ and 421.7 cm$^{-1}$, respectively. The scattering rate, $\gamma$, for Drude 1 increases in frequency by about 19.5 cm$^{-1}$ while for Dude 2 $\gamma$ decreases by about 57.5 cm$^{-1}$.
Figure 5.13: These graphs show the actual reflectance (red) and the modeled reflectance (blue) for each temperature for Bi$_2$Se$_3$. 
CHAPTER VI
CONCLUSIONS

The results indicate the plasma frequency of certain topological insulators is temperature dependent. For Bi$_2$Te$_3$ and Sb$_2$Te$_3$ the plasmon temperature dependence is different from Bi$_2$Se$_3$ and Bi$_{0.0985}$Sb$_{0.015}$. While the plasma edges for Bi$_2$Te$_3$ and Sb$_2$Te$_3$ shift to higher frequency as the temperature decreases, the plasma edge for Bi$_2$Se$_3$ and Bi$_{0.0985}$Sb$_{0.015}$ shift to lower frequency. This was indicated by their reflectance curves and the spectral loss function. In Bi$_2$Se$_3$ there is a phonon mode observed, while there are none in Bi$_2$Te$_3$, Sb$_2$Te$_3$ and Bi$_{0.0985}$Sb$_{0.015}$. Also in Bi$_2$Se$_3$ there is an absorption dip at 50 cm$^{-1}$ that is not understood at the current time.

In all four samples, Bi$_2$Te$_3$, Sb$_2$Te$_3$, Bi$_2$Se$_3$ and Bi$_{0.0985}$Sb$_{0.015}$, the reflectance shows magnetic field dependence especially around the plasma frequency. The Bi$_2$Se$_3$ spectra also shows a strong magnetic field dependence at 50 cm$^{-1}$, which is not observed in the other samples. The understanding as to what is actually happening to the charge carriers under these conditions at the plasma frequency is still under analysis.

The Drude-Lorentz fits show that the main characteristics of the spectra can be modeled. This is especially true for Bi$_2$Te$_3$, Sb$_2$Te$_3$ and Bi$_{0.0985}$Sb$_{0.015}$. There fits, although not quite perfect, are well described for a classical model. As for Bi$_2$Se$_3$ the
fits can model the two absorption dips rather well, but after the plasma frequency they are not in good agreement with data, especially as the temperature decreases. Overall, the model can replicate the data to an extent, but the model cannot explain the fine details around the plasma frequency for all four samples.
BIBLIOGRAPHY


[3] Stojilovic, N, A. Koncz. *Normal state charge dynamics of Fe$_{1.06}$Te$_{0.88}$S$_{0.14}$ superconductor probed with infrared spectroscopy*. cond-mat.supr-con (2010).


