Optical Properties of $\text{Sb}_2\text{Te}_3$, and Dilute Magnetic Semiconductors $\text{Sb}_{1.97}\text{V}_{0.03}\text{Te}_3$ and $\text{Sb}_{1.94}\text{Cr}_{0.06}\text{Te}_3$

by

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Abstract

This thesis reports on the optical properties of the dilute magnetic semiconductors, Sb$_{1.97}$V$_{0.03}$Te$_3$ and Sb$_{1.94}$Cr$_{0.06}$Te$_3$, along with the parent compound Sb$_2$Te$_3$. These materials develop a ferromagnetic state at low temperature with Curie temperatures of 22 K and 16 K respectively. All three samples were oriented such that the electric field vector of the light was perpendicular to the c-axis. The reflectance profile of these samples in the mid-infrared (500 to 3000 cm$^{-1}$) shows a pronounced plasma edge which retracts with decreasing temperature. The far-infrared region of these samples exhibits a phonon at $\approx$ 60 cm$^{-1}$ which softens as temperature decreases. Kramers-Kronig analysis and a Drude-Lorentz model were employed to determine the optical constants of the bulk samples. The real part of the optical conductivity is shown to consist of intraband contributions at frequencies below the energy gap ($\approx$ 0.26 eV) and interband contributions at frequencies above the energy gap. The temperature dependence of the scattering rate show that a mix of phonon and impurity scattering are present, while the signature of traditional spin disorder (magnetic) scattering was difficult to confirm.
# Contents

Abstract ................................................................. ii

Contents ................................................................. iii

List of Tables ........................................................... v

List of Figures .......................................................... vi

Acknowledgements ......................................................... ix

1 Introduction .......................................................... 1
  1.1 Introduction ......................................................... 1
  1.2 Materials ............................................................ 3
    1.2.1 Crystal Structure of Sb(Bi) Chalcogenides .................. 3
    1.2.2 Sb$_2$Te$_3$ ................................................... 5
  1.3 Magnetism in Tetradymite DMS .................................. 8
    1.3.1 Vanadium Doped Sb$_2$Te$_3$ ................................. 9
    1.3.2 Chromium Doped Sb$_2$Te$_3$ ................................ 12
  1.4 Goal and Theme of the Thesis ................................ 12

2 Theory ................................................................. 16
  2.1 Theory ............................................................. 16
    2.1.1 Lorentz Model ............................................... 18
    2.1.2 Drude Model ................................................ 20
    2.1.3 Reflection .................................................. 21
    2.1.4 Kramers Kronig Relations ................................ 23
    2.1.5 Reflectance in Metallic Systems ............................ 24
    2.1.6 Reflectance in Doped Semiconductors ..................... 27
    2.1.7 Experimental Uncertainty and Reflectance Measurements 27

3 Methods ............................................................... 30
  3.1 Samples .......................................................... 30
    3.1.1 Fourier Transform Spectroscopy ............................ 30
    3.1.2 Finite Resolution Effects ................................ 32
    3.1.3 Sampling .................................................... 33
  3.2 Experimental Procedure ......................................... 34
    3.2.1 Temperature Variation ..................................... 35
4 Results and Discussion ................................................. 42
  4.1 Reflectance Measurements ........................................... 42
    4.1.1 Extrapolated Reflectance Data for KK analysis ............... 42
    4.1.2 Kramers-Kronig Optical Conductivity ............................ 51
    4.1.3 Scattering ...................................................... 56
    4.1.4 Conclusion ..................................................... 65

Bibliography ............................................................... 70
## List of Tables

1.1 A list of atomic radii for Sb, Te, and various transition metal ions ([23]).

3.1 List of various optical elements and sources used in this work to obtain the reflectance measurements over a broad range of frequencies.
List of Figures

1.1 Trends in the miniaturization of the ipod, its increased storage capacity, and increase in sales. .......................................................... 2
1.2 The crystal structure of Sb$_2$Te$_3$. Left: Trigonal unit cell. Right: Hexagonal conventional cell. Typical lattice constants for Sb$_2$Te$_3$ are $a_{hex} = 4.25\, \text{Å}$, $c_{hex} = 30.35\, \text{Å}$. Reproduced from [3]. .................................................. 4
1.3 Diamagnetic behavior of the susceptibility of Sb$_2$Te$_3$. [18]. ........................................ 5
1.4 Top: Hall coefficient $R_H$ as a function of temperature for Sb$_{2-x}$V$_x$Te$_3$ single crystals. Bottom: In plane electrical resistivity as a function of temperature for Sb$_{2-x}$V$_x$Te$_3$ single crystals. The current was measured perpendicular to the c axis [20]. The Curie temperature varies with doping concentration (denoted by x) from 1 to 23 K and can be seen in the Sb$_{1.97}$V$_{0.03}$Te$_3$ sample from the point of steep decline in resistivity to the left of the graph. Values for the Curie temperatures were estimated by Dyck et al. through analysis of susceptibility measurements. Reproduced from [20]. .............. 6
1.5 Four unit cells of antimony telluride demonstrating the possible anti-site defect locations. (a) Defect free Unit cell illustrating six possibilities for the exchange of the Te atom marked 0 with Sb atoms marked 1-6. (b) Anti-site defect showing Sb in Te2 site. (c) Anti-site defect showing Sb in Te1 site. (d) Anti-site defect showing Te in Sb site. ............................................. 7
1.6 Magnetization of Sb$_{1.97}$V$_{0.03}$Te$_3$ [20]. The hard magnetic axis is shown as the magnetization perpendicular to the c-axis, while the easy axis of magnetization occurs when the applied field is parallel to the c-axis. ........................................ 11
1.7 Top: Hall coefficient $R_H$ as a function of temperature for Sb$_{2-x}$Cr$_x$Te$_3$ single crystals. Bottom: In plane electrical resistivity as a function of temperature for Sb$_{2-x}$Cr$_x$Te$_3$ single crystals. The current was measured perpendicular to the c axis [25]. The Curie temperature varies with doping concentration (denoted by x) from 7 to 17 K and can be seen from the point of steep decline in resistivity to the left of the graph. Reproduced from [25]. .............................................. 13
1.8 Right: Temperature dependence of the magnetization $M$ cooling in B = 1000 G (Gauss) parallel to the c axis and in-plane resistivity $\rho$ for Sb$_{2-x}$Cr$_x$Te$_3$ single crystals with x = 0.047 (triangles) and x = 0.095 (circles). Open symbols represent $M$, and solid symbols represent $\rho$. Left: Inverse magnetic susceptibility as a function of temperature for Sb$_{2-x}$Cr$_x$Te$_3$ single crystals. The lines in inverse susceptibility plot are linear fits, which illustrate the ferromagnetic positive Curie-Weiss temperatures. Reproduced from [25]. .................................................. 14
2.1 Reflectivity of an undamped free carrier gas as a function of frequency. Reproduced from [26]. .......................................................... 25
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>Experimental reflectance of aluminum as a function of energy. The experimental data are compared to the free electron model with $\hbar \omega_p = 15\text{eV}$. The dotted curve represented no damping. The dashed line includes damping ($\tau = 1/\gamma$). Reproduced from [26].</td>
<td>26</td>
</tr>
<tr>
<td>2.3</td>
<td>$\varepsilon_2$ obtained from KK analysis of a theoretical set of reflectance data, which was extrapolated with $R \propto \omega^{-4}$ from 6, 10, 25, and 50 eV. Reproduced from [28].</td>
<td>29</td>
</tr>
<tr>
<td>3.1</td>
<td>A schematic view of a simple Michelson interferometer. Reproduced from [30].</td>
<td>31</td>
</tr>
<tr>
<td>3.2</td>
<td>Cryostat with flow-through liquid He input. Thermocouple gauges were used to check the temperature of the sample as well as the temperature of the liquid He bayonet.</td>
<td>36</td>
</tr>
<tr>
<td>3.3</td>
<td>The sample holder was coupled to a cold-finger cryostat with flow-through liquid He input by a flexible metal conduit (Ag or Cu). Thermocouple gauges were used to check the temperature of the sample as well as the temperature of the liquid He bayonet.</td>
<td>37</td>
</tr>
<tr>
<td>3.4</td>
<td>Simplified optical path. The sample and reference are mounted at 90 degrees from one another. A stepper motor rotates the sample holder between measurements so that the reference and the sample experience the same optical path.</td>
<td>38</td>
</tr>
<tr>
<td>3.5</td>
<td>Top: Images of the plates used to secure the silver conduit. Bottom: Ag conduit rotated in two positions: the left shows the mirror in the optical path, and right image shows the sample in the optical path.</td>
<td>39</td>
</tr>
<tr>
<td>3.6</td>
<td>The thermal conductivity of the specimens of copper, silver and gold. Ag1 samples are 99 percent pure Ag wires. Ag2 samples polycrystalline annealed samples. The precise purity of Ag2 samples was not mentioned in [33].</td>
<td>40</td>
</tr>
<tr>
<td>4.1</td>
<td>Reflectance of $\text{Sb}_2\text{Te}_3$ as a function of wavenumber (cm$^{-1}$).</td>
<td>43</td>
</tr>
<tr>
<td>4.2</td>
<td>Reflectance of $\text{Sb}<em>{1.97}\text{V}</em>{0.03}\text{Te}_3$ as a function of wavenumber (cm$^{-1}$).</td>
<td>44</td>
</tr>
<tr>
<td>4.3</td>
<td>Reflectance of $\text{Sb}<em>{1.94}\text{Cr}</em>{0.06}\text{Te}_3$ as a function of wavenumber (cm$^{-1}$).</td>
<td>45</td>
</tr>
<tr>
<td>4.4</td>
<td>Reflectance of $\text{Sb}<em>{1.97}\text{V}</em>{0.03}\text{Te}_3$ as a function of wavenumber (Taken by Jesse Hall from McMaster University). Notice the similarity in the plasma edge at 50 K and 12 K.</td>
<td>46</td>
</tr>
<tr>
<td>4.5</td>
<td>Reflectance measurements of $\text{Bi}_2\text{Te}_3$ as a function of temperature. Reproduced from [34]. Notice the plasma edge which moves to lower energy with increasing temperature.</td>
<td>47</td>
</tr>
<tr>
<td>4.6</td>
<td>Far-infrared reflectance of $\text{Sb}<em>{1.97}\text{V}</em>{0.03}\text{Te}_3$ (black) with a comparison of a Drude model (red) versus a Drude-Lorentz model (green).</td>
<td>48</td>
</tr>
<tr>
<td>4.7</td>
<td>Far infrared reflectance of $\text{Sb}<em>{1.97}\text{V}</em>{0.03}\text{Te}_3$ as a function of wavenumber (cm$^{-1}$). Notice the phonon at $\approx 60$ cm$^{-1}$ which moves to lower energy with decreasing temperature.</td>
<td>49</td>
</tr>
<tr>
<td>4.8</td>
<td>Far infrared reflectance of $\text{Sb}<em>{1.94}\text{Cr}</em>{0.06}\text{Te}_3$ as a function of wavenumber (cm$^{-1}$). Notice the phonon at $\approx 60$ cm$^{-1}$ which moves to lower energy with decreasing temperature.</td>
<td>50</td>
</tr>
<tr>
<td>4.9</td>
<td>Room temperature reflectance measurements of $\text{Bi}_2\text{Te}_3$ as a function of energy, where 1meV $= 8.064$ cm$^{-1}$. Reproduced from [35].</td>
<td>51</td>
</tr>
<tr>
<td>4.10</td>
<td>Reflectance of $\text{Sb}<em>{1.94}\text{Cr}</em>{0.06}\text{Te}<em>3$ at 300 K including extrapolated region. In this plot, our reflectance data is shown from 50 cm$^{-1}$ to 10000 cm$^{-1}$, while reflectance data from 10000 cm$^{-1}$ to 40000 cm$^{-1}$ was taken by Jesse Hall at McMaster University for the $\text{Sb}</em>{1.97}\text{V}_{0.03}\text{Te}_3$ sample. The extrapolated reflectance region covered the frequency range from 40000 cm$^{-1}$ to 200000 cm$^{-1}$.</td>
<td>52</td>
</tr>
<tr>
<td>4.11</td>
<td>The real part of the conductivity for $\text{Sb}_2\text{Te}_3$ as a function of wavenumber. Note that 8064 cm$^{-1}$ corresponds to a photon energy of 1 eV.</td>
<td>53</td>
</tr>
</tbody>
</table>
4.12 The real part of the conductivity for $Sb_{1.97}V_{0.03}Te_3$ as a function of wavenumber. Note that 8064 cm$^{-1}$ corresponds to a photon energy of 1 eV. .................. 54

4.13 The real part of the conductivity for $Sb_{1.94}Cr_{0.06}Te_3$ as a function of wavenumber at low frequency. Arrows on the graph denote the onset of interband absorption. ... 55

4.14 Connection between the real part of the conductivity and the DC conductivity as well as the scattering rate (gamma). Reproduced from [36]. .................. 56

4.15 Scattering rates obtained through fits of a Drude-Lorentz model. Red solid circles represents measurements taken at McMaster. Note the similarity to Figure 4.16. .. 57

4.16 Temperature dependence of the scattering rate obtained by the FWHM of the optical conductivity. The scattering rate for $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$ were found to be $0.49 \pm 0.04$ cm$^{-1}$K$^{-1}$, $0.51 \pm 0.04$ cm$^{-1}$K$^{-1}$, and $0.49 \pm 0.03$ cm$^{-1}$K$^{-1}$ respectively. .................. 58

4.17 Room temperature reflectance for $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$. .... 59

4.18 Room temperature Mid infrared reflectance of $Sb_{2-x}Cr_xTe_3$. The samples are numbered according to the concentration of Cr in the lattice, where 1. $x=0$, 2. $x=0.01$, 3. $x=0.035$, and 4. $x=0.07$ respectively. .................. 60

4.19 Room temperature mid-infrared reflectance of $Sb_{2-x}Fe_xTe_3$. The samples are numbered according to the concentration of Fe in the lattice, where 1. $x=0$, 2. $x=0.002$, 3. $x=0.005$, 6. $x=0.02$, and 7. $x=0.06$ respectively .................. 61

4.20 Room temperature mid-infrared reflectance of $Sb_{2-x}In_xTe_3$. The samples are numbered according to the concentration of In in the lattice, where 1. $x=0$, 2. $x=0.05$, 3. $x=0.098$, 4. $x=0.22$, 5. $x=0.29$, and 6. $x=0.41$, respectively. Reproduced from [39]. 62

4.21 Temperature dependent scattering rate for, static disorder scattering $\sigma_{sd}$, phonon scattering $\sigma_{ph}$, and magnetic scattering $\sigma_{ph}$. Reproduced from [41]. .................. 63

4.22 The plasma frequency ($\omega_p^2$) are plotted with the inverse Hall coefficient (1/R$_H$) as a function of temperature. Open circles plot carrier concentrations measured by the Hall Effect ($\sigma \propto 1/R_H$). Solid circles plot carrier concentrations measured optically ($\sigma \propto \omega_p^2$). Purple: McMaster $Sb_{1.97}V_{0.03}Te_3$ measurements. Red: Brock $Sb_{1.97}V_{0.03}Te_3$ measurements .................. 66

4.23 (a) Temperature dependent AC and DC resistivity of Au and AuFe. The solid dots refer to AC resistivity oof AuFe films (6 at. percent Fe) measured at 1.05 THz. The dashed line correspond to DC resistivity for bulk AuFe with 5 atomic percent of Fe. The solid linerefers to the DC resistivity of bulk Au. (b) The temperature dependent magnetic contribution to the AC resistivity shown by the open circles; for comparison the AC resistivity of the AuFe film is shown as solid dots. Reproduced from [43]. ... 67

4.24 Concentration of Cr across a boule of $Sb_{1.96}Cr_{0.04}Te_3$. .................. 68
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Chapter 1

Introduction

1.1 Introduction

Today, there is hardly an aspect of our daily lives that has not been enhanced by technology. The advancements in microelectronics and communications technology, in particular, are largely responsible for the increase in speed and storage capacity that have made handheld devices an indispensable appendage for many people. In many ways, it is consumer demand for more powerful, portable smart-electronics, which has led to the advent of more high capacity miniaturized storage drives. It is necessary to consider only the evolution of something like the Ipod (Figure 1.1), for example, to observe how consumer demand has influenced technological advancement in this field. Nevertheless these trends cannot persist indefinitely, and physical limitations have made it impossible to extend miniaturization by the fabrication process alone. An alternative solution involves manipulating the fundamental properties of the materials involved; creating a new regime of information processing. This is called spintronics (or spin based electronics), and it is a developing field in which the spin of the electron is used for data processing [2]. In fact, "metallic spintronic devices have already demonstrated success with the development of hard disk read heads and magnetic random access memory (MRAM) [2]".

The development of spintronic technologies involves generating spin polarized currents, maintaining spin polarization, varying the spin state, and detecting polarized currents.

Ferromagnetic materials were the early candidates for spintronic technologies since their Curie temperatures ($T_c$) are above room temperature. In addition, running a current through a ferromagnetic material provides the simplest way to create a spin polarized current [3]. These materials were ultimately abandoned as candidates for spintronic devices as large conductivity mismatches led to low spin injection efficiencies [4] at the metal-semiconductor interface.
Chapter 1. Introduction

Figure 1.1: Trends in the miniaturization of the iPod, its increased storage capacity, and increase in sales. [1].
The next phase in the development of spintronic materials involved the growth and testing of so-called dilute magnetic semiconductors. Dilute magnetic semiconductors (DMS) are made of a semiconductor host which is doped with a small concentration of transition metal (TM) or rare-earth elements [5]. The first attempts involved type II-VI semiconductors, which were alloyed with MnTe [3]. However, obtaining ferromagnetic samples was found to be difficult as direct exchange between the Mn ions resulted in either paramagnetism or antiferromagnetism [6, 7].

More recently, DMS compounds based on Mn doped III-V semiconductors have been heavily studied because the host materials used in these compounds are already found in integrated circuit and optoelectronic devices [2]. Mn doped III-V DMS materials have shown some promise; however, the bulk solubility limit of these materials results in Curie temperatures far below room temperature. Even with the application of non-equilibrium thin film techniques, the highest Curie temperature observed in a III-V DMS material was a Mn doped GaAs sample with $T_c = 170\text{K}$ [?].

While much of the research on DMS materials is comprised of Mn doped III-V and II-VI systems, research on DMS materials based on TM doped $Sb_2Te_3$ has recently emerged. These new DMS materials, with tetradymite crystal structure, are interesting because they offer an alternative setting to study the behavior of DMS materials, compared to the more traditional wurtzite or zinc blende DMS structures.

1.2 Materials

1.2.1 Crystal Structure of Sb(Bi) Chalcogenides

Sb(Bi) chalcogenides are members of the semiconductor family $A^V_2B^VI_3$ (where $A = Sb$ or $Bi$ and $B = Te$ or $Se$), and the atoms in these semiconductors crystallize in a tetradymite-type structure. The term tetradymite was originally used specifically to describe the crystal structure of the mineral $Bi_2Te_2S$, but because Sb(Bi) chalcogenides share a similar structure to $Bi_2Te_2S$ and have been intensely studied, the term tetradymite was adopted as a general term to denote the structure of this family of compounds. This crystal structure can be described by a Bravais lattice constructed of rhombohedral (or trigonal) primitive cells (Figure 1.2, left), or by a larger hexagonal conventional
Figure 1.2: The crystal structure of Sb$_2$Te$_3$. Left: Trigonal unit cell. Right: Hexagonal conventional cell. Typical lattice constants for Sb$_2$Te$_3$ are $a_{\text{hex}} = 4.25\,\text{Å}$, $c_{\text{hex}} = 30.35\,\text{Å}$. Reproduced from [3].

The atomic arrangement is best described in terms of a layered structure, much like that of a sandwich, where each sandwich consists of five mono-atomic sheets. The sequence of layers to make an Sb$_2$Te$_3$ sandwich, for example, is Te$_1$-Sb-Te$_2$-Sb-Te$_1$, where the numbers 1 and 2 denote differently bonded tellurium atoms. Bonds between Te$_1$ and Sb atoms are predominantly ionic, while bonding between Te$_2$ and Sb atoms is mainly covalent. Neighboring sandwiches (between Te$_1$-Te$_1$ sheets) are weakly held together by van der Waals type interactions [10, 11, 12].
Chapter 1. Introduction

1.2.2 Sb₂Te₃

Antimony telluride is a diamagnetic (Figure 1.3), narrow gap \( (E_g \approx 0.26 \text{ eV} \ [13]) \) semiconductor compound that tends to crystallize in a non-stoichiometric fashion. As a result, Sb₂Te₃ exhibits a high concentration of p-type carriers \( \approx 10^{19} \text{ cm}^{-3} \) and a metallic resistivity (Figure 1.4). A natural excess of Sb in the Sb₂Te₃ lattice is the result of antisite defects. The existence of these defects in Sb and Bi tellurides has been confirmed in many studies \([14, 15, 16]\) and are characterized by the replacement of one atom in the lattice with the atom which is in excess. Since there are Te₁ and Te₂ sites for which Sb can substitute, there are a total of three possibilities for antisite defects in the unit cell (Figure 1.5) \([17]\); however, the antisite defects in Sb₂Te₃ are predominantly characterized by the substitution of a Te atom by an Sb atom.

Horák et al. \([14]\) suggest that the formation of antisite defects in tetradymite-type \( (A^Y_2 B^V_3) \) crystals is caused by the low polarity between A-B bonds. They found the formation energy of the
Figure 1.4: Top: Hall coefficient $R_H$ as a function of temperature for Sb$_{2-x}$V$_x$Te$_3$ single crystals. Bottom: In plane electrical resistivity as a function of temperature for Sb$_{2-x}$V$_x$Te$_3$ single crystals. The current was measured perpendicular to the c axis [20]. The Curie temperature varies with doping concentration (denoted by x) from 1 to 23 K and can be seen in the Sb$_{1.97}$V$_{0.03}$Te$_3$ sample from the point of steep decline in resistivity to the left of the graph. Values for the Curie temperatures were estimated by Dyck et. al. through analysis of susceptibility measurements. Reproduced from [20].
Figure 1.5: Four unit cells of antimony telluride demonstrating the possible anti-site defect locations. (a) Defect free Unit cell illustrating six possibilities for the exchange of the Te atom marked 0 with Sb atoms marked 1-6. (b) Anti-site defect showing Sb in Te2 site. (c) Anti-site defect showing Sb in Te1 site. (d) Anti-site defect showing Te2 in Sb site. Reproduced from [17].
antisite defect to be $E_0 = 0.35$ eV. Additionally, the formation energy of Bi$_2$Te$_3$ was calculated by Miller and Che-Yu Li [14] and was found to be 0.40 eV. According to Horák et al. [19], the lower formation energy obtained for Sb$_2$Te$_3$ is due to the smaller difference in bond electronegativity between Sb and Te than between Bi and Te.

T. Thonhauser et al. [17] continued this work by employing first principle calculations to obtain the formation energy of antisite defects for Sb$_2$Te$_3$, as well as the formation energy of Sb and Te vacancies. In addition to obtaining results which were in reasonable agreement with Horák et al. [19], T. Thonhauser et al. [17] found that the formation energy of the vacancies were nearly twice that of the antisite defects and that the most favorable antisite defect included a substitution of Te$_1$ atoms with Sb.

1.3 Magnetism in Tetradyrmite DMS

The addition of a small amount of magnetic impurity has been demonstrated to result in ferromagnetism in Sb(Bi) chalcogenides; however, these dilute magnetic semiconductors only exhibit ferromagnetism when the dominant carriers are holes (p-type). DMSs are characterized by the dilute nature of their magnetic dopants, which results in a large enough average distance between the magnetic impurities such that they cannot interact directly. Since these materials exhibit a large number of carriers and have moments which are thought to be unable of interacting directly, it has been suggested that the mechanism for ferromagnetism in these materials is carrier induced via indirect coupling [20].

The Ruderman-Kittel-Kasuya-Yoshida (RKKY) theory describes long range indirectly coupled interactions. Within the RKKY picture, free carriers are spin-polarized to some degree based on their distance from the magnetic ions. This model is used to describe the interaction between the free carriers (p or s) and localized states (d or f) of the magnetic impurities [21]. Carriers that are, at any instance, closer to the magnetic ion will be polarized more strongly than those which are further away. As a result, spin polarization of the carriers forms long range interactions of a sinusoidal nature over which the magnetic information is passed from one impurity to the next [21].
Chapter 1. Introduction

The second-order interaction between two spins is given in Kittel [21] by;

\[ H = \vec{I}_n \cdot \vec{I}_m \frac{4J^2m_ek_f^4}{(2\pi)^3} F(2k_f r) \]  \hspace{1cm} (1.1)

In which, \( \vec{I}_{n,m} \) are the moments, \( k_f \) is the Fermi wavevector, \( j \) is a coupling constant, and \( m_* \) is the effective mass of the carriers. The function \( F(x) \), where \( x=2k_f r \), is called the range function and accounts for the oscillatory nature of the interaction [21]. The range function is given by Kittel [21] is;

\[ F(x) = \frac{xcosx - sinx}{x^4} \]  \hspace{1cm} (1.2)

Looking at the range function in the limit of small \( x \), it becomes apparent that for small \( x \), \( F(x) \rightarrow -1/6x \) [21]). This is to say that for \( x \) less than the first zero of \( F(x) \), the interaction is ferromagnetic. In DMS materials the distance between nearest neighbor magnetic impurities is much smaller than the period of oscillation, although not all DMS behavior is described by the RKKY interaction picture. In fact, III-V DMS materials doped with Mn are not normally treated under the RKKY picture because Mn atoms not only act as magnetic impurities but also acceptors, which results in many charge carriers (holes) with Mn 3d character.

1.3.1 Vanadium Doped Sb\(_2\)Te\(_3\)

The first set of results describing a DMS based on TM doped Sb\(_2\)Te\(_3\) was published by Dyck et al. [20] in 2002. They had successfully grown crystals of Sb\(_{2-x}\)V\(_x\)Te\(_3\) (0 ≤ x ≤ 0.03) by the modified Bridgman method. Their results showed that the resistivity profile of Sb\(_{2-x}\)V\(_x\)Te\(_3\) exhibits metallic behaviour that is similar to Sb\(_2\)Te\(_3\), but with higher resistivity at all temperatures. In addition to the increase in resistivity compared to the parent material Sb\(_2\)Te\(_3\), Sb\(_{2-x}\)V\(_x\)Te\(_3\) also exhibits a magnetic transition, characterized by a small hump in the resistivity curve near the transition temperature (Figure 1.4). As Figure 1.4 illustrates, increasing the concentration of Vanadium in these samples increases the resistivity (at all temperatures) and pushes T\(_c\) to higher temperatures. These variations in resistivity could possibly result from a reduction of antisite defects [22], a change in scattering, or a combination of the two.
Another interesting feature of these materials is the increase in the measured Hall coefficient \( R_H \) near the onset of the magnetic transition (Figure 1.4, top). Ordinarily, this would translate to a large reduction in the carrier concentration near \( T_c \), as the Hall coefficient is inversely proportional to the number of carriers. However; this feature could arise because of an increase in spontaneous magnetization (near \( T_c \)) [20], which can be explained by the Anomalous Hall effect (AHE), in which the Hall resistivity, \( \rho_H \), is expressed as:

\[
\rho_H = R_o B + R_s M
\]  

(1.3)

Here, \( R_o \) is the ordinary Hall coefficient, \( R_s \) the anomalous Hall coefficient, and \( M \) the magnetization of the samples. When samples are at temperatures much greater than \( T_c \), \( M \) is negligible, and the ordinary Hall effect applies. As the internal magnetization becomes larger upon the onset of the ferromagnetic state it contributes to the total magnetic field experienced by the conduction electrons. As a result more electrons are pushed to one side of the sample, significantly altering the Hall voltage.

In order to investigate the effects related to transition metal (TM) ions in DMSs, it is important to identify the most likely electron configuration of the transition metal ion, as it may appear in the lattice. The transition metal typically substitutes for the Sb [22, 20] sites requiring the ion to donate three of its electrons for bonding. This is because ions of similar sizes are more likely to substitute for one another. Table 1.1 lists the ionic radius of a few TM ions in comparison to Sb and Te. In the case of bulk Sb\(_{2-x}V_x\)Te\(_3\) crystals, Vanadium is estimated to be in the \( V^{+3} \) state. Susceptibility measurements carried out by Dyck et al. [20] (Figure 1.6) demonstrate ferromagnetic behaviour in the doped samples. Two values of the effective Bohr magneton \( (\mu_{eff}) \) number for Sb\(_{1.97}V_{0.03}\)Te\(_3\) were obtained via the Curie-Weiss law \( (\mu_{eff} = 2.6\mu_B) \) and magnetic saturation \( (\mu_{eff} = 2.3\mu_B) \).

These values are in reasonable agreement with the theoretical value of \( \mu_{eff} = 2.8\mu_B \) for Vanadium in the \( V^{+3} \) state, with total spin \( S = 1 \) [24].
Table 1.1: A list of atomic radii for Sb, Te, and various transition metal ions ([23]).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Covalent Radius (Å)</th>
<th>Ionic Radius (Å)</th>
<th>Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb$^{3+}$</td>
<td>0.90</td>
<td>0.76</td>
<td>VI</td>
</tr>
<tr>
<td>Te$^{2-}$</td>
<td>2.07</td>
<td>2.21</td>
<td></td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>0.78</td>
<td>0.64</td>
<td>VI</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.755</td>
<td>0.615</td>
<td>VI</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.69</td>
<td>0.55</td>
<td>VI</td>
</tr>
<tr>
<td>In$^{3+}$</td>
<td>0.94</td>
<td>0.80</td>
<td>VI</td>
</tr>
</tbody>
</table>

Figure 1.6: Magnetization of Sb$_{1.97}$V$_{0.03}$Te$_3$ [20]. The hard magnetic axis is shown as the magnetization perpendicular to the c-axis, while the easy axis of magnetization occurs when the applied field is parallel to the c-axis.
1.3.2 Chromium Doped Sb$_2$Te$_3$

The resistivity profiles of Sb$_{2-x}$Cr$_x$Te$_3$ samples share the fundamental features with that of the Sb$_{2-x}$V$_x$Te$_3$ samples (Figure 1.7). One may note, however, that the resistivity of Vanadium doped samples in the paramagnetic temperature regime is larger than that of their Chromium doped counterparts at equal doping concentration. Vanadium samples appear to have a greater level of static scattering, which is possibly due to the way that Cr interacts with the native defects of the host lattice [22]. As discussed previously (section 1.2.2), antisite defects native to Sb$_2$Te$_3$ are thought to be related to the bond polarity between Sb and Te atoms. Replacing an Sb atom for a TM ion results in a change in bond polarity, which could further result in a reduction in the number of antisite defects, and possibly holes.

As shown above, the Anomalous Hall Effect is a linear combination of the ordinary Hall coefficient ($R_0$) and the anomalous Hall coefficient ($R_s$), “where $R_s$ is the sum of two contributions proportional to $\rho$ and $\rho^2$, known as skew scattering and jump scattering, respectively [25]”. Dyck et al. [25] found $R_s \propto \rho$, suggesting that the AHE in Sb$_{2-x}$Cr$_x$Te$_3$ is likely due to skew scattering related to magnetic impurities in the lattice.

Plots of the inverse susceptibility show signs of a ferromagnetic transition below the appropriate transition temperature (Figure 1.8). Transition temperatures associated with the Cr samples are lower than those of the Vanadium samples, despite having a larger moment associated with the Cr$^{3+}$ ($S = 3/2$) atom. Although Sb$_{1.97}$V$_{0.03}$Te$_3$ has half the dopant concentration of Sb$_{1.94}$Cr$_{0.06}$Te$_3$, the V doped ($T_c = 23$ K) samples have a $T_c$ seven degrees higher than the Cr doped ($T_c = 16$ K) samples. Dyck et al. [25] used the Curie-Weiss law to estimate the effective Bohr Magneton number for the Cr samples. These values were found to be $3.5\mu_B$, $3.10\mu_B$, $3.12\mu_B$, and $2.98\mu_B$, for $x = 0.031$, $0.047$, $0.069$, and $0.095$, respectively. These results suggest that the Cr atom is indeed in the $3^+$ valence state ($\mu_B$ ($S=3/2$) = 3.87).

1.4 Goal and Theme of the Thesis

The goal of the thesis was to measure the temperature dependence of the scattering rate in Sb$_2$Te$_3$, Sb$_{1.97}$V$_{0.03}$Te$_3$, and Sb$_{1.94}$Cr$_{0.06}$Te$_3$ using Fourier transform infrared reflectance spectroscopy. Near
Figure 1.7: Top: Hall coefficient $R_H$ as a function of temperature for Sb$_{2-x}$Cr$_x$Te$_3$ single crystals. Bottom: In plane electrical resistivity as a function of temperature for Sb$_{2-x}$Cr$_x$Te$_3$ single crystals. The current was measured perpendicular to the c axis [25]. The Curie temperature varies with doping concentration (denoted by x) from 7 to 17 K and can be seen from the point of steep decline in resistivity to the left of the graph. Reproduced from [25].
Figure 1.8: Right: Temperature dependence of the magnetization $M$ cooling in $B = 1000$ G (Gauss) parallel to the $c$ axis and in-plane resistivity $\rho$ for $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ single crystals with $x = 0.047$ (triangles) and $x = 0.095$ (circles). Open symbols represent $M$, and solid symbols represent $\rho$. Left: Inverse magnetic susceptibility as a function of temperature for $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ single crystals. The lines in inverse susceptibility plot are linear fits, which illustrate the ferromagnetic positive Curie-Weiss temperatures. Reproduced from [25].
normal incidence reflectance measurements allow us experimental access to the dielectric function of a solid. The dielectric function holds information regarding the frequency dependence of the electronic transitions, bound oscillations (phonons), and free carrier oscillations in a solid. The following chapter outlines several models for the dielectric function of metals and insulators and how they are related to reflectance measurements.

In order to measure the temperature dependence of the scattering rate below the transition temperature for the DMS samples, it was necessary to take measurements below their Curie temperatures. The pre-existing cryostat utilized for this type of work at Brock University was capable of cooling asamples down to 45 K. Since the Curie temperatures of the DMS samples in this work were below 45 K, it was necessary to decrease the low temperature limit of the pre-existing system. The goal for the low temperature limit of the system was 10 K as this temperature would accommodate the lowest Curie temperature of the samples (\( T_c \) of \( \text{Sb}_1\text{.94Cr}_0\text{.06Te}_3 \approx 16 \text{ K} \)). Chapter 3 discusses the modifications which were made to the cryostat and some difficulties associated with achieving sub-10 K temperatures without abandoning the original design completely.
Chapter 2

Theory

2.1 Theory

Under Maxwell’s theory of optical propagation, light is treated as electromagnetic waves and the atoms or molecules of a dielectric material are modelled as classical dipole oscillators [26, 27]. This classically derived model provides a general overview of the optical properties of solids, and enables the calculation of the frequency dependence of the complex dielectric constant [26]. The complex dielectric constant allows us access to the frequency dependence of the complex index of refraction, and thus enables the examination of the absorptive and dispersive nature of solids [26, 27]. Maxwell’s model assumes that there are two main types of oscillators within a medium: bound, and unbound (or free). The category for bound electron oscillators is broken into two: atomic oscillators, and vibrational oscillators. In insulators and semiconductors, bound electron oscillators are responsible for the largest contribution at frequencies below their energy gap, whereas in metals and doped (or degenerate) semiconductors free oscillators are the dominant mode of oscillation at lower frequencies.

The atomic oscillator model assumes that bonds between electrons and the nucleus are represented by a spring. Within this picture, small displacements between the electron and the positively charged nucleus create an electric dipole, which vibrates at a characteristic frequency, $\omega_0$. The relationship between, $\omega_0$ and K (the bond strength) is:

$$\omega_0 = \sqrt{\frac{K}{m_r}}$$  \hspace{1cm} (2.1)

where $m_r$ is the reduced mass of the system and be calculated as in equation 2.2, with $m_e$ the mass of the electron and $m_n$ the mass of the nucleus.
There are several dipoles associated with every atom, which account for one atom's many transition frequencies. This is evident by atomic absorption and emission spectra, which occur over a wide range of frequencies [26, 27]. The dipole oscillator model can be used to understand interactions between external electromagnetic waves and the atom. This model assumes that the forces due to the electric field provided by the external electromagnetic wave are very small compared to the binding forces which hold the electrons to the nucleus. Furthermore, in this model, the magnetic field of the external electromagnetic wave is neglected as the magnetic force is much less than that of the electric force [26, 29, 27].

Consider an external electromagnetic wave of frequency $\omega$ interacting with an atom. Its alternating electric field imposes a force on the electron/nucleus system and drives oscillations at that frequency. If $\omega$ is equal to one of the natural frequencies of the atom, then resonance will occur resulting in a larger amplitude oscillation. This resonance event is also accompanied by the transfer of energy from the external wave to the atom, achieving absorption. If the frequency of the external wave does not coincide with any of the natural frequencies of the atom, then no absorption occurs and the atom appears transparent to those frequencies.

In this case, the external wave drives non-resonant oscillations at frequency $\omega$, which causes a phase lag in the wave interacting with the atom. The phase lag is a feature of forced oscillators and is caused by damping [26, 27]. The oscillating atoms act as Huygen point sources, which re-radiate destructive wavelets of the incoming wave in all directions, cancelling all wave fronts except for in the direction of propagation [26, 27]. The phase lag acquired through this process retards the propagation of the wavefront, thus lowering the velocity of the wave while it travels through the material. This reduction of the velocity in the material is related to its refractive index.

Ionic materials contain oppositely charged atoms. In crystalline solids, atoms are arranged in a lattice structure, where the atoms are considered bound to a particular position in the crystal lattice. If vibrations between two oppositely charged atoms occur, an oscillating dipole moment is achieved [26, 27]. This event is similar to the oscillations within the atoms discussed above.
Vibrational oscillations (phonons) are excitations of the bound atoms in the lattice. The excitation of the modes can be accomplished thermally or optically and can be represented by two atoms separated by a spring representing the molecular bond between them. If oppositely charged atoms begin to vibrate about equilibrium positions, an oscillating electric dipole is created in similar fashion to the atomic oscillator model. Oscillations in this regime occur at lower frequencies (typically Far-IR), which is a consequence of a larger reduced mass, as seen in equation 2.2, with the electron and nucleus masses replaced by those of the charged atom. These lower frequency oscillations are a feature of molecular oscillators and as a result are apparent in the infrared spectral region [26, 27]. While both vibrational and atomic oscillations are bound oscillators, in practice they can be treated as two distinct types of dipoles because of their sharp resonances which occur at very different frequencies. This renders the resonant effects of bound electrons negligible near the frequencies of the lattice vibrations [26, 29, 27].

The previous dipole models are based on bound oscillators; however, metals and heavily doped semiconductors have a significant number of free electrons. Free electrons are not bound to any atoms and they do not experience a restoring force when displaced from equilibrium. This implies that both the spring constant and natural resonance frequency of this type of oscillator is zero [26].

### 2.1.1 Lorentz Model

The Lorentz oscillator model is based on bound dipole oscillations. When acted upon by an external electromagnetic field, the motion of the electron is described by the following differential equation:

\[
\frac{d^2 \vec{r}}{dt^2} + m_0 \gamma \frac{d\vec{r}}{dt} + m_0 \omega_0^2 \vec{r} = -e \vec{E}
\]  

(2.3)

where \( m_0 \) is the mass of the electron, \( \gamma \) is the damping constant, \( e \) is the charge, \( \omega_0 \) is the resonant frequency, and \( \vec{E} \) is the electric field component of the electromagnetic wave. Movement of the nucleus can be neglected, as its mass is much greater than that of the electron [26, 27].

Consider a monochromatic source which interacts with an atom. The source AC electric field will drive oscillations at its own frequency, \( \omega \). In this case the solution to the equation of motion
above has the form:

\[ \tilde{\tau} = \frac{-e\tilde{E}}{(\omega_0^2 - \omega^2 - i\gamma\omega)} \]  \hspace{1cm} (2.4)

If \( N \) is the number of atoms per unit volume, the resonant polarization is then given by:

\[ \tilde{P} = N\tilde{\tau} \]  \hspace{1cm} (2.5)

\[ = Ne\tilde{\tau} \]  \hspace{1cm} (2.6)

\[ = \frac{-e^2N\tilde{E}}{m_0(\omega_0^2 - \omega^2 - i\gamma\omega)} \]  \hspace{1cm} (2.7)

Equation 2.7 can be used to obtain the complex dielectric function \( \tilde{\varepsilon} \). The electric displacement, \( \tilde{D} \), of the material is related to the electric field and polarization through the following equation:

\[ \tilde{D} = \varepsilon_0\tilde{E} + \tilde{P} = \varepsilon_0\tilde{\varepsilon}\tilde{E} \]  \hspace{1cm} (2.8)

By combining equations 2.7 and 2.8, the dielectric function is found to be:

\[ \tilde{\varepsilon} = 1 + \frac{\omega_p^2}{(\omega_0^2 - \omega^2 - i\gamma\omega)} \]  \hspace{1cm} (2.9)

Here the so called plasma frequency is defined as:

\[ \omega_p^2 = \frac{e^2N}{\varepsilon_0m_0} \]  \hspace{1cm} (2.10)

The dielectric function is an optical response function for a given medium, and can be split into its real (\( \varepsilon_1 \)) and imaginary (\( \varepsilon_2 \)) portions resulting in the following terms:

\[ \varepsilon_1 = 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \]  \hspace{1cm} (2.11)

\[ \varepsilon_2 = \frac{\omega_p^2\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \]  \hspace{1cm} (2.12)

The Lorentz model applies to semiconductors and insulators; however, to fit real materials a sum of several Lorentz oscillators is needed [26, 27]. The complex dielectric function used to fit multiple
bound oscillators is given by:

\[
\varepsilon = \varepsilon_\infty + \sum_j \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}
\]  

(2.13)

Here, each bound oscillator labelled, by \( j \), has its own characteristic resonance, damping constant, and plasma frequency. The addition of \( \varepsilon_\infty \) is used to describe contributions of high frequency oscillations which are out of the field of interest.

### 2.1.2 Drude Model

Metals and doped semiconductors feature a large number of free electrons. In metals, the large densities of free electrons originate from valence states associated with the metal atoms [26, 27] and are relatively constant with respect to temperature. The carrier nature in doped semiconductors is complicated because of interactions between the host lattice and impurity states associated with the dopant. Consider the induced oscillations of a free electron resulting from an external electromagnetic wave. The equation of motion for the displacement of the electron is:

\[
m_0 \frac{d^2 \vec{r}}{dt^2} + m_0 \gamma \frac{d \vec{r}}{dt} = -e \vec{E}
\]  

(2.14)

Notice that this is the equation of motion used to describe the displacement of a Lorentzian oscillator (2.3) without the third term on the left hand side. This is the result of the absence of a restoring force.

The same logical progression used with the Lorentz model is applied here to retrieve the dielectric function, which is given as:

\[
\varepsilon = 1 + \frac{\omega_p^2}{\omega^2 - i\gamma\omega}
\]  

(2.15)

Under the Drude model, \( \omega_p \) represents the plasma frequency of the free electron gas.

This can then be separated into its real (\( \varepsilon_1 \)) and imaginary (\( \varepsilon_2 \)) portions to yield:

\[
\varepsilon_1 = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2}
\]  

(2.16)

\[
\varepsilon_2 = \frac{\omega_p^2 \gamma}{\omega(\omega^2 + \gamma^2)}
\]  

(2.17)
As with the Lorentz oscillator model, the Drude model can be used to describe real metals. Real metals and semiconductors, however, are complex systems which are assumed to have many oscillators of all three varieties described so far in this chapter. A more complete description can be obtained with the sum of a Drude oscillator and several Lorentz oscillators (which is known as the Drude-Lorentz model) as illustrated by the following equation [26]:

\[ \varepsilon = \varepsilon_\infty - \frac{\omega_p^2}{\left(\omega^2 - i\gamma\omega\right)} + \sum_j \frac{\omega_{pj}^2}{\left(\omega_{0j}^2 - \omega^2 - i\gamma_{j}\omega\right)} \]  

(2.18)

### 2.1.3 Reflection

Previously the complex dielectric function \( \varepsilon \) was described as it pertains to the atomic oscillator models. The complex dielectric function of a solid can be found through normal incident reflectivity measurements. To illustrate the connection between reflectance and the complex dielectric function it is convenient to introduce a complex index of refraction \( \tilde{N} \), as described in equation 2.19, with \( n \) the real part of the complex index of refraction and \( k \) the extinction coefficient.

\[ \tilde{N} = n + ik = \sqrt{\varepsilon} \]  

(2.19)

The complex index of refraction allows us to relate the dielectric function to the propagation of electromagnetic waves in the following manner:

\[ \vec{E}(z, t) = E_0 e^{i(\tilde{N}kz - \omega t)} \]  

(2.20)

where \( E_0 \) is the amplitude of the wave, \( z \) is the direction of propagation, \( \kappa \) is the wave vector, and \( \omega \) is the angular frequency. The wave vector satisfies the following relations:

\[ \kappa = \frac{2\pi}{\lambda} = \frac{\omega}{v} = \frac{\omega}{c} \]  

(2.21)

Here, \( \lambda \) is the wavelength and \( v \) is the velocity of the travelling wave in the medium. Making
substitutions from equations 2.19 and 2.21 into 2.20, the propagating electric field now becomes:

$$\vec{E}(\vec{r}, t) = E_0 e^{-i(\vec{k} \cdot \vec{r})} e^{i(\omega \varepsilon_2 z - \omega t)}$$  \hspace{1cm} (2.22)

From this equation, it becomes apparent that the role of $k$ is to attenuate the wave as it travels into the material.

Recall that the complex dielectric function can be broken into its real and imaginary parts, $\varepsilon_1$ and $\varepsilon_2$. Using the relation shown in equation 2.19, it can be seen that:

$$\bar{\varepsilon} = (n + ik)^2$$  \hspace{1cm} (2.23)

From which equations 2.24 and 2.25 can be discerned immediately.

$$\varepsilon_1 = n^2 - k^2$$  \hspace{1cm} (2.24)

$$\varepsilon_2 = 2nk$$  \hspace{1cm} (2.25)

Maxwell's equations along with the appropriate boundary conditions result in the reflectance in terms of the refractive index and the extinction coefficient [26, 27]. Normal incidence reflection is then given by:

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$  \hspace{1cm} (2.26)

Solving equations 2.24 and 2.25 for $n$ and $k$ we can see that the reflection at normal incidence is intimately related to the complex dielectric function, as evidenced by equations 2.27 and 2.28.

$$n = \sqrt{\frac{1}{2} \left( \varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1 \right)}$$  \hspace{1cm} (2.27)

$$k = \sqrt{\frac{1}{2} \left( \varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1 \right)}$$  \hspace{1cm} (2.28)
2.1.4 Kramers Kronig Relations

The models discussed previously can be used to describe the optical response functions, through which the phenomenon of dispersion is understood. These response functions were assumed to be of a complex nature, and it was shown that the real and imaginary parts of these parameters are intimately connected, and this is because they are derived from a single complex variable [26, 27]. The optical constants are, in actuality, linear response functions that describe the absorption (real) and change in phase (imaginary) of an electromagnetic wave as it interacts with a solid [26, 27]. In general, a complex linear response function can be defined as:

\[
\tilde{G}(\omega) = G_1(\omega) + iG_2(\omega)
\] (2.29)

where \( G_1(\omega) \) describes the dissipative processes, and \( G_2(\omega) \) describes the phase related processes. The relationship between real and imaginary parts of \( \tilde{G}(\omega) \) are given by:

\[
G_1(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega'G_2(\omega')}{(\omega'^2 - \omega^2)} d\omega'
\] (2.30)

\[
G_2(\omega) = -\frac{2}{\pi\omega} P \int_0^\infty \frac{\omega'^2G_1(\omega')}{(\omega'^2 - \omega^2)} d\omega'
\] (2.31)

Here, \( P \) represents the principal part of the integral. These integral equations are known as the Kramers-Kronig (or dispersion) relations.

These relations are of great importance, as they allow us to recover the phase-related portion of a response function, which is lost during reflectance (transmission) measurements [26, 27]. In order to recover the phase-related portion of the optical constants, there is a dispersion relation between reflectance (intensity) measurements and their corresponding phase information. Reflectance \( R(\omega) \) is a measure of the ratio between the incident and reflected intensity of light. The reflectance \( R(\omega) \), can be described by equation 2.32:

\[
R(\omega) = r^2 = \left| \frac{E_r}{E_i} \right|^2
\] (2.32)
where $E_r$ is the reflected electric field and $E_i$ is the incident field amplitude. $E_r$ and $E_i$ are connected through the complex reflectivity amplitude in the following way:

$$E_r = re^{i\theta(\omega')} E_i$$  \hspace{1cm} (2.33)

The dispersion relation which connects $R(\omega)$ and $\theta(\omega')$ is [27]:

$$\theta(\omega) = \frac{\omega}{\pi} P \int_0^{\infty} \ln \left( \frac{R(\omega)}{R(\omega')} \right) \frac{d\omega'}{(\omega'^2 - \omega^2)}$$  \hspace{1cm} (2.34)

Equation 2.34 can be solved using any one of a variety of numerical integration techniques which are normally calculated using graphical software. The results of this calculation discussed herein were obtained using Simpson’s rule. Once $\theta(\omega)$ has been calculated the real and imaginary parts of the index of refraction can be obtained through the following equations;

$$n(\omega) = \frac{1 - r^2}{1 + r^2 - 2r \cos(\theta)}$$  \hspace{1cm} (2.35)

$$k(\omega) = \frac{2r \sin(\theta)}{1 + r^2 - 2r \cos(\theta)}$$  \hspace{1cm} (2.36)

Equations, 2.35 and 2.36 can then be used to obtain the real and imaginary parts of the dielectric constant as shown in equations 2.24 and 2.25.

### 2.1.5 Reflectance in Metallic Systems

 Metallic systems are unique in that they consist of a large number of free electrons (or holes in doped semiconductors). Under the Drude model, charge carriers in metallic systems act similar to how a gas atom behaves according to the kinetic theory of gases [26, 27]. In the presence of an electric field, charge carriers are accelerated between collisions. The time between collisions is known as the scattering time ($\tau = 1/\gamma$), and is characteristic of a particular scattering mechanism.

The reflectance profile of metallic systems is dominated by its plasma frequency ($\omega_p$). Figure 2.1 shows the reflectance of an undamped ($\gamma = 0$) metallic system. An implication of the Drude model
Figure 2.1: Reflectivity of an undamped free carrier gas as a function of frequency. Reproduced from [26].
Figure 2.2: Experimental reflectance of aluminum as a function of energy. The experimental data are compared to the free electron model with $\hbar \omega_p = 15\text{eV}$. The dotted curve represented no damping. The dashed line includes damping ($\tau = 1/\gamma$). Reproduced from [26].
is that the dielectric function turns from negative to positive as the frequency goes from below to above the plasma frequency [26, 27]. This results in the highly reflective nature of metals below the plasma frequency, as well as some degree of transparency beyond \( \omega_p \). Figure 2.2 illustrates that the addition of scattering results in a reduction in reflectance values (below 100%) at frequencies below \( \omega_p \).

2.1.6 Reflectance in Doped Semiconductors

It is possible to change some of the fundamental properties of a semiconductor by introducing impurities. The introduction of these impurities can result in an excess number of electrons (n-type) or holes (p-type). The Drude model is a suitable model to study the optical properties of doped semiconductors [26, 27]. Since electrons and holes are moving in valence and conduction bands, we make the assumption that the carriers behave like particles with an effective mass \( m_* \). Hence,

\[
\omega_p^2 = \frac{4\pi e^2 N}{m_*}
\]  

(2.37)

As a consequence of semiconductors containing a smaller number of carriers than metals, the plasma edge (onset of \( \omega_p \)) is shifted into the infrared spectral range.

Plasma edge behaviour is intimately connected to the carrier dynamics in doped semiconductors. It is for this reason that reflectance measurements are used to assist in making estimations of the carrier concentration and carrier effective mass. Unfortunately \( N \) and \( m_* \) cannot be distinctly identified by reflectance measurements alone, therefore Hall measurements are normally employed to separate the carrier concentration from the effective mass. Since Hall measurements directly measure the concentration of carriers while the spectral weight is a ratio of the carrier concentration to the effective mass. Therefore, using the carrier concentrations obtained by Hall measurements, it is possible to calculate the effective mass of the carrier as long as the spectral weight is known.

2.1.7 Experimental Uncertainty and Reflectance Measurements

No experiment is perfect, and reflectance spectroscopy is no exception. The largest source of uncertainty associated with determining the complex dielectric function and the complex conductivity
from reflectance measurements come from the Kramers Kronig relations. In metallic systems, such as those studied in this thesis, the reflectance approaches one as the frequency approaches zero. The difficulties associated with ensuring that $R=1$ at low frequencies (below $\omega_p$) are experimentally driven and thus require careful measurements to obtain accurate results. Fortunately, in this frequency range experimental uncertainty can be reduced by comparing the real part of the optical conductivity at zero frequency to experimentally determined DC conductivity data. At frequencies that are greater than $\omega_p$, the largest contribution to the uncertainty in reflectance measurements comes from the extrapolations used to perform the Kramers Kronig analysis. As an example, Nilsson and Munkby [28] studied the error introduced by Kramers Kronig analysis by comparing the effects of several high frequency extrapolations on a set of theoretical reflectance data. A common approach when choosing a high frequency extrapolation is to use an extrapolation in the form [28]:

$$R \propto \omega^{-s}$$

(2.38)

Figure 2.3 shows a plot of $\epsilon_2$ obtained from a set of theoretical reflectance data (solid line) as well as $\epsilon_2$ obtained by Kramers Kronig analysis with use of equation 2.38 and $s=4$ for the extrapolated regions. Nilson and Munkby examined the effect of beginning the extrapolation at several frequencies, $\omega=6$ eV, $\omega=10$ eV, $\omega=25$ eV, and $\omega=50$ eV. From figure 2.3, it can be seen that extrapolations that started at $\omega=6$ or 10 eV were not good, whereas the extrapolation which began at $\omega=50$ eV was. This example illustrates how important it is to choose the high frequency extrapolation carefully in order to minimize the error associated with a Kramers Kronig analysis.
Figure 2.3: $\varepsilon_2$ obtained from KK analysis of a theoretical set of reflectance data, which was extrapolated with $R \propto \omega^{-4}$ from 6, 10, 25, and 50 eV. Reproduced from [28].
Chapter 3

Methods

3.1 Samples

This thesis reports on the temperature dependent optical properties of Sb$_2$Te$_3$, Sb$_{1.97}$V$_{0.03}$Te$_3$, and Sb$_{1.94}$Cr$_{0.06}$Te$_3$ single crystal samples with $\vec{E} \perp$ to the c-axis. The samples were donated to Dr. D.A. Crandles by Dr. C. Uher (University of Michigan) and Dr. P. Lostak (University of Pardubice). All three samples were grown using the Bridgman method (vertical orientation), where stoichiometric amounts of Sb, Te, and TM ion, were melted together at an anealing temperature of 1003 K for 24 hours and then lowered through a temperature gradient of 400 K/5 cm at a rate of 1.3 mm/h. The samples were then subjected to microprobe analysis in order to obtain their stoichiometry. The following sections are intended to give a brief account of Fourier transform reflectance spectroscopy, how the measurements in this thesis were obtained, and the changes which were made to the cryostat in order to perform lower temperature measurements. Additionally, some difficulties associated with temperature varied measurements and a table of the various optical elements used in this work are included in the following sections.

3.1.1 Fourier Transform Spectroscopy

A fourier transform (FT) spectroscopy system can be thought of as consisting of four main components which are: the interferometer (and optical elements); the source; the detector; and a computer. The basic design of a Michelson interferometer, illustrated in figure 3.1, consists of a moving mirror, a fixed mirror, and a beamsplitter.

As source radiation enters the interferometer the beam splitter reflects approximately half the incident radiation and transmits the rest. Therefore the source radiation is now separated into two paths. When one path is changed in length, via the moving mirror, the packets of radiation now
Figure 3.1: A schematic view of a simple Michelson interferometer. Reproduced from [30].
take different amounts of time to reach the detector. Due to the temporal coherence properties of light, variations in path length allow for interference between the two packets at the detector. The intensity of the radiation which reaches the detector is recorded as a function of mirror position, which is called an interferogram. It can be shown that the Fourier transform of the interferogram results in a power spectrum which is the intensity as a function of frequency. While calculus offers a concise illustration of the transform from the time domain to the frequency domain, a heuristic approach will be offered here. Consider a coherent source consisting of one wavelength as it travels through the Michelson interferometer. As the moving mirror is displaced, varying degrees of interference occur between the two paths, ranging from in phase constructive interference to out of phase destructive interference. The outcome is a sinusoidal graph which depicts intensity as a function of time. Hence, the interferogram for a monochromatic source looks is a sine or cosine function. The function of a Fourier transform is to find the frequency of the interferogram. The Fourier transform of an interferogram produced by a monochromatic source is a delta function power spectrum graph. Further, a spectrum passing through the Michelson interferometer would yield an interferogram consisting of the sum of each sinusoidal function produced by the spectrum. The Fourier transform then acts as a search function, picking out each of the frequencies and their corresponding intensities resulting in a power spectrum covering the spectral range. It is important to note that the power spectrum is not a direct measure of reflectance since it is also affected by the emission spectrum of the source, the sensitivity of the detector, the transmission of various windows in the light path, as well as sample surface irregularities.

3.1.2 Finite Resolution Effects

In the previous section it was mentioned that the Fourier transform of a sine or cosine graph is a delta function. However, FT spectroscopy is a technique that uses a broadband source. Since broadband sources provide a continuum of light, it is immediately evident that two problems arise: 1. Sampling a large number of points leads to increased memory requirements and longer Fourier transform times, and 2. Sampling a larger number of points infers sampling narrower spacing between wavenumbers (wavelengths). This is a physical limitation of FT spectroscopy systems as
the path difference provide by the moving mirror is finite.

To illustrate this, let us consider a doublet with a spacing of 0.1 cm\(^{-1}\). In order to go through one complete beat frequency we would require a minimum path difference of \(\Delta \nu^{-1}\) which implies a minimum path difference of 10 cm. This is because of the inverse relationship between resolution and the path difference created by the moving mirror. As a comparison, the Bruker IFS 66 V/s spectrometer used to perform this work has a maximum resolution of 0.25 cm\(^{-1}\), which corresponds to a 4 cm displacement of the moving mirror.

### 3.1.3 Sampling

A consequence of measuring a broadband source using an interferometer is that radiation with frequencies far outside the range of interest gets folded back into the spectrum as spurious noise. This effect is known as aliasing [31] and can be corrected by filtering and proper sampling. The Nyquist sampling criteria says that all frequencies within a band should be sampled twice per interval [31] in order to be unambiguously sampled. This means that if the sampling frequency is \(2F\) then only waves with frequencies below \(F\) will be sampled correctly. According to Nyquist, one can avoid aliasing effects by requiring \(\nu_{\text{max}}-\nu_{\text{min}}\) to be larger than \(2\nu_{\text{max}}\) [31]. In addition to proper sampling, optical and electronic filters are normally used to reduce sources of unwanted frequencies.

The number of points \((N_s)\) required to be unambiguously sampled for a given frequency band, \(\nu_{\text{max}}-\nu_{\text{min}}\), with a resolution of \(\delta \nu\) is given by;

\[
N_s = \frac{2(\nu_{\text{max}} - \nu_{\text{min}})}{\delta \nu} \tag{3.1}
\]

One can see that a spectroscopist must be willing to make trade-offs, or the number of points required to retrieve viable data will quickly exceed the amount of memory allocated to the analog to digital converter. An experimentalist must then choose between the resolution of their measurements and the bandwidth they are measuring. As an example, taking measurements as the moving mirror moves both forward and backwards corrects any anti-symmetry within the interferogram [30], but this increases \(N_s\) by a factor of two!
### Table 3.1: List of various optical elements and sources used in this work to obtain the reflectance measurements over a broad range of frequencies.

<table>
<thead>
<tr>
<th>Material</th>
<th>Spectral Range</th>
<th>Detector</th>
<th>Source</th>
<th>Beam Splitter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Sb_2Te_3$</td>
<td>FIR (50-600 cm$^{-1}$)</td>
<td>Bolometer</td>
<td>SiC globar SiC globar W bulb</td>
<td>Mylar (50μm) KBr CaF$_2$</td>
</tr>
<tr>
<td></td>
<td>MIR(500-6000 cm$^{-1}$)</td>
<td>MCT</td>
<td>SiC globar W bulb</td>
<td>KBr CaF$_2$</td>
</tr>
<tr>
<td></td>
<td>NIR (5000-11000 cm$^{-1}$)</td>
<td>MCT</td>
<td>W bulb</td>
<td>CaF$_2$</td>
</tr>
<tr>
<td>$Sb_{1.94}Cr_{0.06}Te_3$</td>
<td>FIR (50-600 cm$^{-1}$)</td>
<td>Bolometer</td>
<td>SiC globar SiC globar W bulb</td>
<td>Mylar (50μm) KBr CaF$_2$</td>
</tr>
<tr>
<td></td>
<td>MIR(500-6000 cm$^{-1}$)</td>
<td>MCT</td>
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</tr>
<tr>
<td></td>
<td>NIR (5000-11000 cm$^{-1}$)</td>
<td>MCT</td>
<td>W bulb</td>
<td>CaF$_2$</td>
</tr>
<tr>
<td>$Sb_{1.97}V_{0.03}Te_3$</td>
<td>FIR (50-600 cm$^{-1}$)</td>
<td>Bolometer</td>
<td>SiC globar SiC globar W bulb</td>
<td>Mylar (50μm) KBr CaF$_2$</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>NIR (5000-11000 cm$^{-1}$)</td>
<td>MCT</td>
<td>W bulb</td>
<td>CaF$_2$</td>
</tr>
<tr>
<td></td>
<td>UV-VIS (9000-50000 cm$^{-1}$)</td>
<td>Mc Master</td>
<td>Mc Master</td>
<td>Mc Master</td>
</tr>
</tbody>
</table>

### 3.2 Experimental Procedure

In order to measure the response of a material fully, it is important to measure the widest band of frequencies possible. To accomplish this, a variety of detectors, beamsplitters, and sources were used in this work. Table 3.1 specifies the optical elements used in completing this work.

In order to obtain the absolute reflectance data, a piece of software called OPUS was used to manipulate the optical spectra. To the user, OPUS treats spectra as common variables and takes input commands the way a calculator does. Therefore, to take the ratio of two spectra the user need only select the desired spectra (quotient), then the function (e.g. division), followed by the second spectrum (divisor), and a click of the “equals” button to complete the calculation.

In order to get the final reflectance measurement, several ratios were calculated. The ratio of the power spectrum of the sample, $I_s$, and the power spectrum of the reference mirror, $I_{ref}$, was calculated upon completion of phase one. Once phase two was complete the gold spectra, $I_{Au}$, was divided by the steel reference mirror, $I_{ref'}$. Gold was chosen because of its uniform reflectivity of about 98.5 percent throughout the IR, allowing for an accurate estimate for the absolute reflectance of a sample. The absolute reflectance was then calculated in the following manner:

$$ R_{Abs} = \frac{I_s}{I_{ref'}} \frac{I_{ref}}{I_{Au}} $$

(3.2)

Note that if there is no variation in the detectors or the source, $I_{ref}/I_{ref'}=1$. 

3.2.1 Temperature Variation

In designing a cryogenic environment it is necessary to simultaneously isolate the sample from its environment, and to have a powerful cooling source. The design employed in this work consisted of a He-4 flow-through system (Figure 3.2), whereby cooling provided by pressurized liquid He, cooled a cold-finger which was connected to the sample holder (Figure 3.3) through flexible metal conduits (Figures 3.4 and 3.5). The sample holder was suspended from the rotation assembly in a high vacuum environment in order to facilitate the in-situ evaporation and provide thermal insulation. Copper was the original candidate for the design of these thermal conduits because it is one of the few metals that maintain its ductility at low temperatures, in addition to excellent thermal conductivity. The flexible nature of the copper braids was necessary to allow for rotation of the sample holder, where the sample and reference were positioned 90 degrees from each other (Figure 3.4). This meant that by rotating the assembly by 90 degrees the reference would replace the sample, while sharing a nearly identical optical path.

Insulating glass rods were used to separate the sample holder from the rotation assembly (Figure 3.3). The glass rods had hemispherical ends, which limited thermal contact between the copper sample holder and themselves. The rotation assembly was connected to the sample holder by a hollow plastic bolt and nuts, which pressed the glass rods against the sample holder, holding them in place. Dr. Timusk (McMaster) was the originator of this design concept which he shared through discussions with Dr. Crandles.

In the aforementioned configuration, the lowest achievable temperature was 45 K [32]; however, the materials used in this study have transition temperatures below 23 K, which made it necessary to improve the temperature limits of the pre-existing system. The goal was to reach 10 K, a temperature below the onset of the ferromagnetic state in either of the materials that were to be investigated. Several options were available to enhance the low temperature limit of the system, which included: improving the insulation; changing the material for the thermal conduit; and/or improving the thermal contact between the conduit and the sample holder.
Figure 3.2: Cryostat with flow-through liquid He input. Thermocouple gauges were used to check the temperature of the sample as well as the temperature of the liquid He bayonet.
Figure 3.3: The sample holder was coupled to a cold-finger cryostat with flow-through liquid He input by a flexible metal conduit (Ag or Cu). Thermocouple gauges were used to check the temperature of the sample as well as the temperature of the liquid He bayonet.
Figure 3.4: Simplified optical path. The sample and reference are mounted at 90 degrees from one another. A stepper motor rotates the sample holder between measurements so that the reference and the sample experience the same optical path.
Figure 3.5: Top: Images of the plates used to secure the silver conduit. Bottom: Ag conduit rotated in two positions: the left shows the mirror in the optical path, and right image shows the sample in the optical path.
Figure 3.6: The thermal conductivity of the specimens of copper, silver and gold. Ag1 samples are 99 percent pure Ag wires. Ag2 samples polycrystalline annealed samples. The precise purity of Ag2 samples was not mentioned in [33]. Reproduced from [33].
Because the low temperature thermal conductivity of Ag was better than that of copper (Figure 3.6), and since this was true at high temperatures (300 K, not shown in graph) as well, Ag was chosen to replace the copper as the thermal conduit. Instead of Ag braided lines, 99.999 percent pure silver sheets were used in order to increase the area of thermal contact at the sheet/sample holder and sheet/cold finger interfaces. Figure 3.5 illustrates how the Ag sheets were fixed to both the sample holder and the cold finger. On the cold finger side, a copper disk was machined to compress open flaps of Ag against the cold finger. Six layers of Ag were used to conduct heat away from the sample. The stack of sheets was separated such that three sheets were bent to each side of the copper disk and a small amount of thermal paste was applied between each sheet, and to the cold finger, to ensure optimal thermal contact.

Attaching the silver sheets to the sample holder was more challenging. It required a modular design as the thermal conduit needed to be removed after each experiment to change the sample. This was accomplished by designing a type of clamp, which was composed of a plate of silver with dimension of 3 X 2 X 0.2 cm$^3$, and a copper back-plate of the same dimensions (Figure 3.5). The copper plates were machined with beveled slits cut out of them to allow for penetration of the silver sheets. Once the copper back-plate was threaded onto the stack of silver sheets, the Ag plate was pressed on top and then screwed in place. This resulted in a sandwich of Ag sheets and thermal paste pressed between the two plates. The sandwich could then be attached to the sample holder by two 1mm hex screws. These changes increased the thermal contact on both sides of the thermal conduit while maintaining the ability to rotate the sample. As a result, the improved system was able to lower the temperature to 20K. In order to reach lower temperatures with the current design, it is suspected that improved radiation shielding will be required.
Chapter 4

Results and Discussion

4.1 Reflectance Measurements

The results of temperature dependent, mid-infrared reflectance measurements of Cr doped and V doped antimony telluride as well as $Sb_2Te_3$ are illustrated in Figures 4.1, 4.2, 4.3. The reflectance measurements for this thesis were taken in 25 degree increments from 20 K to 300 K. It was the goal of this work to take reflectance measurements below the transition temperatures of these materials, but lowering the temperature below 20 K proved to be difficult without additional modifications to the experimental apparatus. Since below $T_c$ temperatures were not achieved, a group from McMaster University was asked to assist with some low temperature measurements of the Vanadium sample. The reflectance shown in Figure 4.4 illustrates that there is very little difference in the reflectance of $Sb_{1.97}V_{0.03}Te_3$, from 20 K to 12 K.

All three reflectance curves show a pronounced plasma edge that softens with decreasing temperature. The plasma edge is associated with free carrier absorption, and is the predominant feature throughout the spectral range covered by the measurements used in this thesis. A similar trend was observed in the isostructural $Bi_2Te_3$ by Thomas et. al. [34](Figure 4.5).

4.1.1 Extrapolated Reflectance Data for KK analysis

Since it is impossible to measure the entire spectral range, extrapolations were made in order to extend both the high and low portions of the frequency range. In the low frequency range (below 100 cm$^{-1}$), it is normally possible to use what is called the Hagen-Rubens approximation for reflectance in metals. The Hagen-Rubens approximation is obtained by taking the low frequency limit of the Drude oscillator. However, this extrapolation neglected the phonon which was visible near 60 cm$^{-1}$. Instead, a modified Drude model was used with a Lorentz oscillator added in to emulate
Figure 4.1: Reflectance of $Sb_2Te_3$ as a function of wavenumber (cm$^{-1}$).
Figure 4.2: Reflectance of $Sb_{1.97}V_{0.03}Te_3$ as a function of wavenumber (cm$^{-1}$).
Figure 4.3: Reflectance of $Sb_{1.94}Cr_{0.06}Te_3$ as a function of wavenumber ($cm^{-1}$).
Figure 4.4: Reflectance of $Sb_{1.97}V_{0.03}Te_3$ as a function of wavenumber. Reflectance data was obtained at 20 K and 12 K by Jesse Hall at McMaster University. Notice the similarity in the plasma edge at 50 K and 12 K.
Chapter 4. Results and Discussion

Figure 4.5: Reflectance measurements of $\text{Bi}_2\text{Te}_3$ as a function of temperature. Reproduced from [34]. Notice the plasma edge which moves to lower energy with increasing temperature.
Chapter 4. Results and Discussion

Figure 4.6: Far-infrared reflectance of $Sb_{1.97}V_{0.03}Te_3$ (black) with a comparison of a Drude model (red) versus a Drude-Lorentz model (green).

The presence of the phonon in these spectra (Figure 4.6). The far-infrared optical properties of Cr and V doped antimony telluride were investigated by A. Madubounu [32], who demonstrated the influence of an optical phonon near 60 cm$^{-1}$ that softens with decreasing temperature, in agreement with our reflectance measurements of the far infrared as shown in figures 4.7 and 4.8.

Reflectance measurements from 800 cm$^{-1}$ to 88000 cm$^{-1}$ obtained by Harbeke and Greenaway [35] (Figure 4.9) on $Bi_2Te_3$, provided valuable information regarding the profile of the reflectance at high frequency. Their work demonstrated a large dip in reflectance near 50000 cm$^{-1}$, which was included in the extrapolation. Additionally, room temperature reflectance measurements of $Sb_{1.97}V_{0.03}Te_3$ (obtained by McMaster University) were used to adjust the levels of reflectance for the
Figure 4.7: Far infrared reflectance of $Sb_{1.97}V_{0.03}Te_3$ as a function of wavenumber ($cm^{-1}$). Notice the phonon at $\approx 60$ cm$^{-1}$ which moves to lower energy with decreasing temperature.
Figure 4.8: Far infrared reflectance of $Sb_{1.94}Cr_{0.06}Te_{3}$ as a function of wavenumber (cm$^{-1}$). Notice the phonon at $\approx 60$ cm$^{-1}$ which moves to lower energy with decreasing temperature.
Figure 4.9: Room temperature reflectance measurements of $Bi_2Te_3$ as a function of energy, where $1\text{meV} = 8.064\text{ cm}^{-1}$. Reproduced from [35].

spectral range between $15000\text{ cm}^{-1}$ and $45000\text{ cm}^{-1}$. The resulting extrapolation is demonstrated in Figure 4.10, and extends from $10000\text{ cm}^{-1}$ to $200000\text{ cm}^{-1}$. It was assumed that the reflectance in the high energy region was the same for all three samples and was temperature independent. These assumptions were considered to be reasonable given that these regions are far removed from the plasma frequency and therefore contribute less to the KK integral.

4.1.2 Kramers-Kronig Optical Conductivity

One advantage of the Kramers-Kronig relations is that they are a model-independent way to extract the optical constants from reflectance measurements. One trade off is that KK analysis enhances
Chapter 4. Results and Discussion

Figure 4.10: Reflectance of $Sb_{1.94}Cr_{0.06}Te_3$ at 300 K including extrapolated region. In this plot, our reflectance data is shown from 50 cm$^{-1}$ to 10000 cm$^{-1}$, while reflectance data from 10000 cm$^{-1}$ to 40000 cm$^{-1}$ was taken by Jesse Hall at McMaster University for the $Sb_{1.97}V_{0.03}Te_3$ sample. The extrapolated reflectance region covers the frequency range from 40000 cm$^{-1}$ to 200000 cm$^{-1}$. 
Figure 4.11: The real part of the conductivity for $Sb_2Te_3$ as a function of wavenumber. Note that 8064 cm$^{-1}$ corresponds to a photon energy of 1 eV.

the noise associated with reflectance measurements. KK analysis was applied to the sets of reflectance shown in section 4.1 in order to explore the temperature related effects of the frequency dependent conductivity. The real part of the optical conductivity for $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$ are illustrated in Figures, 4.11, 4.12, 4.13, respectively.

Note the similar structure in all three figures. The real part of the optical conductivity appears to contain contributions from both intraband and interband transitions, which we can distinguish. The intraband or free carrier contributions to the real part of the optical conductivity are those near $\omega = 0$ to $\omega \approx E_{gap}$. The energy gap of Sb$_2$Te$_3$ occurs very near 2000 cm$^{-1}$ or 0.25 eV. At room temperature, the intraband contributions for all three samples appear to come from frequencies
Figure 4.12: The real part of the conductivity for $Sb_{1.97}V_{0.03}Te_3$ as a function of wavenumber. Note that 8064 cm$^{-1}$ corresponds to a photon energy of 1 eV.
below $\approx 2000$ cm$^{-1}$, which marks the onset of the interband absorption. As the temperature decreases, the intraband portion begins to narrow as the peak is shown to increase as the frequency approaches zero. This is consistent with DC resistivity measurements which demonstrate increasing conductivity as temperature decreases. Figure 4.13 illustrates the beginning of interband absorption which is denoted by arrows and is near 2000 cm$^{-1}$ ($\approx 0.25$ eV). In semiconductors it is common for the energy gap to widen at lower temperatures. This is reflected by the fact that interband absorption begins closer to 2300 cm$^{-1}$ at low temperature for both the pure sample and the Cr doped sample, as illustrated in figures, 4.11 and 4.13. This trend is also apparent in the V doped sample as illustrated in figure 4.12.
4.1.3 Scattering

The reflectance of $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$ was measured at various temperatures to ultimately obtain their respective temperature dependent scattering rates. Note the narrowing of the intraband contribution as temperature decreases in figures, 4.11, 4.12, and 4.13. Figure 4.14 illustrates the relationship between the real part of the conductivity and the scattering rate for a simple Drude dielectric function. Similar scattering rates of the carriers can be extracted from either Drude-Lorentz fits of the reflectance (Figure 4.15) or directly from the full width at half maximum (FWHM) of the intraband contribution to the real part of the optical conductivity (Figures 4.14 and 4.16).

The scattering rates are shown in Figure 4.16, and illustrate temperature dependent scattering behavior which is similar across all the samples. Madubounu [32], also investigated the scattering
Figure 4.15: Scattering rates obtained through fits of a Drude-Lorentz model. Red solid circles represent measurements taken at McMaster. Note the similarity to Figure 4.16.
Figure 4.16: Temperature dependence of the scattering rate obtained by the FWHM of the optical conductivity. The scattering rate for $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$. Slopes obtained by the linear fits of $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$ were found to be $0.49 \pm 0.04$ cm$^{-1}$K$^{-1}$, $0.51 \pm 0.04$ cm$^{-1}$K$^{-1}$, and $0.49 \pm 0.03$ cm$^{-1}$K$^{-1}$ respectively.

Rates for these samples and his results are in agreement with those found here.

A plot of the room temperature reflectance (Figure 4.17) of these samples demonstrates that they have very similar carrier concentrations. Lostak et. al. [37], investigated the room temperature mid-infrared optical properties of $Sb_{2-x}Cr_xTe_3$. They claim that the shared minima in the reflectance profile (Figure 4.18) between samples with different concentrations of Cr is evidence that the number of holes remains constant with doping. Unfortunately this does not agree with results obtained by Hall measurements which show that the number of carriers is different in $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$, as well as between $Sb_{2-x}Cr_xTe_3$ samples. Other TM doped $Sb_2Te_3$ have been studied. In fact, the plasma edge in $Sb_{2-x}Fe_xTe_3$ hardens (moves to higher
Figure 4.17: Room temperature reflectance for $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$. 
energy) as the concentration of Fe was increased (Figure 4.19), while the plasma edge softens with the addition of In in $Sb_{2-x}In_xTe_3$ samples (Figure 4.20). Since the behavior of the plasma edge is linked to the behavior of the carriers, these studies illustrate that the carrier concentration of these materials is a complicated function of the dopant type and concentration.

Temperature dependent scattering rates for $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$ demonstrate behavior which is similar to their resistivity. According to Matthiessen’s rule each scattering mechanism can be accounted for independently. Therefore, the total scattering rate is the sum of the rates due to each scattering mechanism [40]. Figure 4.21 illustrates the theoretical contribution to the overall scattering rate as a function of temperature. The dotted plots represent the temperature dependent behavior of three different contributions; phonon scattering, static scattering, and magnetic scattering.
Chapter 4. Results and Discussion

Figure 4.19: Room temperature mid-infrared reflectance of \( Sb_{2-x}Fe_xTe_3 \). The samples are numbered according to the concentration of Fe in the lattice, where 1. \( x=0 \), 2. \( x=0.002 \), 3. \( x=0.005 \), 6. \( x=0.02 \), and 7. \( x=0.06 \) respectively.
Figure 4.20: Room temperature mid-infrared reflectance of $Sb_{2-x}In_xTe_3$. The samples are numbered according to the concentration of In in the lattice, where 1. $x=0$, 2. $x=0.05$, 3. $x=0.098$, 4. $x=0.22$, 5. $x=0.29$, and 6. $x=0.41$, respectively. Reproduced from [39].
Figure 4.21: Temperature dependent scattering rate for, static disorder scattering $\rho_0$, phonon scattering $\rho_{ph}$, and magnetic scattering $\rho_{sd}$. Reproduced from [41].
Carriers in a semiconductor can be scattered by a variety of interactions. Scattering can occur as a result of optical and acoustic phonons, ionized impurities, neutral defects, surface and interfaces, as well as with other carriers (scattering between holes and electrons) [42]. The Lorentz model was discussed in chapter 2, in which the scattering rate was depicted as the inverse of the damping constant in equation 2.3. By end of chapter 2 it was shown how the scattering rate is related to reflectance measurements through the dielectric function. Influential changes in the scattering mechanism are normally depicted in variations in the depth of the reflectance minima. Figures 4.1, 4.2, 4.3 show obvious differences in the depth of reflectance minima at different temperatures and also between the samples. Unkelbach et. al. [45] suggest that the main scattering mechanism in the isomorphic crystal Bi₂Te₃ is acoustic phonon scattering, while by Horak et. al. [22] suggest that there is likely a mixed scattering mechanism at play. Figure 4.16 shows a linear dependence of the scattering rate with temperature which is consistent with contributions from phonon and impurity scattering. In addition, it is difficult to see evidence of magnetic scattering in these samples. As illustrated in Figure 4.21, magnetic scattering is characterized by a steep decline in the scattering rate at temperatures lower than T_c. This was not seen in scattering rates obtained in this work.

It is interesting to note that these materials have similar carrier concentrations but still appear to have very different degrees of static scattering. This would make sense if each sample had a uniquely predominant type of crystal defect. For example, it is well known that antisite defects are the dominant defect in antimony telluride; however, Horak et al. [22] claim that the dominant form of defect changes in Sb₂₋ₓCrₓTe₃ from antisite driven at low concentrations of Cr (x<0.014) to tellurium vacancies at higher Cr (x>0.014) concentrations. This could mean that the sample of Sb₁.₉₄Cr₀.₀₆Te₃ has tellurium vacancies as the predominant defect. Therefore, it is possible that the defect structure in antimony telluride is highly sensitive to dopants which results in changes in the scattering rate.

In the case of the vanadium doped sample, the scattering rate was found to be higher than that of the Cr doped sample and Sb₂Te₃. In addition, the vanadium sample has a higher T_c than the Cr doped sample even though it is doped with half the concentration of magnetic impurity and despite its smaller magnetic moment. In the paramagnetic state magnetic impurity scattering is proportional to S(S+1) [41]. In this case, however, the Cr doped samples, which have a larger
moment exhibit lower scattering rates at all temperatures than the Vanadium sample.

Figure 4.22 shows the change of the plasma frequency as a function of temperature and is compared to the change in the Hall coefficient as a function of temperature. Since the square of plasma frequency is proportional to the number of carriers, a plot like figure 4.22 illustrates the difference between carrier concentrations measured by ordinary Hall measurements and those obtained optically. Note similarity in slope at higher temperatures between the plasma frequency as a function of temperature and the Hall coefficient. The optical plasma edge measurements are not affected by magnetization whereas \( R_H \) measurements are.

Two pieces of evidence suggest that magnetic scattering is not predominant in these materials. Firstly, the scattering rate of \( \text{Sb}_{1.97}\text{V}_{0.03}\text{Te}_3 \) is larger than the scattering rate in \( \text{Sb}_{1.94}\text{Cr}_{0.06}\text{Te}_3 \). If magnetic scattering were predominant one would expect \( \text{Sb}_{1.94}\text{Cr}_{0.06}\text{Te}_3 \) to have larger scattering rates because the spin of Cr is larger, and because the density of the magnetic defects is larger. Secondly, as shown in Figure 4.21 the theoretical contribution of the spin scattering falls off sharply below \( T_c \). This can not be seen in Figures 4.16 or 4.15.

Though low temperature measurements of the scattering rate did not show classic evidence of a magnetic transition (ie, a strong drop in the scattering rate below \( T_c \)), this does not mean that magnetic scattering is not present in these samples. It is more likely that magnetic scattering only provides a small contribution to the overall scattering experienced by the conduction electrons in these samples like those exhibited by AuFe spin glasses [43](Figure 4.23). Further investigation would be needed to answer this question more thoroughly, and could be investigated using magneto-optical spectroscopy.

### 4.1.4 Conclusion

The real part of the optical conductivity was suggested to consist of intraband transitions at frequencies below the energy gap of the material and involved interband transitions at frequencies above the energy gap. The real conductivity of the samples shows a widening of the band gap as the temperature decreases. The Cr sample shows two interband transitions that seem to harden with increasing temperature.
Figure 4.22: The temperature plasma frequency ($\omega_p^2$) are plotted with the inverse Hall coefficient ($1/R_H$) as a function of temperature. Open circles plot carrier concentrations measured by the Hall Effect ($\sigma \propto 1/R_H$). Solid circles plot carrier concentrations measured optically ($\sigma \propto \omega_p^2$). Purple: McMaster $Sb_{1.97}V_{0.03}Te_3$ measurements. Red: Brock $Sb_{1.97}V_{0.03}Te_3$ measurements.
Figure 4.23: (a) Temperature dependent AC and DC resistivity of Au and AuFe. The solid dots refer to AC resistivity of AuFe films (6 at. percent Fe) measured at 1.05 THz. The dashed line correspond to DC resistivity for bulk AuFe with 5 atomic percent of Fe. The solid line refers to the DC resistivity of bulk Au. (b) The temperature dependent magnetic contribution to the AC resistivity shown by the open circles; for comparison the AC resistivity of the AuFe film is shown as solid dots. Reproduced from [43].
Chapter 4. Results and Discussion

Figure 4.24: Concentration of Cr across a boule of $Sb_{1.96}Cr_{0.04}Te_3$. Reproduced from [37].

The effective mass parameter proved to be difficult to accurately obtain as it requires knowledge of the carrier concentration of the actual sample measured. While there is full confidence in the accuracy of the Hall measurements obtained by Dyck et al. [20, 25] shown in Figures 1.4 and 1.7, it was difficult to accurately associate our samples to the appropriate Hall data. This difficulty occurred as a result of the way the crystal develops during the crystal growth process. Since the concentration of the TM dopant varies across the boule and it was routine to peel off layers of the samples in between each set of optical measurements to reveal a clean surface.

An example of the concentration gradient across a boule of Cr doped antimony telluride is shown in figure 4.24. It is estimated that 0.2 to 0.5 cm of each material was stripped away during the many reflectance measurements on our samples made during the course of this work. Since the change in percent by weight of Cr across the boule (figure 4.24) is approximately 0.2 per cm, it is estimated that the uncertainty in the concentration of dopnant concentration of these samples could be as small as 0.003 mol to as large as 0.006 mol, depending on how much material stripped off of the
sample during the course of the study.

In conclusion, the real part of the conductivity and scattering rate for $Sb_2Te_3$, $Sb_{1.94}Cr_{0.06}Te_3$, and $Sb_{1.97}V_{0.03}Te_3$ samples shows intraband and interband absorption features. Furthermore, typical of semiconductors, evidence of band gap widening with decreasing temperature was observed. The scattering rate was obtained as a function of temperature and shows that phonon scattering and static scattering dominate the overall scattering rate of the samples. The difference in scattering rate between the samples could possibly be due to the difference in the dominant form of defect (static disorder) associated to each of the samples.
Bibliography


