Thermoelectric Properties of Bi$_2$Se$_3$ and Copper-Nickel Alloy

DISSERTATION

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By

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Abstract

Thermoelectric effects can be used for fast response temperature sensing, active solid state cooling, and solid state electricity generation from heat. It is favorable to have a material with large thermopower $\alpha$, high electrical conductivity $\sigma$, and low thermal conductivity $\kappa$. The criterion for good thermoelectric materials that have a high energy conversion efficiency is the dimensionless thermoelectric figure of merit, $ZT = \frac{\alpha^2 \sigma}{\kappa} T$. A $ZT$ value of 1 is the current commercialization criterion.

Typically, good thermoelectric materials are semiconductors with large electron effective masses. Doping is a common way to manipulate carrier concentration within a semiconductor class to optimize thermoelectric properties. $\text{Bi}_2\text{Te}_3$ is the paradigm for the class of $(\text{Bi}_{1-x}\text{Sb}_x)_{2}(\text{Te}_{1-y}\text{Se}_y)_3$ thermoelectric alloys that have been successfully commercialized. The $ZT$ values for this class are of order 1. Recently, theorists have predicted that p-type $\text{Bi}_2\text{Se}_3$ could have comparable $ZT$ to the $\text{Bi}_2\text{Te}_3$, but without the expensive element tellurium. In this dissertation, p-type $\text{Bi}_2\text{Se}_3$ was prepared by Bi substitution doping with Ca, Mn, and Pb. Then two independent experimental methods, the transport properties and the Shubnikov–de Hass measurements, were used to establish the effective mass of $\text{Bi}_2\text{Se}_3$. The results show that the effective mass of the $\text{Bi}_2\text{Se}_3$ valence band is lower than theorists have calculated. This work represents the first
experimental study of the valence band of Bi$_2$Se$_3$, and concludes that p-type Bi$_2$Se$_3$ does not have a large enough effective mass to have good thermoelectric properties.

In the second part of this dissertation, thermoelectric metallic alloys are discussed. Metals are the materials used in temperature-sensing, thermocouple applications. An accurate thermocouple requires metal alloys with large thermopower. Copper-nickel alloys have been widely used as the n-type leg of thermocouples under the name “constantan” due to their large thermopower. For this dissertation, a nonmetal element, sulfur, is introduced in the copper-nickel alloy system to improve thermoelectric properties. Preliminary results showing promising improvement of the thermoelectric properties in the copper-nickel alloy system is presented.

This dissertation consists of three chapters and two appendices. Chapter 1 is a review of the fundamentals of thermoelectricity and its application. A literature review is presented on Bi$_2$Se$_3$-related semiconductor materials and thermoelectric metallic metals. Experimental methods used in later chapters are also introduced. Chapter 2 is an experimental study of the valence band of Bi$_2$Se$_3$. This is the first detailed valence band mapping of Bi$_2$Se$_3$. Chapter 3 reports preliminary data of sulfur as a dopant in copper-nickel alloys that improves the thermoelectric properties of the alloy. Appendix A describes a novel thermoelectric combustion chamber design, this design combines the functionalities of combustion chamber, heat exchanger, and thermoelectric generator. Appendix B is a theoretical treatment of the Mott relation, in which a new analytical approximation is given that has better accuracy over a wide range of materials.
Dedication

This document is dedicated to my father, Chongwen Gao, and my mother, Ping Wu.
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First of all, I would like to express my sincere gratitude to my advisor, Dr. Joseph Heremans for his excellent guidance and patience throughout my Ph.D. years. He sets a great example of a true scholar who is devoted to research. I own him his kind instructions. His acute physics sense and knowledge will always inspire me.

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Publications

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Fields of Study

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Table of Contents

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

Dedication ............................................................................................................................. iv

Acknowledgments ................................................................................................................. v

Vita .......................................................................................................................................... vii

Table of Contents .................................................................................................................... ix

List of Tables .......................................................................................................................... xi

List of Figures ......................................................................................................................... xii

Chapter 1: Background of Thermoelectricity .............................................................................. 1

1.1 Introduction to Thermoelectricity ...................................................................................... 1

1.2 Applications of Thermoelectricity .................................................................................... 4

1.3 Optimizing Semiconductor Thermoelectric Materials ...................................................... 16

1.4 Review of tetradymines thermoelectric materials .............................................................. 23

1.5 Introduction to Metallic Thermoelectric Alloys ................................................................. 29

1.6 Experimental Measurements and Error Analysis ............................................................. 32
Chapter 2: Valence Band Structure of Bi₂Se₃ ................................................................. 36

2.1 Introduction ............................................................................................................. 36

2.2 Sample Preparation ............................................................................................... 39

2.3 Experimental Methods .......................................................................................... 42

2.4 Shubnikov-de Haas Oscillation: Introduction ......................................................... 44

2.5 Shubnikov-de Haas Oscillation: Experimental Result ............................................. 50

2.6 Discussion ................................................................................................................ 59

Chapter 3: Metallic Thermoelectric Alloy: A Preliminary Study

of Copper-Nickel Alloys ............................................................................................... 63

3.1 Introduction to Constantan ..................................................................................... 64

3.2 Sample Preparation .................................................................................................. 66

3.3 Thermoelectric Transport Measurement Result ..................................................... 72

3.4 Summary .................................................................................................................. 82

Appendix A: A Design for Thermoelectric Combustion Chambers ......................... 83

Appendix B: Second Order Bethe-Sommerfeld Expansion ........................................ 92

Reference ..................................................................................................................... 106
List of Tables

Table 1. Common thermocouple alloys................................................................. 7

Table 2. Properties of thermocouple materials, data from Refs. [15, 56, 57]........... 30

Table 3. Calculated Bi$_2$Se$_3$ valence band masses for the Γ–Z direction............. 37

Table 4. Summary of the samples used in this study. Sample numbers starting with S identify single crystals, with P for polycrystals. The acceptor impurities used, Mn, Ca, Pb, or Mg, are shown in the nominal composition. The hole concentrations are derived from Hall Effect measurements at 100 K (unless otherwise noted in the table). The symbols in the last column are consistent with the figures throughout this dissertation................................................................. 41

Table 5. Dingle Temperature for all the single crystal samples............................. 58

Table 6. First 9 Bernoulli numbers................................................................. 102
List of Figures

Figure 1. Coefficient of Performance of refrigeration versus the $ZT$ value, figure from Ref. [6].......................................................... 3

Figure 2. The thermoelectric voltage of various common commercial thermocouples; the reference temperature is at 0 °C, modified from Ref. [15]. The types are described in Table 1. ....................................................... 6

Figure 3. Demonstration of zone cooling concept (top) and schematic drawing of an Automotive Climate Control Seat (bottom), figures by Gentherm [11]......... 10

Figure 4. Electricity generation efficiency vs. $ZT$ at various conditions, calculated from Eq. (6)................................................................. 13

Figure 5. PowerPot 5W thermoelectric generator, sells for $149 and can charge phones at campsites. (Source: http://www.powerpractical.com/). ....................... 14

Figure 6. Schematic drawing of thermoelectric properties as a function of the carrier concentration. ................................................................. 17

Figure 7. An example of the Pisarenko plot. Different colors corresponds to different combinations of effective mass and scattering exponent, defined in Eq. (11). 21

Figure 8. Highest $ZT$ vs. $\beta$, modified from Ref. [25].......................................................... 22

Figure 9. Bi$_2$Se$_3$ crystal structure, figure from Ref. [31]....................................................... 24

Figure 10. First Brillouin zone of Bi$_2$Se$_3$ and its high symmetry points. The green circles schematically represent the 6 equivalent bands, modified from Ref. [31]. ........................................................................................................ 25
Figure 11. Price of various metals (5N purity unless indicated) normalized to the price of tellurium, figure from Ref. [37].................................................................26

Figure 12. (a) Thermopower vs. hole concentration for Bi$_2$Se$_3$ and Bi$_2$Te$_3$; (b) projected $ZT$ value for p-type Bi$_2$Se$_3$, calculated for 300 K, from [47]. .........................28

Figure 13. Schematic drawing of thermoelectric properties measurements: (a) thermopower measurement (b) electrical conductivity measurement.............32

Figure 14. Schematic drawing of Hall Effect measurements. .........................34

Figure 15. Experimental temperature dependence of (a) the carrier concentration as measured by the Hall Effect, (b) the thermopower, (c) the mobility, and (d) the resistivity of the single-crystal p-type Bi$_2$Se$_3$ samples studied here. The insert in (a) shows the field-dependence at 10 K of the Hall resistivity, illustrating a simple linear relation indicative of single-band conduction. .........................43

Figure 16. Band structure of Bi$_2$Te$_3$ and Bi$_2$Se$_3$, figure from Ref. [47]..........................44

Figure 17. Calculated hole Fermi surface of Bi$_2$Se$_3$ at hole concentrations of (a) $6\times10^{18}$ cm$^{-3}$ and (b) $4\times10^{19}$ cm$^{-3}$ using the methods developed in Ref. [66]: (a) has the bag region, whereas (b) has both bag and pipe regions. The pipes are connected to the adjacent Brillouin zones. .................................................................45

Figure 18. Trajectory of (a) a free electron in zero field (b) an electron in a quantizing magnetic field. ........................................................................................................47

Figure 19. (a) The Fermi surface of free electrons; (b) the Fermi surface of electrons under magnetic field (The Landau tubes).........................................................47

Figure 20. Density of states. The red line represents the density of states of free electrons; the black curve represents the density of states of Landau levels. ................48
Figure 21. Schematic drawing of the Fermi level oscillation. The blue curve represents the Fermi level. The red curve represents the highest Landau level (ν number) under this Fermi level. The steps coincide with the peaks of the Fermi level.

Figure 22. Angular dependence of Shubnikov–de Haas oscillations trace for all single crystal sample measured. The angle is the elevation angle between the direction of applied magnet field and the basal plane: (1) 0°, (2) 30°, (3) 60°, (4) 90°, (5) 120°, (6) 150°, and (7) 180°. The frames (a)-(d) are for samples S1-S4 (see Table 4).

Figure 23. Polar plot of the cross-sectional area of the Fermi surface, as a function of the elevation angle from the basal plane (0°) toward the trigonal axis (90°). The plots are shown for different doping levels, as indicated.

Figure 24. Characteristic temperature dependence of SdH oscillations amplitudes. The symbols are the experimental data points; (a)-(d) are samples S1-S4, plotted for different values of the magnetic field as indicated. All solid lines are fits to Eq. (29) with a single parameter, an effective mass $m^* = 0.25 m_e$. The Dingle temperatures vary from sample to sample.

Figure 25. Measured (data points) and calculated (lines) density-of-states hole effective mass vs. doping level. The heavy hole mass corresponds to the central “bag” in the Fermi surface, shown in Figure 17(a); the light hole mass corresponds to the “pipes”, as shown in Figure 17(b). Table 4 shows the symbol and color conventions used in this figure.

Figure 26. Thermopower at 300 K versus hole concentration, as measured by the Hall Effect at 100 K for p-type Bi$_2$Se$_3$, see Table 4. Red solid curve and green dashed line corresponds to $m^* = 0.25 m_e$ with $\lambda = -1/2$ (acoustic phonon scattering), and $\lambda = 1/2$ (optical phonon scattering) respectively. The blue solid line is from Figure 12(a).
Figure 27. Maximum ZT estimation for p-type Bi₂Se₃. The green circle encloses the data from this work. ........................................................................................................................................ 62

Figure 28. The thermopower and electron per atom for Cu₁₋ₓNiₓ alloys, compiled from data in Refs. [69, 70]. ........................................................................................................................................ 65

Figure 29. X-Ray Diffraction data of copper-nickel alloys with different sulfur content: (a) shows the overall view; (b) and (c) show the zoomed in view at two different peak locations; (d) shows Ni₃S₂ and Cu₂S, and x corresponds to sulfur nominal concentration (Cu₀.₅Ni₀.₅)₁₋ₓSₓ. ........................................................................................................ 69

Figure 30. Alloy density as a function of nominal sulfur content. The solid line represents the theoretical density calculated by molar mass and lattice constants obtained by XRD data, and x corresponds to sulfur nominal concentration (Cu₀.₅Ni₀.₅)₁₋ₓSₓ in the initial charge use to make the ingots. ........................................ 70

Figure 31. Differential Scanning Calorimetry trace for copper-nickel sample with different sulfur contents; x corresponds to sulfur nominal concentration (Cu₀.₅Ni₀.₅)₁₋ₓSₓ. ........................................................................................................................................ 71

Figure 32. Linseis LSR-3 calibration results. Symbols in the figure are our measurements on the reference sample. The solid black line is the recommended value provided by Linseis. The error bar on the curve is 5%. ................................. 73

Figure 33. Thermopower α of sulfur doped constantan samples ((Cu₀.₅Ni₀.₅)₁₋ₓSₓ, x=1% and 1.25%) from 80 K to 900 K. National Institute of Standards and Technology (NIST) constantan standard reference data are from Ref. [76]. The Cu₀.₅₃Ni₀.₄₇ standard data is provided by the Linseis Company for instrument calibration. ...................................................................................................................... 73

Figure 34. Sample without sulfur (black) shows discrepancy between the cryostat measurement and the Linseis measurement. ........................................................................................................ 75
Figure 35. Resistivity of sulfur doped constantan samples \(((\text{Cu}_{0.5}\text{Ni}_{0.5})_{1-x}\text{S}_x, x=1\% \text{ and } 1.25\%)\) from 80 K to 900 K. Low temperature resistivity data is measured in the cryostat, high temperature resistivity data is measured in the Linseis LSR-3 system is renormalized using the measurement value from the cryostat at the same temperatures. The reference data of Cu$_{0.53}$Ni$_{0.47}$ provided by Linseis is shown................................. 75

Figure 36. Thermoelectric power factor of sulfur doped constantan samples from 80 K to 900 K \(((\text{Cu}_{0.5}\text{Ni}_{0.5})_{1-x}\text{S}_x, x=1\% \text{ and } 1.25\%)\). Reference data of Cu$_{0.53}$Ni$_{0.47}$ provided by Linseis is shown. ................................................................. 76

Figure 37. Thermopower vs. sulfur doping level \(((\text{Cu}_{0.5}\text{Ni}_{0.5})_{1-x}\text{S}_x, x \text{ is sulfur nominal percentage})\). The black squares are taken at 300 K (Linseis and cryostat); the red circles are taken at 875 K (Linseis). The solid points are Linseis reference data at 300 K (square) and 875 K (circle). ................................................................. 77

Figure 38. Hall Effect data. (Cu$_{0.5}$Ni$_{0.5})_{1-x}\text{S}_x, x=0 \text{ and } 1.25\%$. ...................................................... 78

Figure 39. Pisarenko plot for constantan at 320 K. The red crosses are data from Figure 28. The black and blue points are made by us and measured in the cryostat. The black square is the pure sample, and the blue triangle is the copper-nickel alloy sample doped with 1.25% sulfur. The black dotted line is a guide for eyes. (Calculated with effective mass of 15 free electron mass, and scattering exponent of -0.5). ................................................................. 79

Figure 40. Temperature dependence of the thermal conductivity of sulfur doped constantan samples \(((\text{Cu}_{0.5}\text{Ni}_{0.5})_{1-x}\text{S}_x, x=1\% \text{ and } 1.25\%)\) in the temperature range from 300 K to 987 K. Literature reference data of standard constantan from C.Y. Ho et. al. [77] is also shown................................................................. 80

Figure 41. The calculated thermoelectric figure of merit \((ZT)\) of sulfur doped constantan samples \(((\text{Cu}_{0.5}\text{Ni}_{0.5})_{1-x}\text{S}_x, x=1\% \text{ and } 1.25\%)\) from 300 K to 900 K. Reference \(ZT\) of standard constantan from H. Muta [78] is shown.............................. 81
Figure 42. Two-dimensional schematic drawing of the thermoelectric combustion chamber, graph by Dr. Joseph P. Heremans................................................................. 84

Figure 43. Implementation of combustion chamber, by Christine Orovets, Ref. [79]. .................................................................................................................................... 85

Figure 44. Schematic drawing of the thermoelectric combustion chamber design. ........ 87

Figure 45. Fermi energy in a (a) metal and (b) intrinsic semiconductor. ....................... 95

Figure 46. Derivative of the Fermi-Dirac distribution function, $-\frac{\partial f}{\partial E}$. It has a bell-shape curve and vanishes exponentially as the energy is away from the chemical potential $\mu$. Light shaded area is from -3 to 3 and covers 91% of the area under the curve. Dark shaded area is from -2 to 2 and covers 76% of the area under the curve. ........................................................................................................ 98

Figure 47. Comparison of Thermopower calculation in a single parabolic band. The empty circles are accurate numerical integration. The red dashed line corresponds to Eq. (34), and the blue solid curve corresponds to Eq. (52). ................................................................................................................................. 105
Chapter 1: Background of Thermoelectricity

1.1 Introduction to Thermoelectricity

The first thermoelectric phenomenon was discovered in 1821 by Thomas J. Seebeck [1]. He observed that a current will flow in a closed circuit made of two dissimilar metals when the two junctions are at different temperatures. Seebeck initially believed this current was the result of a magnetic effect, as he observed the deflection of a compass magnet near the circuit. However, it was quickly realized that the current was instead an electrical current that induced the magnetic field pursuant to Ampere's Law. If the closed circuit is converted to an open one, then a voltage could be measured that is proportional to the temperature difference between the two junctions, where the proportionality factor is the difference in thermopowers of the two materials. This demonstrates the working principle of thermocouples.

In 1834, Jean C. A. Peltier discovered a second thermoelectric effect, which is the reverse effect of the Seebeck effect [2]. By passing a current through two dissimilar materials, heating or cooling could be induced at their junctions. Thermoelectric modules can be made for active cooling applications using the Peltier Effect.
In 1854 William Thomson, also known as Lord Kelvin, derived the relation between the Seebeck and Peltier Effects and discovered a third thermoelectric effect that does not require two dissimilar materials [3]. When passing a current through a homogeneous conductor in which a temperature gradient is maintained, there is an additional contribution in the heat production rate that depends on the temperature gradient.

During 1909-1911, Edmund Altenkirch [4] first introduced the thermoelectric figure of merit, the $Z$ value.

$$Z \triangleq \frac{\alpha^2 \sigma}{\kappa} \quad (1)$$

where $\alpha$ is the thermopower (also known as the Seebeck coefficient), $\sigma$ is the electrical conductivity, and $\kappa$ is the thermal conductivity. The "thermoelectric figure of merit" $Z$ has the unit of inverse temperature. For convenience, the value $Z$ is often multiplied by the average working temperature. This results in a more commonly used unit-less quantity, the dimensionless thermoelectric figure of merit, known as $ZT$ and as shown in Equation (2) [5].

$$ZT \triangleq \frac{\alpha^2 \sigma T}{\kappa} \quad (2)$$
The $ZT$ value is an important criterion for a material’s thermoelectric performance. Materials with higher $ZT$ values have better performances (higher efficiency, etc.). Figure 1 shows the dependence of the Coefficient of Performance (COP) of Peltier refrigeration as a function of the material’s $ZT$ value [6]. To have a competitive efficiency compared to the traditional vapor-compression based refrigerator, it is necessary to use materials with $ZT$ values larger than one, and to use the segmented module design [6]. However, it is also possible to capitalize on the other advantages of thermoelectric devices and create a niche market even with Peltier devices that have an energy efficiency lower than other methods. State of the art Bi$_2$Te$_3$-based materials for thermoelectric cooling are commercially viable [7], but a major limiting factor of the competitiveness for this system is the cost of tellurium. The advantages and applications of thermoelectric devices will be discussed in Section 1.2; further introduction to Bi$_2$Te$_3$-based material will be in Section 1.4.

![Figure 1. Coefficient of Performance of refrigeration versus the $ZT$ value, figure from Ref. [6].](image)
1.2 Applications of Thermoelectricity

Today, thermoelectricity has both scientific significance, as well as various engineering applications. In scientific research, thermoelectric phenomena are important transport properties. According to the Mott Relation in Eq. (3) (Ref. [8], see Appendix B for more discussion), thermopower is related to the differential of the energy dependent conductivity:

\[ \alpha = -\frac{k_B}{e} \frac{1}{\sigma} \int \sigma_E(E) \cdot \left( \frac{E - \mu}{k_B T} \right) \cdot \left( -\frac{\partial f}{\partial E} \right) dE \]  

(3)

where \( \alpha \) is the thermopower, \( k_B \) is the Boltzmann constant, \( e \) is the electron charge, \( \sigma \) is the conductivity, \( E \) is the energy of the carrier (i.e. electrons or holes), and \( \mu \) is the electrochemical potential. \( T \) is the temperature in absolute units, and \( f \) is the Fermi-Dirac distribution function as in Eq. (4):

\[ f(E) = \frac{1}{1 + \exp \left( \frac{E - \mu}{k_B T} \right)} \]  

(4)

\( \sigma_E(E) \) is not the electrical conductivity, but the “Mott” conductivity. Its integral represents the real conductivity \( \sigma \). The thermopower \( \alpha \) measures a material’s transport properties differently from the electrical measurements. For example, the thermopower measurement is one of the easiest ways to determine whether a material is p-type or n-type, especially in a highly resistive material where the Hall measurement is either too difficult
to measure or does not accurately represent the carrier type of the material. A hopping system is an example in which electrons in the material are closely bounded to the atoms and cannot move freely, except on rare statistical occasions. The electrons conduct electricity by hopping from one atom site to another. In a hopping system, the electrical conduction and valence band are discrete energy levels. Electrons in these bands do not conduct, and the Hall coefficient is no longer a measure of the carrier concentration [9]. In contrast to the Hall Effect, the thermopower of the material still determines whether it is p-type or n-type.

From an engineering perspective, there are three major areas of application for thermoelectricity: (1) temperature sensing, (2) cooling, and (3) energy harvesting. Thermoelectric temperature sensors, or thermocouples, are one of the most frequently used methods for taking temperature measurements. Additionally, thermoelectrics have been successful in several commercially viable niche markets for cooling and energy harvesting. One company, Gentherm, makes thermoelectric car seats and has sold over $0.5 billion in products [10,11]. Another company, Power Practical, makes a thermoelectric cooking pot (PowerPot) and recently received $250,000 of venture capital investment. This startup company has been valued at $2.5 million [12]. In the following paragraphs, each of these three major areas of application for thermoelectricity will be explained respectively.
(1) Temperature Sensing

The use of thermocouples in temperature sensing is one of the oldest applications of thermoelectricity [13]. The market size for temperature sensors in the year 2010 was $3.27 billion and was expected to be $6.05 billion by 2020. This represents an annual growth rate of 5.1% [14]. Typical types of temperature sensors include thermocouples, resistance temperature detectors (RTDs), and pyrometers. Thermocouples, made from metal alloys, have several advantages over RTDs and pyrometers. They have a broad temperature range from -250 °C to 2200 °C [15], a fast response time, long life-time, good repeatability, excellent mechanical properties, require no external power source, and are easy to assemble. By choosing the appropriate type of thermocouple, it can be used in oxidizing or reducing environments.

![Thermoelectric Voltage Graph](image)

Figure 2. The thermoelectric voltage of various common commercial thermocouples; the reference temperature is at 0 °C, modified from Ref. [15]. The types are described in Table 1.
Figure 2 shows common thermoelectric alloys and their performance in different temperature ranges, and Table 1 describes the materials of which they are made. Noticeably, platinum versus platinum-rhodium thermocouples are so reliable that they were once chosen for the International Practical Temperature Scale between 630.74 and 1064.42 °C [15].

Table 1. Common thermocouple alloys.

<table>
<thead>
<tr>
<th>TC type</th>
<th>Positive leg</th>
<th>Negative leg</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>nickel-chromium alloy (Chromel)</td>
<td>copper-nickel alloy (Constantan)</td>
</tr>
<tr>
<td>J</td>
<td>iron</td>
<td>copper-nickel alloy (Constantan)</td>
</tr>
<tr>
<td>T</td>
<td>copper</td>
<td>copper-nickel alloy (Constantan)</td>
</tr>
<tr>
<td>C</td>
<td>tungsten</td>
<td>tungsten-rhenium</td>
</tr>
<tr>
<td>R</td>
<td>platinum-13% rhodium</td>
<td>platinum</td>
</tr>
</tbody>
</table>
(2) Cooling

Thermoelectric cooling applications are usually focused on room temperature or cryogenic temperatures above 180 K. There have been several successful commercial products, including cooling modules for infrared sensors, thermoelectric wine coolers, and, most successfully, the climate control car seats by Gentherm. Thermoelectric cooling is advantageous because it is lightweight, quiet, and spatially focused, making it effective in removing heat from hot spots where most heat is generated.

Sensors, such as infrared detectors, often require the sensing elements to be maintained at a certain temperature to have their specified accuracy. For example, the laser wavelength in a diode laser depends on its temperature. A fast-response cooler is needed to prevent sensors from self-heating or to stabilize the sensor temperature in spite of the environmental temperature fluctuation. Thermoelectric modules are the perfect candidate for this type of job due to their almost instantaneous response time and good scalability. The Peltier Effect depends on the direction of the current flow, which means that when the applied current is reversed, the thermoelectric module will switch from heating to cooling or vice versa. The reversibility of a Peltier cooler makes it the perfect choice to build a fast-response temperature stabilizer using feedback controls. The response time is much faster than fluid-based temperature control mechanisms. In addition, the Peltier modules are solid state devices that give no vibrations that may affect sensor accuracy. As a result,
thermoelectric modules have been widely used as temperature regulators for infrared detectors, X-ray detectors, and lasers generators.

Thermoelectric modules can also be used to cool electronic units. One of the limiting factors of Moore's Law in Central Processing Units (CPUs) is heat dissipation. The heat generated from a chip-set can be unevenly distributed, and the bottle-neck is usually a few hot spots where the temperature is the highest. Therefore, it is beneficial to have a cooling mechanism that cools the hot spots locally. It is possible to make the small thermoelectric cooling devices required for such a local application because of the good scalability of thermoelectric modules. This is not possible for fluid-based cooling mechanisms or vapor-compressor chillers. Thermoelectric modules can be used in direct contact with the chip and quickly remove heat from the spots [16]. Then, the heat can be further dissipated by radiators and/or fans.
Zone cooling applications for passenger vehicles are another commercially viable use for thermoelectric cooling. Figure 3 (top) shows a zone cooling concept for thermoelectric coolers: the vehicle cabin is divided into zones that are individually air-conditioned by different thermoelectric modules. This concept demonstrates the possibility, in principle, of providing cooling or heating solely to the driver, or turned on for individual passengers as needed, rather than for the entire vehicle at once. This could save on vehicle fuel efficiency, as well as providing a more tailored riding experience.

Figure 3 (bottom) shows a schematic drawing of a commercial automotive climate control seat manufactured by Gentherm [11]. In this application, a thermoelectric module is combined with a fan to distribute cooled or heated air from within the body of the car.
seat. Again, superior comfort levels and energy savings can be achieved in vehicles that implement these thermoelectric modules due in part to their fast start-time as compared to a traditional air-conditioner or heater. Despite the advantages in comfort and fuel economy, this application of thermoelectric modules is not yet widespread.

(3) Energy Harvesting

Thermal energy is one of the most abundant forms of energy, because it is the form taken by all energy waste mechanisms. Low temperature waste heat has poor quality. It is difficult to turn it into useful work because of the second law of thermodynamics. Electricity presently is one of the most desirable forms of energy. From the first law of thermodynamics, it is possible to convert between heat and electricity. However, due to the limitation of the second law of thermodynamics, while it is possible to convert electricity entirely to heat, it is not possible to convert heat entirely to electricity. The heat to electricity energy conversion efficiency is limited by the Carnot efficiency, which is the maximum efficiency at which a heat engine can operate when set between a heat source at the temperature $T_H$ and a cold source at the temperature $T_C$, as shown in (5). The Carnot efficiency is defined as:

$$\eta_{\text{max}} = 1 - \frac{T_C}{T_H} \quad (5)$$

Thermal energy is usually released from chemical energy in combustion processes and then converted to mechanical work in engines or turbines. This work is further transformed into
electrical energy in alternators or dynamos. Only a fraction of heat energy can be converted to electricity and the rest is rejected as waste heat. For example, fossil-fuel-fired power plants have an average of 30–45% thermal efficiency (depending on the type of fuels). A modern natural gas-fired plant can have an efficiency of up to 55% [17]. Waste heat is also a by-product of many industrial productions, such as foundries, and accounts for a large portion of the energy loss. Heat recuperators are often installed in factories to harvest part of the waste heat energy to improve the overall energy efficiency.

Thermoelectric energy harvesting is one of many ways to convert heat to electricity. Thermoelectric generators had a market of $32 million as of 2012 and it is projected to be $950 million by 2022 [18]. Yet, thermoelectric energy generation faces a lot of challenges, mainly due to the low $ZT$ values of currently available thermoelectric materials. The thermoelectric conversion efficiency is only a fraction of the Carnot efficiency, as demonstrated by Equation (6).

$$\eta_{TE} = \eta_{max} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_C/T_H}$$ (6)
Figure 4. Electricity generation efficiency vs. $ZT$ at various conditions, calculated from Eq. (6).

Figure 4 shows the overall thermoelectric efficiency as a function of $ZT$ at various hot end temperatures, while the cold end temperature is maintained at 400 K. Despite their relatively low efficiency, thermoelectrics excel when the energy availability outweighs the efficiency. This is especially true in applications requiring power below 1 kilowatt (kW) [19], because conventional heat engines lose efficiency with decreasing energy scale. Thermoelectric cooking/power devices, such as the PowerPot, and Radioisotope Thermoelectric Generators (RTGs) are two examples for thermoelectric application in energy harvesting at a low power level (less than 1 kW, perhaps less than 100 W).
Figure 5. PowerPot 5W thermoelectric generator, sells for $149 and can charge phones at campsites. (Source: http://www.powerpractical.com/).

A 5W thermoelectric portable generator / cooking pot, known as “PowerPot”, that retails for $149 is shown in Figure 5. The working principle of this portable generator is the same as a coal fired power plant, despite their 8 orders of magnitude difference in energy scales. Thermal energy is released from the chemical energy of fuel. This thermal energy is then converted to electricity. The difference from the coal fired power plant is that the PowerPot uses thermoelectric modules, whereas the power plant uses gas and steam turbines to convert heat to electricity at much higher energy output levels of 100 MW~1 GW.

The PowerPot uses the temperature difference between the flame and the boiling temperature of water to charge small electronic devices. This precisely demonstrates the idea that thermoelectricity has its advantage where the energy availability is more important than the efficiency. The PowerPot can also be viewed as an example of cogeneration. One can get boiling water, camp fire (warmth, light), and electricity all at the
same time. For camping and hiking excursions, a significant concern is the total weight of equipment that must be carried on the person. Therefore, a cooking pot that serves extra duty as a thermoelectric generator that can charge small devices, such as phones and GPS locators, is an enticing option. The applications for this type of small thermoelectric generator have applications beyond those of the weekend warrior; similar weight concerns also apply to powering space probes.

RTGs are thermoelectric generators that converts heat produced by radioactive material into electricity. RTGs have been used to power satellites, space probes, and, most recently, the Curiosity Mars rover. RTGs have a longer service time than fuel cells and batteries, and operate when there is not enough sunlight for solar cells. A common RTG device is the Systems for Nuclear Auxiliary Power (SNAP). A typical heat source is $^{238}\text{PuO}_2$ and it is used to power probes travelling far from the Sun [20]. Though less useful for terrestrial applications, RTGs have broad implications for the future of long-range space exploration.
1.3 Optimizing Semiconductor Thermoelectric Materials

As previously discussed, the criterion for determining thermoelectric efficiency, including that of thermoelectric cooling and electricity generation, is the $ZT$ value, as shown previously in Figure 1 and Figure 4. Here, we present a qualitative analysis of the three components that determine the $ZT$ value, and what effect they have on that value: thermopower $\alpha$, electrical conductivity $\sigma$, and thermal conductivity.

In the electricity generation mode of a thermoelectric system, thermopower determines the Seebeck voltage at a given temperature, while the inverse of electrical conductivity describes the amount of Joule heating loss in producing that electricity. Thermal conductivity determines how much heat flows from the hot end to the cold end of a thermoelectric system. The heat conducted from the hot end to the cold end is not converted to electricity and therefore lost. Thus, having a material with low thermal conductivity is superior for thermoelectric efficiency.

In the cooling mode of a thermoelectric system, a high thermopower gives a high Peltier effect, while the inverse of electrical conductivity describes the heat generated by Joule heating. This Joule heating is detrimental to producing the cooling effect. Thermal conductivity causes the heat from the hot end to be conducted to the part intended to be
cooled, which will lower the efficiency and maximum temperature difference that the module can achieve.

![Schematic drawing of thermoelectric properties](image)

Figure 6. Schematic drawing of thermoelectric properties as a function of the carrier concentration.

The major difficulty in thermoelectric material optimization is that the three material properties, $\alpha$, $\sigma$, and $\kappa$ are interrelated. It is difficult to improve one of them without negatively affecting the other two, as can be seen in the schematic drawings in Figure 6. Insulators usually have low $ZT$ values because of their low electrical conductivities. Metal conductors also usually have low $ZT$ values, but because of their low thermopowers and high thermal conductivities. However, semiconductors have a reasonable balance between the thermopower, electrical conductivity, and thermal conductivity, and their $ZT$ values could be good.
The $ZT$ values are re-written in the following way to better understand how we could decouple the three material properties and to improve a material’s $ZT$ value. The thermal conductivity of a material can be separated into the electronic contribution and the lattice (phonon) contribution, $\kappa = \kappa_e + \kappa_L$. The electronic portion of thermal conductivity is related to the electrical conductivity, $\sigma$, by the Wiedemann-Franz Law, as in Eq. (7):

$$\kappa_e = LT\sigma$$  \hspace{1cm} (7)

where $L$ is the Lorenz ratio. For free electrons, such as in metals, $L$ equals a universal constant $2.45 \times 10^8 \text{ V}^2\text{K}^{-2}$. [21, 22] For electrons in semiconductors, $L$ deviates by at most 30% from this value. Therefore, to a first order approximation, we assume $L$ is a constant, and then the $ZT$ value is reduced to Eq. (8):

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T = \frac{\alpha^2}{L} \cdot \frac{1}{1 + \frac{\kappa_L}{\kappa_e}}$$  \hspace{1cm} (8)

The electrical conductivity can be written as in Eq. (9)

$$\sigma = ne\mu$$  \hspace{1cm} (9)

where $\mu$ is the mobility of electrons or holes. This can be further written as in Eq. (10):

$$\mu = \frac{e\tau}{m^*}$$  \hspace{1cm} (10)

where $\tau$ is the relaxation time of carriers between scattering events. A further simplification is to write the relaxation time as a power law of energy:
\[ \tau(E) = \tau_0 E^\lambda \]  

(11)

where \( \lambda \) is called the scattering exponent. Schematically, \( \lambda = -\frac{1}{2} \) is indicative of carrier scattering on acoustic phonons, \( \lambda = \frac{1}{2} \) of scattering on polar optical phonons, and \( \lambda = \frac{3}{2} \) of scattering on ionized impurities, such as acceptor impurities.

Now it is possible to derive the thermopower from the Mott Relation as in Eq. (3):

\[ \alpha = \frac{k_B}{e} \left[ \frac{K \left( \frac{5}{2} + \lambda, x_F \right)}{K \left( \frac{3}{2} + \lambda, x_F \right)} - x_F \right] \]  

(12)

where \( x_F \) is the reduced Fermi level, \( x_F = \frac{E_F}{k_B T} \). The integral \( K(r, x) \) is defined as the following:

\[ K(r, x) = \int x^r \left( -\frac{\partial f}{\partial x} \right) \, dx \]  

(13)

where \( f \) is defined as in Eq. (4), but with a transformation of variable \( x = \frac{E - \mu}{k_B T} \) into a dimensionless form: \( f(x) = \frac{1}{1 + \exp(x)} \). The total carrier concentration, \( n \), can be calculated by Fermi statistics, as in Eq. (14):

\[ n = \frac{(2m^* k_B T)^{3/2}}{3\pi^2 \hbar^3} K \left( \frac{3}{2} + \lambda, x_F \right) \]  

(14)

From Eq. (12) and (14), it is possible to plot the thermopower as a function of the carrier concentration, \( \alpha(n) \), using the Fermi levels as an independent variable. This is
known as the Pisarenko plot [23]. Here, the scattering coefficient $\lambda$ and the density of states effective mass $m^*$ are the two material-dependent parameters. Figure 7 is an example of a Pisarenko plot. Note that two different combination of $\lambda$ and $m^*$ can give similar curves. For example, $m^* = 0.4 m_e, \lambda = -\frac{1}{2}$ and $m^* = 0.2 m_e, \lambda = \frac{1}{2}$ give two curves that are close together. Therefore, by experimentally measuring the thermopower vs. the carrier concentration, we cannot uniquely determine $\lambda$ and $m^*$ at once. One additional measurement is still needed to derive the two parameters. In my study on p-type Bi$_2$Se$_3$ described in Chapter 2 of this dissertation, a Shubnikov-de Haas (SdH) oscillation measurement is used to determine the effective mass of the valence band of Bi$_2$Se$_3$. 
Figure 7. An example of the Pisarenko plot. Different colors corresponds to different combinations of effective mass and scattering exponent, defined in Eq. (11).

Now, all three components of thermoelectrics in Eq. (1) are expressed in terms of the new variables: the lattice thermal conductivity, $\kappa_L$; the mobility, $\mu$; the scattering exponent, $\lambda$; the density of states effective mass, $m^*$; and the Fermi level. Optimizing a semiconductor’s thermoelectric properties inside one given class of materials is usually done by changing the Fermi level. It is possible to theoretically calculate the highest $ZT$ value by varying the Fermi level for given $\kappa_L, \lambda, \mu, m^*$, and the temperature as input parameters. These input parameters are combined into a simple material parameter, the $\beta$ value:
\[ \beta \overset{\text{def}}{=} \left( \frac{T}{300} \right)^{5/2} \left( \frac{m_{\text{DOS}}}{m_e} \right)^{3/2} \frac{\mu}{\kappa_L} \]  

(15)

The maximum ZT value increases monotonically with increasing \( \beta \) value, as seen in Figure 8. A more detailed discussion can be found in Refs. [24,25].

![Figure 8. Highest ZT vs. \( \beta \), modified from Ref. [25].](image)

In summary, for any new class of semiconductor thermoelectric materials, its potential is determined by important material parameters: the lattice thermal conductivity, \( \kappa_L \); the mobility, \( \mu \); the scattering coefficient \( \lambda \); and the density of states effective mass, \( m^* \). Once these basic properties of the class are established, the optimization process can
take place. The Fermi level can be changed by doping to achieve the optimized $ZT$ value. The following section will give a brief review of one particular semiconductor case: Bi$_2$Se$_3$. In Chapter 2, the basic valence band parameters of Bi$_2$Se$_3$ are studied experimentally for the first time to evaluate the potential of p-type Bi$_2$Se$_3$ as a new candidate of thermoelectric semiconductor material.

1.4 Review of tetradymites thermoelectric materials

Tetradymite is the name given to a naturally occurring mineral, Bi$_2$Te$_2$S. The word tetradymites is generalized to refer to the class of crystals that includes Bi$_2$Te$_3$ and (Bi$_{1-x}$Sb$_x$)$_2$(Te$_{1-y}$Se$_y$)$_3$ alloys. From 1950~1980, three decades of fast progress improved the $ZT$ value of Bi$_2$Te$_3$-based tetradymites from less than 0.3 to about 1 [26, 27, 28]. The tetradymites were the first material system to achieve high $ZT$ and be commercialized. Currently, Bi$_2$Te$_3$ and its alloys are still the best commercial thermoelectric material for room temperature applications [7]. In recent years, nanostructuring has been introduced as a new method to reduce the thermal conductivity, $\kappa$, and has resulted in improvement of the $ZT$ values for tetradymites. A $ZT$ value of 1.56 was achieved in lab settings as a result of nanostructuring [29,30].
Tetradymite Bi$_2$Te$_3$ and Bi$_2$Se$_3$ crystals have the same rhombohedral structure, R$\overline{3}m$. The hexagonal cell is formed by stacking quintuple layers [31], and the crystal structure of Bi$_2$Se$_3$ is shown in Figure 9.

An example of one quintuple layer of Bi$_2$Se$_3$ is:

Se1-Bi1-Se2-Bi1’-Se1’

Se1, Se2 and Se1’ denote selenium atoms at different locations in the lattice structure. The Se1’-Se1 bonds are considered to be Van der Waals bonds [32,33], while the Bi-Se bonds are covalent-ionic [32,34,35]. The weakness of Se1’-Se1 Van der Waals bonds between
two quintuple layers are responsible for easy cleavage along basal planes (perpendicular to the c-axis).

Perpendicular to the cleavage plane, we can identify the c-axis, also known as the trigonal axis, which is named for its 3-fold rotational symmetry. The crystal also has an inversion symmetry center at the Γ point of the Brillouin zone. As a combined result of these two symmetry properties, the off-center points may have 6 equivalent points in the Brillouin zone, as shown schematically in Figure 10.

![Figure 10](image)

Figure 10. First Brillouin zone of Bi$_2$Se$_3$ and its high symmetry points. The green circles schematically represent the 6 equivalent bands, modified from Ref. [31].

Although Bi$_2$Te$_3$ is already a commercial thermoelectric material, the high material cost of the element tellurium limits its large scale applications. The current price of tellurium is about $133/kg, compared to the price of bismuth which is about $20/kg and the price of selenium is about $60/kg [36]. Figure 11 shows the price of elements commonly used for thermoelectric applications. The value is normalized for tellurium price
In addition to this, the United States Department of Energy anticipates a supply shortfall of tellurium by 2025 [38]. Selenium belongs to the same VI-A group as tellurium in the periodic table. Therefore, it has similar chemical properties. Recent studies have shown promising results in replacing the tellurium in PbTe system with selenium, and the PbSe material has reached a ZT value of 1.5 at 900 K [39]. Bi$_2$Se$_3$ based material have been theoretically evaluated as a tellurium-free substitute for Bi$_2$Te$_3$-based thermoelectric material in order to increase the commercial competitiveness of thermoelectric modules for room temperature cooling applications. However, we will show in Chapter 2 that the theory upon which these predictions are based is not corroborated by experiments.

![Figure 11. Price of various metals (5N purity unless indicated) normalized to the price of tellurium, figure from Ref. [37].](image)
Bi$_2$Se$_3$ can form solid solutions with Bi$_2$Te$_3$ [40]. The optimization studies [41] aimed at obtaining $ZT$ values in the Bi$_2$Te$_x$Se$_{3-x}$ alloy system have been focused on the Te-rich ($x \geq 1.5$) region [28]. While Bi$_2$Te$_3$ can be easily doped either p-type or n-type, the defect chemistry of Bi$_2$Se$_3$ is such that material prepared at thermodynamic equilibrium is always n-type [42, 43]. The only report [44] on p-type Bi$_2$Se$_3$ before this decade has not been repeated. The nature of native defects in Bi$_2$Se$_3$ is still an open debate. There are two opinions: Analytis et al. [45] argue that the defects are Se vacancies, while Huang et al. [46] claim that there are Bi$_{Se}$ anti-site defects and additional layers. In the early days, researchers once predicted that the detailed valence band structure of Bi$_2$Se$_3$ was “not too important because Bi$_2$Te$_x$Se$_{3-x}$ alloys with substantial Se are generally used as the n-type material” [28]. N-type Bi$_2$Se$_3$ has never been a good thermoelectric material and is no longer considered because the conduction band is unfavorable [28, 42, 43]. Recent discovery of p-type dopants in Bi$_2$Se$_3$ and the theoretical prediction of $ZT$ value larger than 1 in Bi$_2$Se$_3$ [47] rekindles the interest in the valence band structure of Bi$_2$Se$_3$. Several new acceptor impurities have been discovered recently for Bi$_2$Se$_3$, including Ca [48], Mn [49], Mg [50, 51, 52], and Pb (See Chapter 2 for detail). Yet, it is suspected that the native defects of Bi$_2$Se$_3$ still exist, even in the presence of these chemical acceptors. Further, we do not know if the p-type material is compensated, or if the acceptor impurities alleviate the donor action of the native defects.

The electronic band structure of Bi$_2$Se$_3$ is different from Bi$_2$Te$_3$ in that Bi$_2$Te$_3$ has 6-fold band degeneracy for both its conduction band and valence band, whereas Bi$_2$Se$_3$
conduction band has only one minimum in the center (Γ point) of the Brillouin zone. Without the benefit of 6-fold degeneracy, the conduction band of Bi$_2$Se$_3$ has a low density of states effective mass of about 0.21 $m_e$, where $m_e$ is the free electron mass [42, 43]. Therefore, Bi$_2$Se$_3$ is a poor candidate for material of high $ZT$ value. The valence band, however, is more elusive. It was recently predicted theoretically that the valence band of Bi$_2$Se$_3$ could be favorable to producing a high-$ZT$ thermoelectric material [47]. Figure 12 shows the predicted thermopower and $ZT$ value for p-type Bi$_2$Se$_3$. The prediction shows the optimum $ZT$ above 1 at 300 K. This inspired our interest in characterizing p-type Bi$_2$Se$_3$ for room temperature cooling thermoelectric applications, which constitutes Chapter 2 in this dissertation.

![Figure 12: Thermopower vs. hole concentration for Bi$_2$Se$_3$ and Bi$_2$Te$_3$](image)

![Figure 12: Projected ZT value for p-type Bi$_2$Se$_3$](image)

Figure 12. (a) Thermopower vs. hole concentration for Bi$_2$Se$_3$ and Bi$_2$Te$_3$; (b) projected $ZT$ value for p-type Bi$_2$Se$_3$, calculated for 300 K, from [47].
1.5 Introduction to Metallic Thermoelectric Alloys

Although metallic alloys are useful for thermocouple temperature measurements, they are not used presently as thermoelectric materials for power generation [53]. As early as 1885, Lord Rayleigh considered the possibility of using German-silver (a copper-nickel alloy, similar to constantan) and iron to build a thermopile for energy conversion. He concluded that “the steam-engine and dynamo are not likely to be superseded by a German-silver and iron thermopile” [54]. Today, there is still no commercial metallic thermoelectric energy harvesting devices because of the low ZT values (usually < 0.2) of metals compared to those of semiconductors (close to or above 1). In metallic alloys, thermal conductivity is usually dominated by electronic contributions, which follows the Wiedemann-Franz Law in Eq. (7). In the extreme limit valid for metals, $\kappa_L / \kappa_e \to 0$, then the ZT value is simply proportional to the thermopower $\alpha$ squared.

$$ ZT = \frac{\alpha^2}{L} \cdot \frac{1}{1 + \frac{\kappa_L}{\kappa_e}} \approx \frac{\alpha^2}{L} \quad (16) $$

To have a ZT of 1, which is the commercial standard for semiconductor thermoelectric materials, and using the free electron value for $L$, the thermopower needs to be larger than 156 $\mu$V/K. However, typical metals usually have a thermopower less than 10 $\mu$V/K at room temperature [15]. The few exceptions that have thermopowers close to or exceeding 10$\mu$V/K are nickel, chromium, iron, and platinum in elemental metals; and Constantan
(Cu-Ni), Chromel (Ni-Cr), Alumel (Ni-Mn-Al-Si), Nicrosil (Ni-Cr-Si-Mg), and Nisil (Ni-Si) in alloys. The thermoelectric power factor is given as:

\[ PF \equiv \alpha^2 \sigma \]  \hspace{1cm} (17)

While the \( ZT \) of metals is low, their thermoelectric power factor could typically be 3 times higher at a high temperature (100 \( \mu \text{W/cm} \cdot \text{K}^2 \)) than that of semiconductors (usually less than 30 \( \mu \text{W/cm} \cdot \text{K}^2 \), Ref. [55]), but not usually at room temperature, see Table 2.

Table 2. Properties of thermocouple materials, data from Refs. [15, 56, 57].

<table>
<thead>
<tr>
<th></th>
<th>Constantan</th>
<th>Copper</th>
<th>Iron</th>
<th>Chromel</th>
<th>Pt13%Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point °C</td>
<td>1220</td>
<td>1083</td>
<td>1490</td>
<td>1427</td>
<td>1850</td>
</tr>
<tr>
<td>Resistivity at 20°C (( \mu \Omega \cdot \text{cm} ))</td>
<td>48.9</td>
<td>1.724</td>
<td>9.67</td>
<td>70.6</td>
<td>19.6</td>
</tr>
<tr>
<td>Temperature Coefficient Resistance (0-100°C)</td>
<td>-1.0×10^{-5}</td>
<td>4.3×10^{-4}</td>
<td>6.5×10^{-3}</td>
<td>4.1×10^{-4}</td>
<td>1.56×10^{-3}</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>552</td>
<td>241</td>
<td>345</td>
<td>655</td>
<td>317</td>
</tr>
<tr>
<td>Thermopower (( \mu \text{V/K} ))</td>
<td>-39</td>
<td>1.83</td>
<td>10</td>
<td>22</td>
<td>1</td>
</tr>
<tr>
<td>Thermal conductivity at 20°C (W/m · K)</td>
<td>21</td>
<td>377</td>
<td>68</td>
<td>19</td>
<td>37</td>
</tr>
<tr>
<td>Power Factor at 20°C (( \mu \text{W/cm} \cdot \text{K}^2 ))</td>
<td>31</td>
<td>2</td>
<td>10</td>
<td>6.9</td>
<td>0.05</td>
</tr>
<tr>
<td>( ZT ) (20°C)</td>
<td>0.04</td>
<td>1.5×10^{-4}</td>
<td>4×10^{-3}</td>
<td>0.01</td>
<td>4×10^{-5}</td>
</tr>
</tbody>
</table>

If thermoelectric alloys could be used in heat recovery, they would have the following advantages over the semiconducting thermoelectric materials: (1) the melting temperatures of metals and metal alloys are usually higher than semiconductors, and operating at a higher temperature could also increase the higher Carnot efficiency limit (Eq. (5)); (2) many alloys (e.g. nickel alloys) can be welded together, forming strong mechanical connections, which is a task difficult for semiconductor materials; (3) metals
can be formed into desirable shapes; and (4) alloys have much better mechanical properties. The tensile strength of constantan is 552 MPa (see Table 2, data compiled from Refs. [15, 56, 57]), which is much larger in comparison to semiconductor thermoelectric materials: 0.84 MPa for PbTe and 6.14 MPa for TAGS-85 ([58]). In Chapter 3, we attempted to improve the thermoelectric property in constantan and preliminary data are reported.
1.6 Experimental Measurements and Error Analysis

This dissertation focuses on the experimental characterizations of thermoelectric materials. The following measurement techniques were used.

\textit{Thermopower and Resistivity Measurements}

![Figure 13. Schematic drawing of thermoelectric properties measurements: (a) thermopower measurement (b) electrical conductivity measurement.](image)

The measurement technique is shown schematically in Figure 13; the sample is shown as the rectangular parallelepiped. The red and blue wires denote thin copper (red) and constantan wires (blue) (~25 µm diameter). They are soldered together to make type-T thermocouples and can measure the temperature at the two points of the sample as shown in Figure 13. A voltage, $\Delta V$, can also be measured between the two copper wires (red). In
Figure 13(a), a heat flux is sent through the sample and a temperature gradient is created across the sample. \( \Delta V \) is then a measure of the thermopower which can be calculated from:

\[
\alpha = -\frac{\Delta V}{\Delta T}
\]  

(18)

In Figure 13(b), a current is sent through the sample and the resistance of the sample can be calculated:

\[
R = \frac{\Delta V}{I}
\]  

(19)

where \( R \) is the resistance of the sample. The resistivity, \( \rho \), can be calculated from the resistance \( R \) and the dimension of the sample. Conductivity, \( \sigma \), is the inverse of resistivity:

\[
\rho = \frac{R \cdot A}{l}
\]  

\[
\sigma = \frac{l}{R \cdot A}
\]  

(20)

where \( l \) is the distance between the two points from with the voltage, and \( A \) is the cross-sectional area of the sample.

Figure 13 shows the principle of our measurements of transport properties at low temperature in a Janis conventional liquid nitrogen flow cryostat from 78 K to 420 K. High temperature thermopower and resistivity were measured in a commercial Linseis LSR-3 system from 300 K up to 900 K. The principle is also similar to Figure 13, but this instrument cannot be used to determine thermal conductivity.
Thermal Conductivity Measurements

Thermal conductivity was measured differently in two separate ranges. From 480 K to 1000 K, it was measured using a flash-diffusivity method (Anter Flashline 3000). At 300 K, it was measured using the time-domain thermo-reflectance method in Professor J. C. Zhao’s group by Dr. Changdong Wei (data at 300 K is reported in this dissertation, but in principle this method can be used to measure thermal conductivity at higher temperature [59]). The thermal conductivity measurements were done by my colleague, Dr. Richard L. J. Qiu. I will present his data, since the $ZT$ value requires thermal conductivity data, but I will not discuss in detail the thermal conductivity measurement techniques.

Hall Effect Measurements

![Figure 14. Schematic drawing of Hall Effect measurements.](image)

The Hall Effect is used to determine the carrier concentration in solids where electrical conduction is governed by electrons in the conduction or valence bands. A current is sent through the sample perpendicular to an applied magnetic field. Electron
movement will be deflected by the Lorentz force, and a transverse voltage can be measured perpendicular to both the current and the applied magnetic field direction; see Figure 14. The transverse Hall resistance is defined as the following:

\[ R_{\text{Hall}} = \frac{\Delta V}{I} \]  \hspace{1cm} (21)

where \( \Delta V \) is the transverse voltage and \( I \) is the current sent through the sample. For more details, see Ref. [60].

The carrier concentration \( n \), can then be calculated by:

\[ n = -\frac{1}{e} \frac{B}{R_{\text{Hall}} \cdot th} \]  \hspace{1cm} (22)

where \( n \) is the carrier concentration, \( e \) is the electron charge, \( B \) is the magnetic field, \( R_{\text{Hall}} \) is the transverse Hall resistance, and \( th \) is the sample thickness.

**Error Analysis**

For low temperature thermoelectric properties measured in the cryostat, error in thermopower \( \alpha \) is less than 2%. Error in \( \rho \) is around 3%, and mainly comes from errors in measurements of sample geometry.

For high temperature measurement in the LSR-3 system, the error in thermopower is around 5% and error in resistivity is around 3%. Thermopower and resistivity results match well with the cryostat data. The combined error in \( ZT \) is estimated to be on the order of 10 to 15%. 

35
Chapter 2: Valence Band Structure of Bi$_2$Se$_3$

This dissertation relies on work that I, along with several co-authors, published in *Physical Review B* [61]. In crafting that published work, my contribution included growth of single crystal samples, thermoelectric transport and Shubnikov-de Haas (SdH) measurement, results analysis, and composition of the experimental portion of the paper [61]. Co-author Bin He made the polycrystalline samples and measured their thermoelectric properties. Those results are presented in a Pisarenko plot in Figure 26. Co-author David Parker completed the band structure calculation, including the calculated Fermi surface and effective mass (Figure 16 and Figure 17). He also discussed the possible cause for the discrepancy between the experimental result and theoretical calculation, as well as drafting the theoretical portion of the paper. Co-author Ioannis Androulakis made Mg doped polycrystalline samples and measured their transport properties.

2.1 Introduction

As outlined in Chapter 1, the interest in substituting selenium for tellurium in tetradymites thermoelectrics stimulates this work. In particular, p-type Bi$_2$Se$_3$ has been calculated [47] to be a promising thermoelectric material; see Figure 12. However, the
literature on the band structure calculations of Bi$_2$Se$_3$ shows a large discrepancy. Theorists cannot agree on the location of the valence band maximum or the effective mass of the valence band. Such information is critical in determining the potential of Bi$_2$Se$_3$ as a thermoelectric material. Mishra’s [62] and Parker’s [47] calculations show that the valence band maximum should be at the Γ point, but they also show that, away from the Γ point, there is a secondary maximum. This will be discussed here in further detail. Zhang’s [31] and Larson’s [63] calculations show instead that the valence band maximum of Bi$_2$Se$_3$ is not at the Γ point, and therefore should have 6-fold degeneracy. The effective mass calculations by these theorists have a wide variance, as summarized in Table 3. Despite these theoretical calculations, no prior experimental work has been done to study the actual valence band structure of Bi$_2$Se$_3$. Investigation the valence band structure of p-type Bi$_2$Se$_3$ as a new material will help to determine the potential of Bi$_2$Se$_3$ as a thermoelectric material, and it is also helpful to solve the dispute of these different theoretical calculations.

Table 3. Calculated Bi$_2$Se$_3$ valence band masses for the Γ–Z direction.

<table>
<thead>
<tr>
<th>Publication</th>
<th>Calculated mass (units of $m_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mishra et al [62]</td>
<td>0.36</td>
</tr>
<tr>
<td>Parker et al [47]</td>
<td>0.80</td>
</tr>
<tr>
<td>Zhang et al [31]</td>
<td>2.20</td>
</tr>
<tr>
<td>Larson et al [63]</td>
<td>0.56</td>
</tr>
</tbody>
</table>
Experiments are designed to take property measurements that can then be compared with theoretical calculations. For example, thermopower, as a function of the carrier concentration (the “Pisarenko” plot), can be obtained from both experiments and calculations. However, the calculated and experimentally determined Pisarenko curve have contributions from both the band structure (effective mass) as well as scattering. The Pisarenko plot alone cannot exclude the effect from the scattering and therefore does not necessarily confirm or dispute the result of the band structure calculation. Fortunately, it is possible to design experiments to separate the contributions from the band structure and the scattering effect. Thus, we use magnetic quantum oscillations as one way of measuring the properties of band structure without the complication of the scattering effect. The oscillations observed in measurements of the resistance versus high magnetic field are called Shubnikov-de Haas (SdH) oscillations. The shape of the Fermi surface can be measured from the SdH oscillations periods. The effective mass can also be derived from the Dingle analysis of the temperature decay of the SdH oscillations amplitudes.

For Bi$_2$Se$_3$, the measurements I obtained experimentally can be compared with theoretical calculations of the same properties. This comparison will yield valuable information about the valence band structure of Bi$_2$Se$_3$. Here, the thermoelectric transport properties and the SdH oscillation measurement are made on several single crystal Bi$_2$Se$_3$ samples and these measurements are compared to theoretical calculations. Pisarenko relation results confirm the SdH measurements.
2.2 Sample Preparation

A total of 4 single crystals and 6 polycrystalline samples were prepared for this study; sample identification and properties are summarized in Table 4. For the single crystals, 99.999% pure Bi and Se were weighed into quartz ampoules and acceptor impurities (Ca or Mn) were added in appropriate amounts to dope Bi$_2$Se$_3$ p-type. The ampoules were evacuated to $10^{-6}$ Torr, sealed, and the elements were then melted and reacted at 1073 K. Single crystals of Bi$_2$Se$_3$ were grown by slow cooling, using a modified horizontal Bridgman method described in Ref. [48]. The single crystals cleave easily perpendicular to the c-axis, as expected. We limit our discussion to self-consistent data on small individual cleaved samples with a characteristic size of 0.2 mm $\times$ 1 mm $\times$ 4 mm, in which we were able to confirm sufficient homogeneity via the presence of quantum oscillations in the resistivity measurements. The polycrystalline samples were prepared by ball milling and spark plasma sintering. Stoichiometric or off-stoichiometric Bi$_2$Se$_3$ doped with Mg or Pb (see Table 4 for details) were weighed and loaded into a quartz ampoule. The ampoule was evacuated to $10^{-6}$ Torr, sealed, and then heated to 1073 K where it was kept overnight to ensure homogeneity. The furnace was turned off and the ingot was allowed to gradually cool to room temperature. The sample was removed from the ampoule and ground by hand. The resulting powder was then formed into a pellet by Spark Plasma Sintering (SPS) at 623 K under 50 MP of pressure. The sintered pellet was cut into a 6 mm
× 2 mm × 2 mm rectangular parallelepiped for transport measurements. The electrical and thermal properties of the disks cannot be expected to be isotropic, since the process favors the alignment of the c-axis of the Bi$_2$Se$_3$ polycrystals with the pressing direction. To account for this, small parallelepipeds were cut out, and the thermopower and Hall coefficients were measured with the heat and charge currents in the plane of the pressing; i.e., preferentially aligned in the basal plane of the crystallites.

A summary of the properties of all samples is given in Table 4.
Table 4. Summary of the samples used in this study. Sample numbers starting with S identify single crystals, with P for polycrystals. The acceptor impurities used, Mn, Ca, Pb, or Mg, are shown in the nominal composition. The hole concentrations are derived from Hall Effect measurements at 100 K (unless otherwise noted in the table). The symbols in the last column are consistent with the figures throughout this dissertation.

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Nominal composition</th>
<th>Hole concentration ((10^{18} \text{ cm}^{-3}))</th>
<th>Thermopower (@300 \text{ K (µV/K)})</th>
<th>Symbol in this paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Bi(<em>{1.97})Mn(</em>{0.03})Se(_3)</td>
<td>5.7@100 K</td>
<td>146</td>
<td>▲</td>
</tr>
<tr>
<td>S2</td>
<td>Bi(<em>{1.95})Ca(</em>{0.05})Se(_{2.975})</td>
<td>14@100 K</td>
<td>140</td>
<td>■</td>
</tr>
<tr>
<td>S3</td>
<td>Bi(<em>{1.98})Ca(</em>{0.02})Se(_{3.03})</td>
<td>14@100 K</td>
<td>144</td>
<td>△</td>
</tr>
<tr>
<td>S4</td>
<td>Bi(<em>{1.99})Ca(</em>{0.01})Se(_{3.03})</td>
<td>16@100 K</td>
<td>134</td>
<td>□</td>
</tr>
<tr>
<td>P1</td>
<td>Bi(<em>{1.98})Pb(</em>{0.02})Se(_{3.01})</td>
<td>9.3@100 K</td>
<td>109</td>
<td>▼</td>
</tr>
<tr>
<td>P2</td>
<td>Bi(<em>{1.96})Pb(</em>{0.04})Se(_{3.01})</td>
<td>9.8@100 K</td>
<td>93</td>
<td>▼</td>
</tr>
<tr>
<td>P3</td>
<td>Bi(<em>{1.96})Mg(</em>{0.02})Se(_3)</td>
<td>8.5@100 K</td>
<td>131</td>
<td>×</td>
</tr>
<tr>
<td>P4</td>
<td>Bi(<em>{1.99})Mg(</em>{0.01})Se(_{3.06})</td>
<td>13@300 K</td>
<td>131</td>
<td>°</td>
</tr>
<tr>
<td>P5</td>
<td>Bi(<em>{1.98})Mg(</em>{0.02})Se(_{3.03})</td>
<td>14@100 K</td>
<td>114</td>
<td>×</td>
</tr>
<tr>
<td>P6</td>
<td>Bi(<em>{1.96})Mg(</em>{0.04})Se(_{3.06})</td>
<td>18@300 K</td>
<td>116</td>
<td>◦</td>
</tr>
</tbody>
</table>
2.3 Experimental Methods

The resistivity, \( \rho \), and low-field Hall coefficient, \( R_H \), of the single crystals were measured in a Quantum Design Physical Property Measurement System (PPMS) from 2 K to 300 K. The thermopower, \( \alpha \), and the Hall coefficient of the polycrystalline samples were measured in a Janis cryostat from 77 K to 300 K in magnetic fields up to 13 kOe.

The hole concentration, \( p \), is obtained using \( p = 1/(R_H e) \), where \( e \) is the elementary electron charge, assuming that the Hall prefactor is in unity. The hole concentrations of the single crystals are shown in Figure 15(a). The temperature dependence of thermopower is measured on the same samples and shown in Figure 15(b). The Drude mobility is calculated using \( \mu = R_H/\rho \) and shown in Figure 15(c), while the temperature dependence of resistivity is shown in Figure 15(d). All of the samples show metallic behavior, as demonstrated by the increases in \( \rho \) and \( \alpha \), with temperature. Further, the carrier concentration appears temperature independent from 2 K to 200 K and varies little with temperatures above that. Some of this temperature variation may be due to variation of the Hall prefactor. The hole concentrations (Table 4) were calculated from the low-temperature (\( T \leq 100 \) K) value of \( R_H \). The mobility decreases monotonically with increasing temperature, indicating that the charge carriers are scattered predominantly by phonons. The measured carrier concentrations and the mobilities both have an error bar of 5%, mostly from sample geometry measurement (error bars are not shown in the figures to improve readability). The p-type Bi\(_2\)Se\(_3\) single crystals have a room temperature mobility
~500 cm²V⁻¹s⁻¹, less than the electron mobilities in typical n-type Bi₂Se₃ single crystals, which can reach above 1000 cm²V⁻¹s⁻¹ around room temperature.

Figure 15. Experimental temperature dependence of (a) the carrier concentration as measured by the Hall Effect, (b) the thermopower, (c) the mobility, and (d) the resistivity of the single-crystal p-type Bi₂Se₃ samples studied here. The insert in (a) shows the field-dependence at 10 K of the Hall resistivity, illustrating a simple linear relation indicative of single-band conduction.
2.4 Shubnikov-de Haas Oscillation: Introduction

In this section, a brief background introduction to the magnetic quantum oscillation is given, followed by the experimental study of Bi$_2$Se$_3$ valence structure. The electronic band structure of a solid describes the energy spectrum of all the possible wave-functions in the solid. Figure 16 is an example of the band structure (dispersion relation) of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ [47]. The band theory can give much information about the material’s properties based on the electronic band structure. The Fermi surface is defined as an equi-energetic surface in reciprocal space that has an energy equal to the Fermi energy. The study of Fermi surfaces is of great importance in understanding the materials’ thermoelectric properties.

Figure 16. Band structure of Bi$_2$Te$_3$ and Bi$_2$Se$_3$, figure from Ref. [47].

Parker and Singh [47] calculated the Fermi surfaces of p-type Bi$_2$Se$_3$, and plotted them from band structure calculations. Figure 17 is a plot of valence band Fermi surface of Bi$_2$Se$_3$ at two different hole concentrations.
We map the cross-sections of these Fermi surfaces by magnetic quantum oscillations. Specifically, in this work, the SdH measurement technique is used in which the oscillation of resistance is measured as a function of the applied magnetic field and the angles between the field and the crystallographic axes of the samples.

![Figure 17. Calculated hole Fermi surface of Bi$_2$Se$_3$ at hole concentrations of (a) 6×10$^{18}$ cm$^{-3}$ and (b) 4×10$^{19}$ cm$^{-3}$ using the methods developed in Ref. [66]: (a) has the bag region, whereas (b) has both bag and pipe regions. The pipes are connected to the adjacent Brillouin zones.](image)

To introduce the SdH quantum oscillation measurement technique, we start by writing the electron energy in motion. For electrons moving in free space, the dispersion relation near the top or bottom of each band is as in the following Eq. (23):
\[ E = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m^*} \]  \hspace{1cm} (23)

where \(k_x, k_y, k_z\) are the \(x, y, z\) components of the wave vector, \(m^*\) is the effective mass, and \(\hbar\) is the reduced Planck constant. The density of available states is then:

\[ D(E) = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E} \hspace{1cm} (24)\]

\(D(E)\) describes the number of available states at a given energy interval.

Under a strong external magnetic field, the path of electron motion in a solid changes drastically due to presence of the Lorentz force. Schematic drawings of electron trajectories with and without magnetic fields are shown in Figure 18. In a field applied along the \(z\) direction, the energy dispersion relation of an electron in strong magnetic field changes to Eq. (25):

\[ E = \frac{\hbar^2 k_z^2}{2m^*} + \hbar \omega_c \left( \nu + \frac{1}{2} \right) \hspace{1cm} (25)\]

where \(k_z\) is still the \(z\) component of the wave vector, but in the \(x\) and \(y\) directions (perpendicular to the magnetic field), the energy is quantized into Landau levels. \(\nu\) is the Landau level index, \(\omega_c = \frac{|eB_z|}{m^*}\) is the cyclotron frequency, and \(B_z\) is the magnetic field. Eq.(25) shows that the orbital motion of the electrons around the \(z\) axis now have quantized energy in the \(x\) and \(y\) directions.

The energy dispersion in Eq. (24) is isotropic in the \(x, y,\) and \(z\) directions, and the equi-energy surface is spherical; see Figure 19(a). For the dispersion relation with the magnetic field, the energy levels for electrons in a magnetic field are called the Landau
levels. The spherical Fermi surfaces of free electrons in zero field changes into a quantizing field and becomes a series of tubular shapes, as shown schematically in Figure 19(b).

Figure 18. Trajectory of (a) a free electron in zero field (b) an electron in in a quantizing magnetic field.

Figure 19. (a) The Fermi surface of free electrons; (b) the Fermi surface of electrons under magnetic field (The Landau tubes).
The free electron density-of-states has a square root dependence on the electron energy as in Eq. (24). It can be shown schematically as the red line in Figure 20. The density states for electrons in a quantizing magnetic field changes to Eq. (26), and is shown as the black curve in Figure 20. More detailed discussions can be found in Ref. [65]

\[
D(E) = \frac{(2m^*)^{3/2} \omega_c}{4\pi^2 \hbar^2} \sum_{v=0}^{\infty} \frac{1}{\sqrt{E - \hbar \omega_c (v + \frac{1}{2})}}
\]

Figure 20. Density of states. The red line represents the density of states of free electrons; the black curve represents the density of states of Landau levels.
Figure 21. Schematic drawing of the Fermi level oscillation. The blue curve represents the Fermi level. The red curve represents the highest Landau level ($\nu$ number) under this Fermi level. The steps coincide with the peaks of the Fermi level.

Note that the energy of the wave-functions in Eq. (25) has a linear dependence on the external magnetic field given by $\omega_c$. The position and relative height in density of state (Eq. (26)) also changes with the applied magnetic field. As the external field is changed continuously, the energy spectrum of electrons changes accordingly. At 0 K, electrons will occupy the available states with the lowest energy. The Fermi energy changes with applied magnetic field such that the integral of the density of states below the Fermi energy gives the carrier concentration, as in Eq. (27), which does not change with the field because it is set by the doping level of the sample.
\[ \int_0^{E_F} D(E,B) \, dE = n \] (27)

As a result of the principle of minimum energy, the electron configuration will change each time a Landau level passes the Fermi surface. A numerical simulation result of Eq. (27) in Figure 21 shows how the Fermi energy oscillates with the applied magnetic field. The physical properties of the electrons also oscillate with the Fermi energy as a result of changing density of states near the Fermi level. Therefore, by continuously measuring quantities such as resistivity (SdH oscillations) or magnetic susceptibility (de Haas-van Alphen oscillation) while sweeping the magnetic field, an oscillatory behavior in \(1/B\) is expected. From the oscillation frequency, the cross-sectional area of the Fermi surface can be calculated by Eq. (28) [65]:

\[ a_F = \frac{2\pi e}{\hbar \Delta(1/B)} \] (28)

2.5 Shubnikov-de Hass Oscillation: Experimental Result

The existence of high-mobility p-type single crystal Bi\(_2\)Se\(_3\), presented in this work, makes it possible to study the valence band of p-type Bi\(_2\)Se\(_3\) experimentally, and to compare the results with the calculations. We show in Figure 17 the hole Fermi surface (generated by Parker from data in Ref. [47] using code in Ref. [64]) for hole concentrations of \(6\times10^{18}\) cm\(^{-3}\) and \(4\times10^{19}\) cm\(^{-3}\), respectively. The Fermi surface from calculation in Figure
17(a) has a “bag-shape” pocket centered around the Γ-point. In Figure 17(b) there are six additional topologically open pieces, “pipes,” which connect to the adjacent Brillouin zones. At lower carrier concentrations, the pipes separate from the bag. The bag now becomes a topologically closed surface, and the pipes transform into small, ellipsoidal, and separated pockets that are also topologically closed. At lower concentrations still, only the central bag remains, as shown in Figure 17(a).

SdH oscillations were measured in a PPMS from 2 K to 12 K in magnetic fields up to 140 kOe. The cleaved single crystal samples were mounted on a horizontal rotator, and the angular dependence of the SdH oscillations was measured by varying the orientation of the sample relative to the applied magnetic field. The elevation angle was set at 90° when the applied field is aligned with the trigonal axis. No attempt was made to align the electrical current with the azimuthal angle in the basal plane.

Raw traces of the SdH oscillations observed in the resistivity as a function of elevation angle on the samples S1-S4 are shown in Figure 22. The main period as a function of the inverse of the field is obvious and periodic, and Fourier transforms of these traces have been determined. The accuracy (standard deviation) on the main oscillation period is about 3%. Other minor peaks also appear in the Fourier transforms, but they are likely to be artifacts, as they are not robust enough, vis-à-vis changes in the numerical treatment, to be identified as real SdH periods. In the analysis we considered only the main period, which is the one visible to the naked eye in Figure 22. The cross-section of the Fermi surface, $a_F$, is
in the plane normal to the applied magnetic field can be directly calculated from the period of the oscillation [65] by Equation (28).

We identify the main period to be associated with the Fermi surface centered at Γ-point in Figure 17. Polar plots of the periods \([\Delta(1/B)]^{-1}\) as a function of the elevation angle are shown for all samples (identified by their hole concentration as measured by the Hall Effect in Figure 23. The polar plots show how the Fermi surface cross-sectional area increases with increasing carrier concentration. Anomalies in cross-sectional area appear in the more highly doped samples in the vicinity of 105°, which we associate with appearance of the open orbits, as illustrated in Figure 17(b).
Figure 22. Angular dependence of Shubnikov–de Haas oscillations trace for all single crystal sample measured. The angle is the elevation angle between the direction of applied magnet field and the basal plane: (1) 0°, (2) 30°, (3) 60°, (4) 90°, (5) 120°, (6) 150°, and (7) 180°. The frames (a)-(d) are for samples S1-S4 (see Table 4).
Figure 23. Polar plot of the cross-sectional area of the Fermi surface, as a function of the elevation angle from the basal plane (0°) toward the trigonal axis (90°). The plots are shown for different doping levels, as indicated.

We now discuss the comparison between the shapes and sizes of the Fermi surfaces as calculated, shown in Figure 17, and the cross-section, as measured in Figure 23. Starting with sample S1, and using the crude assumption that the Fermi surface is spherical at this concentration, the period of the SdH oscillations at 0° (950 kG) would correspond to a hole concentration of $5.2 \times 10^{18} \text{ cm}^{-3}$, while the period at 90° (1220 kG) corresponds to a hole concentration of $7.6 \times 10^{18} \text{ cm}^{-3}$. These values bracket the measured hole concentration obtained from Hall measurements of $5.7 \times 10^{18} \text{ cm}^{-3}$. Thus, it is reasonable to conclude that
the holes occupy a Fermi surface with relatively little anisotropy, which is most likely the central “bag” at the Γ point in Figure 17(a). Additional bands are not expected at this concentration, and are indeed not seen.

Sample S2 (1.4×10^{19} cm^{-3} holes) shows a bump at a 120° angle, which indicates the onset of an extension of the “bag-shaped” Fermi surface in that direction and the beginning of the formation of the “pipe-like” structures. Applying the same spherical Fermi surface approximation used above to sample S2 (which is a clearly unrealistic model for describing the behavior of this sample), the corresponding period of the SdH oscillations at 0° (123 kOe) would yield a hole concentration of \( p = 7.7 \times 10^{18} \) cm^{-3}. In reality, the Hall measurement gives 1.4×10^{19} cm^{-3}. Hall measurements are less accurate than SdH measurements because they involve a measurement of the sample geometry and an assumption about the Hall prefactor equal to 1. Thus, we conclude from this discrepancy that the shape of the Fermi surface must be considerably non-spherical. This behavior becomes even more pronounced in samples S3 and S4, where the SdH oscillations period disappears completely near 105°. This implies that the cross-section of the Fermi surface normal to that direction is open. In other words, it reaches the boundary of the first Brillouin zone and connects to the Fermi surface of the next Brillouin zone, such that the carrier orbits encompass all Brillouin zones and the holes never complete a cyclotron orbit.

SdH measurements also make it possible to measure the holes’ cyclotron effective mass by the Dingle analysis method [65], based on the temperature dependence of the amplitude of the SdH oscillations. The amplitude of the SdH oscillations is reduced by a
reduction factor, $R_T$, given as a function of the average carrier effective cyclotron mass, $m^*$, on the orbit and applied magnetic field $H$ (Ref. [65]):

$$R_T = \frac{147 \frac{m^*}{m_e} \frac{T(K)}{H(kOe)}}{\sinh \left[ 47 \frac{m^*}{m_e} \frac{T(K)}{H(kOe)} \right]}$$

(29)

where $m_e$ is the free electron mass. This analysis is carried out for each sample, at multiple values of the field and the temperature, and using two fitting parameters: the cyclotron mass $m^*$ and the Dingle temperature, which is a measure of the sample defect density [65]. Figure 24 illustrates how all $T$-dependences of the amplitudes taken at various values of the applied field aligned along the c-axis (normalized to the value at 2 K and $1.36 \times 10^6$ Gauss) fit Eq. (29) well for one single value for all samples of the valence band effective mass $m^* = 0.25\pm0.05 \, m_e$. This is not much different from the conduction band mass of 0.21 $m_e$.[42, 43]. Furthermore, values for the average in-plane effective mass are the same for all 4 samples of different carrier concentrations (see Figure 25), and for those doped with two different acceptor impurities (Ca and Mn). The Dingle temperatures do vary from sample to sample (30 K for the Mn-doped sample; 9 – 17 K for the Ca-doped ones. See Table 5 for detail.). However, these temperatures yield no information beyond the observation that Mn doping affects the phase coherence length of the electrons on Landau levels more than Ca-doping, presumably because of the d-electrons in Mn$^{2+}$. 

56
Figure 24. Characteristic temperature dependence of SdH oscillation amplitudes. The symbols are the experimental data points; (a)-(d) are samples S1-S4, plotted for different values of the magnetic field as indicated. All solid lines are fits to Eq. (29) with a single parameter, an effective mass $m^* = 0.25 \, m_e$. The Dingle temperatures vary from sample to sample.
Table 5. Dingle Temperature for all the single crystal samples.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Dingle Temperature(K)</th>
<th>Relaxation time τ (10^{-14}s)</th>
<th>Dingle mobility (\text{cm}^2/\text{s})</th>
<th>Hall mobility (10 K) (\text{cm}^2/\text{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>30.5</td>
<td>4.00</td>
<td>280</td>
<td>1343</td>
</tr>
<tr>
<td>S2</td>
<td>8.8</td>
<td>14</td>
<td>972</td>
<td>1686</td>
</tr>
<tr>
<td>S3</td>
<td>17.1</td>
<td>7.10</td>
<td>500</td>
<td>1926</td>
</tr>
<tr>
<td>S4</td>
<td>17.9</td>
<td>6.80</td>
<td>478</td>
<td>1398</td>
</tr>
</tbody>
</table>

Figure 25. Measured (data points) and calculated (lines) density-of-states hole effective mass vs. doping level. The heavy hole mass corresponds to the central “bag” in the Fermi surface, shown in Figure 17(a); the light hole mass corresponds to the “pipes”, as shown in Figure 17(b). Table 4 shows the symbol and color conventions used in this figure.
Figure 26. Thermopower at 300 K versus hole concentration, as measured by the Hall Effect at 100 K for p-type Bi$_2$Se$_3$, see Table 4. Red solid curve and green dashed line corresponds to $m^* = 0.25 m_e$ with $\lambda = -\frac{1}{2}$ (acoustic phonon scattering), and $\lambda = \frac{1}{2}$ (optical phonon scattering) respectively. The blue solid line is from Figure 12(a).

2.6 Discussion

The Dingle analysis [65] gives an effective mass of 0.25 $m_e$ for all the p-type Bi$_2$Se$_3$ samples. To verify this value for $m^*$ independently, the results of both single crystal and polycrystalline samples are analyzed by the Pisarenko plot $\alpha(p)$ in Figure 26. This plot gives an independent evaluation of the experimental effective mass, albeit one that depends on an assumption about electron scattering. The calculated “Pisarenko curves” must assume a value for the scattering exponent $\lambda$ as in the relaxation time approximation $\tau(E) = \tau_0 E^\lambda$ (See Eq. (11) in Chapter 1 Section 1.3). Ionized impurity scattering ($\lambda = \frac{3}{2}$)
is mostly a low-temperature effect and would not be present in the Pisarenko plot of thermopower taken at 300 K. The temperature dependence of mobility in Figure 15(c) is characteristic of phonon scattering. Therefore, we show “Pisarenko curves” with two possibilities of phonon scatterings in Figure 26: $m^* = 0.25 \, m_e$ with $\lambda = -\frac{1}{2}$ (acoustic phonon scattering), and $\lambda = \frac{1}{2}$ (optical phonon scattering). The samples with $p < 10^{19}$ cm$^{-3}$ fall on the lowest curve ($m^* = 0.25 \, m_e$ with $\lambda = -\frac{1}{2}$), which is consistent with the mass from the SdH data. Some deviation is observed for $p > 10^{19}$ cm$^{-3}$, but it is not large enough to explain the discrepancy between theory [47] and the experimental results presented here. It is also not possible to ascertain whether this is due to an increase in effective mass or a change in scattering mechanism. Moreover, the SdH mass reported here is average cyclotron mass in the basal plane, whereas the Pisarenko plot measures the total density-of-states mass. Because of this, the density of states and cyclotron masses are equal only for a spherical Fermi surface. Figure 23 shows that the hole Fermi surface departs only slightly from spherical when $p \leq 6 \times 10^{18}$ cm$^{-3}$, so that the fact that a mass of 0.25 $m_e$ explains the $\alpha(p)$ results well in that concentration range shows that transport and SdH results are consistent. When the carrier concentration reaches above about $1.4 \times 10^{19}$ cm$^{-3}$, the Fermi surface deviates from spherical and the average density of states mass increases above the basal-plane cyclotron mass. This is again shown in Figure 26 at higher hole concentrations ($p \geq 1.4 \times 10^{19}$). All the experimental $\alpha(p)$ data points in Figure 26 are compatible with the effective mass value obtained from the SdH measurements, but are significantly below the
theoretical calculated values presented in Ref. [47]. Similar data points below the calculated curve [47] were also reported by Cava’s group [48].

Measurement of the Fermi surface of p-type Bi$_2$Se$_3$ confirms that at low doping levels, the holes fill in the pocket at the Γ point. This confirms Parker’s [47] and Mishra’s [62] calculated position of the valence band maximum. At high doping levels (> 1.4×10$^{19}$ cm$^{-3}$), there is evidence for the presence of the “pipes”, in agreement with Parker’s calculation. The Fermi surface therefore has secondary bands connected to the Γ point pocket. However, none of the single crystal samples showed a second oscillation period within the experimental sensitivity. Therefore, the picture of 6 secondary bands detached from the main Γ point pocket is not put in evidence by the experimental observation. It is possible that the additional bands started out connected to the Γ point pocket, rather than starting out as isolated pockets and then connecting to Γ point pocket at a higher carrier concentration. However, it is likely that a sample with the precise density of holes to see this possibility experimentally simply was not available.

The discrepancy in effective masses is directly responsible for the lower thermopower in the experiment relative to the theoretical predictions in Ref. [47]. Since the same calculation techniques have several recent successes in PbSe [66] and SnTe [67], in our original publication [61], Parker ascribed this discrepancy to the weak Van der Waals bond layers that are present in Bi$_2$Se$_3$ but not in PbSe or SnTe. For more discussion on Parker’s analysis of the theory, see Ref. [61].
With the experimental data and assuming the same lattice conductivity in Parker’s calculation, we plot the $\beta$ value (Eq. (15) in Chapter 1) on Figure 27. Following the technique described in Chapter 1.3 to estimate the $ZT$ of a new thermoelectric material, the $ZT$ value of p-type Bi$_2$Se$_3$ is expected to be limited to less than 0.5 at 300 K.

![Figure 27](image)

Figure 27. Maximum $ZT$ estimation for p-type Bi$_2$Se$_3$. The green circle encloses the data from this work.

In summary, we observe experimentally that the value of the density-of-states effective mass for the valence band of Bi$_2$Se$_3$ is significantly smaller than had been theoretically predicted. This in turn affects the calculated theoretical thermopower. From this, we conclude that the prospects of p-type Bi$_2$Se$_3$ as a thermoelectric material are not as promising as originally predicted.
Chapter 3: Metallic Thermoelectric Alloy:
A Preliminary Study of Copper-Nickel Alloys

This chapter discusses a new copper-nickel alloy for thermoelectric energy harvesting applications. The thermoelectric properties of a copper-nickel alloy with sulfur inclusion is reported here. The new alloys set a record high thermopower and power factor for the Cu-Ni alloy family. The new material could be used to make more sensitive thermocouples or used for high temperature waste heat recovery. The role of sulfur in copper-nickel alloys presently is not fully understood; therefore, only experimental results are presented. My contribution to the research into these alloys is that I crafted several Cu-Ni-S alloy samples, measured thermoelectric properties and the Hall Effect in the cryostat (low temperature), and measured thermoelectric properties at high temperatures. Dr. Richard L. J. Qiu crafted the majority of the Cu-Ni-S samples; conducted X-Ray Diffraction (XRD), density and Differential Scanning Calorimetry (DSC), and thermal conductivity measurements; and measured additional high temperature thermoelectric properties.
3.1 Introduction to Constantan

Copper and nickel form solid solutions in the entire composition range [68]. Constantan usually refers to copper-nickel alloys in a certain composition range, typically, a composition around Cu_{0.53}Ni_{0.47}. Constantan has a low temperature coefficient of resistivity of 10 ppmK^{-1} (at 20 °C) (See Table 2 in Chapter 1); therefore, it is usually used in standard resistors (hence the name “constant”an). Constantan also has a large negative thermopower of -39 µV/K at 20 °C. It is used as the n-type leg material for type E, J, and T thermocouples. Table 2 in Chapter 1 shows properties of constantan along with other thermoelectric alloys. The melting point of constantan is about 1220 °C, and it can reliably operate in an oxidizing environment up to 750 °C [15]. Figure 28 shows the thermopower and carrier concentration of copper-nickel alloys as a function of copper content in the alloy. Carrier concentration data are from Ref. [69] and thermopower data are from [70]. Pure copper has a small positive thermopower of 4 µV/K at 20 °C. Pure nickel has a negative thermopower of -17.6 µV/K. When copper and nickel are alloyed between 20% and 80% of copper concentration, the thermopower reaches a more negative value. Meanwhile, electron concentrations in this region are lower than in pure copper or nickel (Figure 28). Although the use of a “Pisarenko plot” is generally limited to discussions of semiconductors and not metallic alloys, it is possible to plot the thermopower as a function of the carrier concentration of this alloy to achieve a “Pisarenko”-like plot. This
“Pisarenko” plot is shown later in this chapter in Figure 39, together with data on our samples for comparison. Significantly, the large negative thermopower values near room temperature of Cu-Ni alloys are observed in alloys covering a wide range of Cu to Ni concentration around 1:1 ratio. The lack of sensitivity of thermopower to composition is useful in a thermoelectric material for thermocouples. In this study, the Cu-Ni ratio was kept at 1:1 while sulfur was added into the alloys.

Figure 28. The thermopower and electron per atom for Cu$_{1-x}$Ni$_x$ alloys, compiled from data in Refs. [69, 70].

Sulfur is a typical trace impurity in constantan. According to Ref. [71] and [72], constantan typically contains about 0.024 wt% (weight percentage) of sulfur, and, according to Ref. [72], this level of sulfur inclusion has no effect on the thermopower of
such constantan samples compared to the standard reference samples (measured from room temperature to about 900 K).

3.2 Sample Preparation

We report here preliminary data that show that adding sulfur into copper nickel alloys results in improved thermoelectric properties. The sulfur doped constantan samples were prepared using elemental copper and nickel powders (99.9% purity, Alfa Aesar). The sulfur content in the sample was altered by adding nickel sulfide powder (Ni$_3$S$_2$, 99.7% purity, from Sigma Aldrich). Different nominal sulfur concentrations were added to the mix, with composition (Cu$_{0.5}$Ni$_{0.5}$)$_{1-x}$S$_x$, where $x = 0.5\%$, 1\%, 1.25\%, 2\%, and 5\% ($x = 0.005$ is written as 0.5\% for short). Starting materials were weighed and sealed in a stainless steel ball milling jar under argon atmosphere. They were subsequently mixed for 60 minutes in a high energy miller try to improve uniformity. No stainless balls were added into the ball milling jar. (When we tried with balls in the milling jar, the powder formed a sticky substance that coated the wall of the ball milling jar and the surfaces of the balls, and the coating was difficult to remove.) The mixed powder was then sintered into a pellet by Spark Plasma Sintering (SPS) at 673 K under 40 MPa of pressure. In the final step, the sintered pellet was arc melted in argon atmosphere several times to ensure homogeneity, resulting in a metal ingot. During the arc-melting process, the sample contained 5\%
nominal sulfur, the addition of which formed clusters on the sample’s surface during cool-down from the molten state. For samples with less than 5% sulfur, no such clusters were observed. For comparison, standard constantan samples with no sulfur (Cu$_{0.5}$Ni$_{0.5}$) were prepared using copper shot (99.999% purity, Alfa Aesar) and nickel shot (> 99.95% purity, Alfa Aesar) by arc melting; no miller nor SPS were used in the process. Elemental copper and nickel shots were used rather than copper and nickel powder. This makes our reference sample different from the sulfur-containing sample.

All the ingots were cut into parallelepipeds of size approximately 12 mm × 2 mm × 2 mm for thermoelectric transport measurement in the Linseis LSR-3. Parallelepipeds of size 7 mm × 2 mm × 2 mm were used for cryostat measurement. From each ingot, a third sample is cut into about 1 mm thick disks for thermal diffusivity measurement.

5.3 Sample Analysis

According to the equilibrium phase diagram, sulfur has a solubility limit in Cu-Ni alloys of about 0.5% atomic percent [73]. In our study, up to 5% nominal sulfur concentration were added to the copper-nickel alloy.

The X-Ray Diffraction (XRD) data in Figure 29 show that with increasing sulfur nominal addition, the peaks shift to lower angles, corresponding an increase in the lattice constants. In the 5% sulfur sample, there are clearly additional peaks that corresponds to
the appearance of secondary Ni$_3$S$_2$ and Cu$_{1.8}$S phases. The increase in lattice constant is confirmed by the density measurements by Archimedes’ method, as shown in Figure 30. Samples have lower density when more sulfur is added. The solid line in Figure 30 represents the theoretical density calculated by molar mass and lattice constants obtained by XRD data shown in Figure 29. Density data deviate from this solid line when more than 1.25% nominal sulfur were added to Cu-Ni alloy, which is again an indication of a phase separation.
Figure 29. X-Ray Diffraction data of copper-nickel alloys with different sulfur content: (a) shows the overall view; (b) and (c) show the zoomed in view at two different peak locations; (d) shows Ni$_3$S$_2$ and Cu$_2$S, and $x$ corresponds to sulfur nominal concentration $(\text{Cu}_{0.5}\text{Ni}_{0.5})_{1-x}S_x$. 
Figure 30. Alloy density as a function of nominal sulfur content. The solid line represents the theoretical density calculated by molar mass and lattice constants obtained by XRD data, and \( x \) corresponds to sulfur nominal concentration \( (\text{Cu}_{0.5}\text{Ni}_{0.5})_{1-x}\text{S}_x \) in the initial charge used to make the ingots.

Next, we performed a Differential Scanning Calorimetry (DSC) study. In a DSC heat trace measurement, the heat flow is measured as a function of temperature when a piece of sample from the ingot was heated and cooled down. This is a sensitive way to detect secondary phases. Figure 31 shows DSC heat traces for the undoped Cu-Ni alloy and alloys with 0.5%, 1%, 1.25%, 2%, and 5% nominal sulfur addition. With 0.5% sulfur inclusion, the latent heat traces are clean. This agrees with the literature [73] that suggests that the solubility of sulfur in copper-nickel alloys is 0.5%. The 1.25% and 2% samples show peaks at 104 °C and 525 °C that correspond to the presence of \( \text{Cu}_2\text{S} \) [74] and \( \text{Ni}_2\text{S}_3 \) [75] phases respectively. At concentrations between 0.5% and 1.25%, only a peak at 104 °C is present, which shows that only the \( \text{Cu}_2\text{S} \) phase is present in the sample.
Figure 31. Differential Scanning Calorimetry trace for copper-nickel sample with different sulfur contents; \( x \) corresponds to sulfur nominal concentration \((\text{Cu}_{0.5}\text{Ni}_{0.5})_{1-x}\text{S}_x\).
3.3 Thermoelectric Transport Measurement Result

High temperature thermopower and resistivity data were measured in Linseis LSR-3, and low temperature thermopower and resistivity data were measured in a cryostat with methods described in Chapter 1. The results of both measurements were compared. In Figure 33, the thermopower measured in the cryostat and the Linseis LSR-3 machine match well with each other for sulfur doped samples, with x=1% and 1.25%. We add to the figure the National Institute of Standards and Technology (NIST) constantan reference data from Ref. [76]. We also note that Cu$_{0.55}$Ni$_{0.47}$ reference data is provided by the Linseis Company for the Cu$_{0.53}$Ni$_{0.47}$ reference sample they provide with the LSR-3 instrument as a standard for instrument calibration. We have measurements on the standard sample provided by Linseis and the results agree within 5% of the reference data, as shown in Figure 32. The Linseis curve in Figure 33 is their recommended standard value from the user manual.
Figure 32. Linseis LSR-3 calibration results. Symbols in the figure are our measurements on the reference sample. The solid black line is the recommended value provided by Linseis. The error bar on the curve is 5%.

Figure 33. Thermopower $\alpha$ of sulfur doped constantan samples ($(Cu_{0.5}Ni_{0.5})_{1-x}S_x$, $x=1\%$ and $1.25\%$) from 80 K to 900 K. National Institute of Standards and Technology (NIST) constantan standard reference data are from Ref. [76]. The $Cu_{0.53}Ni_{0.47}$ standard data is provided by the Linseis Company for instrument calibration.
The thermopower data we measured on our own reference sample without sulfur show a discrepancy between results measured in the cryostat and the LSR-3 Linseis measurement; see Figure 34. The difference between the thermopower measurements in the two instruments are about 10 µV/K in the overlapping temperature range 300~400 K. The cryostat thermopower was lower than, but close to, the reference data. Comparatively, the Linseis data was much higher than the reference data. However, the machine was within calibration accuracy when the high temperature data was taken. The Linseis LSR-3 requires sample length larger than 10 mm; the cryostat measurement requires sample length less than 8 mm. The samples measured in the two instruments were different cuts from the same ingot. All of the samples with sulfur are made by powders because it is easier to ensure homogeneity of sulfur contents. It is possible that since our reference sample was made with copper and nickel shots, it had problems of non-homogeneity and the cuts used in the two instruments might have different compositions. In Figure 33, the x=1% sample was first measured in the LSR-3, then cut short and measured in the cryostat; the x=1.25% sample for the LSR-3 and the cryostat were two different cuts. Both of the sulfur-containing samples show good agreements between the two instruments. Only the measurement results on our own reference sample are inconsistent. The discrepancy in our reference sample has not been resolved at the time of the writing of this thesis.
Figure 34. Sample without sulfur (black) shows discrepancy between the cryostat measurement and the Linseis measurement.

Figure 35. Resistivity of sulfur doped constantan samples ((Cu$_{0.5}$Ni$_{0.5}$)$_{1-x}$S$_x$, $x=1\%$ and $1.25\%$) from 80 K to 900 K. Low temperature resistivity data is measured in the cryostat, high temperature resistivity data is measured in the Linseis LSR-3 system is renormalized using the measurement value from the cryostat at the same temperatures. The reference data of Cu$_{0.53}$Ni$_{0.47}$ provided by Linseis is shown.
Figure 35 shows that the resistivity of both doped and undoped constantan are temperature independent, as expected. Figure 36 shows the thermoelectric power factor calculated from the thermopower and resistivity using Eq. (17). Reference data for Cu_{0.53}Ni_{0.47} provided by Linseis were used for comparison. There is a significant improvement in power factor from our result on our (Cu_{0.5}Ni_{0.5})_{1-x}S_x, x=1% and 1.25% samples, as compared to the reference data.

Figure 36. Thermoelectric power factor of sulfur doped constantan samples from 80 K to 900 K ((Cu_{0.5}Ni_{0.5})_{1-x}S_x, x=1% and 1.25%). Reference data of Cu_{0.53}Ni_{0.47} provided by Linseis is shown.
Figure 37. Thermopower vs. sulfur doping level $(\text{Cu}_{0.5}\text{Ni}_{0.5})_{1-x}\text{S}_x$, $x$ is sulfur nominal percentage. The black squares are taken at 300 K (Linseis and cryostat); the red circles are taken at 875 K (Linseis). The solid points are Linseis reference data at 300 K (square) and 875 K (circle).

The effect of sulfur inclusion on thermopower is shown in Figure 37. The sulfur content in the horizontal axis is the nominal value that was put in the sample. For 300 K data, $x=0.5\%$, 1\%, 1.25\%, 2\%, and 5\% data are measured in the Linseis LSR-3. The 1\% and 1.25\% samples were also measured in the cryostat, and data on them were consistent. The data on the 0\% sample was measured in the cryostat at 300 K. Other samples were not measured in the cryostat because of limited time. All 875 K data were measured in the Linseis LSR-3. The reference data provided by Linseis are shown for comparison. Our result shows that with $x=0.5\%$, already an increase in the thermopower is evident. Our best
room temperature thermopower comes from x=1.25% (atomic percent, corresponds to 0.66 weight percent).

The sulfur doped samples did show improvement over the reference data. This result need further verification due to the inconsistency in the data on our own reference sample.

The Hall Effect measurements in constantan are difficult due to the smallness of the signal that results from the high carrier concentration. However, Hall signals were measured on our x=0 sample and the sample with x=1.25% sulfur. The results are shown in Figure 38, which displays the magnetic field dependence of the Hall resistivity. (See Eq. (22) in Chapter 1.6). It is clear from the data that the 1.25% sample has a higher Hall slope and lower carrier concentration than pure constantan.

Figure 38. Hall Effect data. (Cu0.5Ni0.5)1-xSx, x=0 and 1.25%.
Figure 39. Pisarenko plot for constantan at 320 K. The red crosses are data from Figure 28. The black and blue points are made by us and measured in the cryostat. The black square is the pure sample, and the blue triangle is the copper-nickel alloy sample doped with 1.25% sulfur. The black dotted line is a guide for eyes. (Calculated with effective mass of 15 free electron mass, and scattering exponent of -0.5).

With the Hall data and the thermopower, it is possible to construct the Pisarenko plot for the two samples shown in Figure 38. We also compare that to the literature data reported from Figure 28. Our sample without sulfur is consistent with the literature value [69, 70] when we used the cryostat data, but not the LSR-3 data.
Figure 40. Temperature dependence of the thermal conductivity of sulfur doped constantan samples ((Cu$_{0.5}$Ni$_{0.5}$)$_{1-x}$S$_x$, x=1% and 1.25%) in the temperature range from 300 K to 987 K. Literature reference data of standard constantan from C.Y. Ho et al. [77] is also shown.

The thermal conductivities of the sulfur doped constantan samples are shown in Figure 40. (by Dr. Richard R. J. Qiu). Literature data by C.Y. Ho are shown for comparison [77]. With this data and the power factor result, the $ZT$ value is calculated and shown in Figure 41. Literature data by H. Muta are shown for comparison [78]. The solid green curve shows an estimation of the upper limit of $ZT$ calculated from the thermopower data by Eq. (16) in Chapter 1.5. At high temperature, the electron contribution dominates the thermal conductivity, see Eqs. (7), (8). Our results show that the $ZT$ is the maximum achievable in that type of metal, and that no further improvement can be expected from thermal conductivity reduction.
Figure 41. The calculated thermoelectric figure of merit ($ZT$) of sulfur doped constantan samples ($Cu_{0.5}Ni_{0.5})_{1-x}S_x$, $x=1\%$ and $1.25\%$) from 300 K to 900 K. Reference $ZT$ of standard constantan from H. Muta [78] is shown.
3.4 Summary

Doping copper-nickel alloys with sulfur is reported here to have improved thermoelectric properties of constantan. Data taken in a cryostat show that record high thermopower, power factor, and $ZT$ could be achieved in this material system. Unfortunately, although the data taken from the Linseis LSR-3 show higher thermopower than any literature report, we have a discrepancy in the data taken on our reference sample. This preliminary study shows that doping a few percent of nonmetal elements might be a new way to improve the thermoelectric properties of metallic thermoelectric materials. The results must be confirmed by independent measurements. We also have no microscopic theory about the role of sulfur in the thermopower of Cu-Ni alloy, aside from the observation that sulfur reduces the electron concentration and that this is correlated with thermopower improvement.
Appendix A: A Design for Thermoelectric Combustion Chambers

In this appendix, a new design for thermoelectric combustion chambers is described. This design proposes using metallic thermoelectric alloys to build the body of a combustion chamber. The new design enables this chamber to harvest additional electric power using thermoelectric effects while fulfilling basic functionalities as a combustion chamber/heat exchanger. Such design can be used to build micro generators for distributed electricity generation from household water boilers, for example. This new design avoids the drawback of the low $ZT$ value for metallic thermoelectric material that results from their high thermal conductivity. The thermoelectric conversion efficiency is no longer limited by the low $ZT$ value. Therefore metallic thermoelectric materials may be promising for high temperature applications in thermodynamic topping cycles. My contribution to this proposal is my conception of the three dimensional concentric tube design as an improvement of an earlier planar design by Dr. Heremans.
Design for Thermoelectric Combustion Chamber

In order to use the energy from exhaust to preheat the air and fuel of a combustion process and to harvest energy from the existing temperature difference between a combustion chamber and the environment, the key idea is to develop a counter-flow combustor which is, at the same time, a thermoelectric generator. A two-dimensional concept drawing is shown in Figure 42.

Figure 42. Two-dimensional schematic drawing of the thermoelectric combustion chamber, graph by Dr. Joseph P. Heremans.

This device is at the same time a combustion chamber, a counter-flow heat exchanger, and a thermoelectric power generator. The main part of this generator is made
from n-type and p-type metallic thermoelectric alloys. One the right side of Figure 42, the fuel and oxidizer streams are brought to the point where they mix. This is the location of the flame. The products of the combustion then travel back in a duct (middle path in Figure 42) that goes in the opposite direction of the incoming fuel and oxidizer. Energy from the high temperature flame is directly harvested by the thermoelectric material, the combustion products can still be used for generating steam or other heating purposes. The right side of Figure 42 is a heat source. The benefit of this design is that heat conducted through the thermoelectric material is not lost, as it is in conventional designs, but instead it is carried back into the combustion system by convection.

Figure 43. Implementation of combustion chamber, by Christine Orovets, Ref. [79].
Figure 43 is a planar three dimensional implementation of the design in Figure 42 by Christine Orovets in her undergraduate honor thesis [79]. An issue Ms. Orovet’s experiment encountered was that it is difficult to get a satisfactory seal of the channels for fuel, air and exhaust. In her experiment, the flame leaked from the combustion chamber because it was difficult to design seals that could withstand the high temperature gradient and temperature cycling. I proposed a new three dimensional design based on concentric metallic tubes that will solve this leak problem with a novel structure.

To picture this design in three dimensions, imagine rotating the two-dimensional design in Figure 42 around its central axis. Then we have a coaxial design shape. By modifying it a little, we can have the three-dimensional design. The three-dimensional combustion chamber in this invention is shown in Figure 44. This work is covered by a US utility provisional patent pending: Application number 62/055,050, “Thermoelectric Combustion Chamber”, Joseph. P. Heremans, Yibin Gao.

Figure 44 shows three co-axial tubes: the inner tube is the passage for the fuel, the duct between the inner tube and the middle tube is the exit passage for the exhaust, and the duct between the second tube and the third tube is the passage for the oxidizer (air). On one end of the tube is the combustion chamber (top end in Figure 44(a)); on the other side of the tube is the gas inlet and outlet (bottom end in Figure 44(a), see also Figure 44(d)). The temperature difference between the combustion chamber and the inlet/outlet will be used as the energy source for the thermoelectric alloys (Figure 44(b)). The innermost tube is made from one type of thermoelectric alloys (e.g., n-type), while the tube in the middle
is made from another type of thermoelectric alloys (e.g., p-type) with the opposite sign of thermopower. They make electrical and mechanical contact on the combustion chamber side (top) and they are electrically insulated on the inlet/outlet side. Leads are drawn from electrodes on the two tubes for electrical power output. Heat is conducted from the hot exhaust gas to the cold incoming fuel and oxidizer through the metallic walls.

Figure 44. Schematic drawing of the thermoelectric combustion chamber design.

Figure 44(a) and (b) shows that the inner tube and middle tube go into the outer tube of the combustion chamber. The inner tube and middle tube are made of
thermoelectric alloys, one is p-type and the other is n-type. The polarity does not matter. They are welded together close to the top end (hot side), and are separated by electrically insulating material on the bottom end (cold side, Figure 44(d)).

Figure 44. (Continued) Detailed views of the combustion chamber.

Figure 44(c) is a more detailed drawing of inner tube and middle tube.

1. Innermost tube that is the passage for fuel.

2. Middle tube (duct between middle tube and the inner tube is the passage for out-going exhaust).

3. Top of the inner tube.

4. Nozzle openings of the inner tube where combustion happens.

   Inner tube and middle tube are welded together where they make contact in this area.
5. Holes for out-going exhaust.
7. Exhaust outlet.

Figure 44(d) is a bottom and side view of all three tubes.

22. Bottom of the combustion chamber (the outside tube), made of electrically insulating material.
23. Bottom of the middle tube, made of electrically insulating material.
24. Bottom of the innermost tube, made of electrically insulating material.
25. Exhaust outlet.
26. Fuel inlet; also the lead for output voltage.

Multiple units described above can be connected electrically in parallel or in series to obtain an increase the output voltage.

The thermoelectric output power can be calculated:

\[
P_{TE} = \frac{(S_P + S_N) \Delta T^2}{R_{int}} \frac{R_{Load}}{(R_{int} + R_{Load})^2} \frac{R_{Load}}{R_{Load}/R_{int}} \frac{1}{(1 + R_{Load}/R_{int})^2}
\]

\[=(S_P + S_N)^2 \Delta T^2 \frac{R_{Load}/R_{int}}{(1 + R_{Load}/R_{int})^2}\] (30)
where $P_{TE}$ is the thermoelectric power output, $S_P$ and $S_N$ are thermopower of p-type and n-type material respectively, $\Delta T$ is the temperature difference, and $R_{int}$ and $R_{load}$ are internal resistance and load resistance respectively.

There are two major changes in Eq. (30) compare to the $ZT$ value in Eq. (2). First, the thermal conductivity, $\kappa$, no longer appears explicitly in this equation. This is because the heat transferred through the thermoelectric material is not lost, but is instead used to preheat the air. Preheating air and fuel will significantly improve the combustion efficiency of the chamber [80], and the heat conducted is then not wasted. Second, resistance appears in the equation instead of resistivity. In a device that is evaluated by the $ZT$ value, improvement in efficiency cannot be achieved by changing the dimensions of the material. Here, increasing the cross-sectional area of the thermoelectric leg will increase thermal conductance as well as electrical conductance, so the net effect cancels out. However, in this design, since thermal conductance does not explicitly appear here, changing the cross-sectional area can reduce the internal resistance, and will have a net effect on the power.

The thermoelectric combustion chamber design in Figure 44 could be used potentially for two types of applications. The first use is a natural gas water boiler, in which the electricity generated could power, for example, ventilation or lighting. If the overall efficiency surpasses the 25% break-even efficiency by a large margin, it can be used to build household micro-generator based on natural gas. The second is to use this chamber as a thermoelectric topping cycle combined with an external combustion engine. The flame temperature (~2000 °C) is much higher than household hot water temperature or the
temperature in a steam turbine. A thermoelectric topping cycle can convert the energy from this temperature gradient to electricity and add to the external combustion engine to improve the overall electricity generation efficiency.

Summary

This appendix describes a new design for a thermoelectric combustion chamber. By choosing appropriate p-type and n-type thermoelectric alloys, thermoelectric energy can be harvested to improve the overall efficiency. A high $ZT$ value is no longer the criterion for high efficiency. Thermoelectric alloys, such as the constantan alloys described in Chapter 3, that can withstand high temperature and have a high power factor may be promising in this kind of thermoelectric combustion chamber.
Appendix B: Second Order Bethe-Sommerfeld Expansion

The Mott Relation is a well-known formula that relates the thermopower $\alpha$ to the energy-dependent “Mott” conductivity $\sigma_E(E)$. The Mott Relation is extensively used when interpreting thermoelectric transport data. This chapter is a theoretical treatment of the Mott formula, discussing the many hypotheses that underlay it, which are often overlooked or even misinterpreted. Particular attention is focused on the physical meaning of $\sigma_E$. There are three versions of the Mott Relation: one general, one valid only for metals or strongly degenerately-doped semiconductors, and one valid for near-intrinsic semiconductors. The latter version, valid for lightly-doped semiconductors, is the Pisarenko relation. The version used for metals is a first-order series expansion of the transport integrals around the Fermi energy. However, it diverges when applied to semiconductors that have the Fermi energy at the band edge. We offer here a second-order expansion formula that avoids that divergence and better approximates the thermopower of semiconductors, as long as band conduction applies. There were several people that contributed to my work in this appendix. Dr. Heremans supervised this study and provided useful insights. Dr. G. Jeffrey Snyder and Dr. Bartlomiej Wiendlocha contributed useful discussions on the matter.
In his 1936 book, [81] Sir Nevill F. Mott is presumed to have been the first to give an expression for the thermoelectric power as following:

\[
\alpha = -\frac{k_B}{e} \frac{1}{\sigma} \int \sigma_E(E) \cdot \left(E - \mu\right) \cdot \left(-\frac{\partial f}{\partial E}\right) dE \quad (31)
\]

where \( f \) is the Fermi-Dirac distribution function:

\[
f(E) = \frac{1}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)} \quad (32)
\]

and \( \mu \) is the electrochemical potential, \( k_B \) is the Boltzmann constant, \( T \) is the temperature in absolute unit, \( E \) is the energy of the carrier (i.e. electrons or holes) in discussion, and \( e \) the elementary charge. The key part of this equation is the “Mott conductivity” \( \sigma_E(E) \). \( \sigma_E(E) \) is defined by the fact that its integral gives the actual electrical conductivity \( \sigma \).

\[
\sigma = \int \sigma_E(E) \cdot \left(-\frac{\partial f}{\partial E}\right) dE \quad (33)
\]

Eq. (31) was rigorously derived by Cutler and Mott [8], and is generally valid for electrical transport. For metals and degenerately doped semiconductors, the Bethe-Sommerfeld expansion of this equation around \( \mu \) gives a more famous version of the Mott Relation:

\[
\alpha = -\frac{\pi^2 k_B^2 T}{3 e} \frac{d \ln \sigma_E(E)}{dE} \bigg|_{E=\mu} \quad (34)
\]
Experimentalists have been using Eq. (34) to qualitatively explain why certain semiconductors have better thermopowers than others. The “Mott conductivity”, or “spectral conductivity”, $\sigma_E(E)$, should not be confused with electrical conductivity or anything that can be measured experimentally. The second issue is that the approximations made in the Bethe-Sommerfeld expansion are only valid in the case of metals. It is well-known that good thermoelectric semiconductors are highly-doped semiconductors [82], but typically with doping levels that fall in the regime between fully degenerate statistics (in the case of metals), and the fully dilute limit of Maxwell-Boltzmann statistics used in lightly-doped semiconductors. Here we seek to clarify those points, and to add the second term of the Bethe-Sommerfeld expansion to Eq. (34), which makes it possible to avoid the divergence of Eq. (34) when $\mu$ reaches the band edge. We point out that the derivation is only valid for solids where the conductivity is by band conduction, unlike the original Mott relation Eq.(31).

**Definitions of Key Concepts**

Before delving into mathematical derivations, it is important remind us of some key physics concepts. First, we repeat here the distinction that must be made between chemical potential and Fermi energy [83]. In statistical physics, the definition of chemical potential of a particle is the amount by which the internal energy of a system is increased when
adding one particle from vacuum to it. It is the same quantity $\mu$ that appears in the Fermi-Dirac distribution function; see Eq.(32). In metals, the energy required to remove one electron from the metal is the same as the energy released when adding one electron to the metal, see Figure 45(a), and this energy is defined as the chemical potential. However, this definition immediately raises a difficulty in the case of insulators or intrinsic semiconductors: the energies of adding and removing one electron are not the same. When adding one electron, it will go into the conduction band. But when removing one electron, it must come from the valence band, as illustrated in Figure 45(b). Therefore, the chemical potential is set as the average of the value needed to add and to remove one electron. In an ideal intrinsic semiconductor at 0 K, the chemical potential is in the middle of the band gap. The *Fermi energy* is defined as the energy equal to the chemical potential at absolute zero temperature, but it is not defined at any finite temperature. The *Fermi level* is equivalent to the chemical potential, but is different from the *Fermi energy*.

![Figure 45](image.png)

*Figure 45. Fermi energy in a (a) metal and (b) intrinsic semiconductor.*
Second, we want to emphasize that the term $\sigma_E(E)$ is not the electrical conductivity measured in experiments. As explained by Mott himself, “$\sigma_E(E)$ represents the conductivity the system would have if the energy at the surface of the Fermi distribution were $E$; its variation with $E$ is important in the discussion of the thermoelectric phenomena” (notations changed for consistency). $\sigma_E(E)$ is an imaginary quantity introduced to facilitate analysis, but it cannot be measured experimentally. To avoid confusion, we call $\sigma_E(E)$ the “Mott conductivity”, and reserve the term “electrical conductivity” for the actual conductivity of the sample, $\sigma$.

In the regime of band conduction, Mott conductivity can be expressed by the surface integral following equation [15]:

$$
\sigma_E(E) = \frac{e^2}{4\pi^3\hbar^2} \int \int \tau(k) \left( \frac{\partial E}{\partial k} \right)^2 \frac{dS}{|\nabla_k E|}
$$

(35)

where $\hbar$ is the Planck constant, $k$ is the wave vector, $\tau(k)$ is the relaxation time as a function of the wave vector, and $S$ denotes equi-energy surfaces of energy $E$ in the $k$-space.

The Bethe-Sommerfeld expansion is used to derive Eq. (34) from Eq. (31). As we will show, the limitations due to this series expansion cause Eq. (34) to deviate severely from Eq. (31) when the Fermi level is close to the band edge. We offer an alternative second-order formula to correct for this deviation.

Following John. M. Ziman in his book, “Electrons and Phonons” [84], we start from the transport integrals $L_n, (n = 0,1,2 \ldots)$ to derive electrical conductivity $\sigma$, the
thermopower $\alpha$, and the electronic thermal conductivity $\kappa_e$. The transport integrals are Eq. (36):

$$L_n = \int \sigma_E(E) \cdot \left(\frac{E - \mu}{k_B T}\right)^n \cdot \left(-\frac{\partial f}{\partial E}\right) dE$$  \hspace{1cm} (36)

Then, we can express the thermoelectric transport properties in terms of $L_n$:

$$\sigma = L_0$$  \hspace{1cm} (37)

$$\alpha = -\frac{k_B L_1}{e L_0}$$  \hspace{1cm} (38)

$$L = \frac{\kappa_e T}{\sigma} = \left(\frac{k_B}{e}\right)^2 \left[\frac{L_2}{L_0} - \left(\frac{L_1}{L_0}\right)^2\right] = \left(\frac{k_B}{e}\right)^2 \frac{L_2}{L_0} - \frac{\alpha^2}{\sigma}$$  \hspace{1cm} (39)

$\kappa_e$ is only the electronic contribution to the thermal conductivity; phonon contribution is not included in $\kappa_e$. $L$ in Eq. (39) is the Lorentz ratio, as in the Wiedemann-Franz law.

The integration range of Eq. (36) should be treated with care. From band theory we know that a full band does not conduct electricity, and only the bands that lie close enough to the chemical potential to have carriers thermally need to be included in those integrals. Further, the upper and the lower limits should be in the range of available energy states and should be cut off at the band edge, as there are no possible electrons in the band gap. However, as we will demonstrate here, there is a mathematical technique that, by extending the integration range to from $-\infty$ to $\infty$, can greatly simplify the math. But caution should be taken about when this approximation is valid. We shall also discuss this in the following.
Figure 46. Derivative of the Fermi-Dirac distribution function, \(-\frac{\partial f}{\partial E}\). It has a bell-shape curve and vanishes exponentially as the energy is away from the chemical potential \(\mu\). Light shaded area is from -3 to 3 and covers 91% of the area under the curve. Dark shaded area is from -2 to 2 and covers 76% of the area under the curve.

The transport integrals \(L_n\) involve energy derivatives of the Fermi-Dirac distribution function, \(-\frac{\partial f}{\partial E}\), which is the bell-shaped function that peaks at the chemical potential and extends several \(k_B T\) around it, shown in Figure 46. At several \(k_B T\) away from its center, this function vanishes exponentially. Although the whole energy range of the Mott conductivity is involved in the transport integrals, only the value \(\sigma_E(E)\) within a few \(k_B T\) of the chemical potential contributes significantly to transport properties. As long
as \( \sigma_E(E) \) is accurate enough near \( E - \mu \), Eq. (36) can be evaluated by approximation. Therefore if one applies the first order Taylor expansion of \( \sigma_E(E) \) around \( \mu \) (called the Bethe-Sommerfeld expansion) one would get:

\[
\sigma_E(E) \approx \sigma_E(\mu) + \left[ \frac{d \sigma_E(E)}{dE} \right]_{E=\mu} (E - \mu) \quad (40)
\]

Plug Eq. (40) into Eq. (36):

\[
L_1 = \int \sigma_E(E) \left( \frac{E - \mu}{k_B T} \right) \left( -\frac{\partial f}{\partial E} \right) dE \\
= \sigma_E(\mu) \cdot \int \left( \frac{E - \mu}{k_B T} \right) \left( -\frac{\partial f}{\partial E} \right) dE \\
+ k_B T \left[ \frac{d \sigma_E(E)}{dE} \right]_{E=\mu} \cdot \int \left( \frac{E - \mu}{k_B T} \right)^2 \left( -\frac{\partial f}{\partial E} \right) dE \quad (41)
\]

Note that:

\[
\int_{-\infty}^{\infty} \left( \frac{E - \mu}{k_B T} \right) \left( -\frac{\partial f}{\partial E} \right) dE = 0 \quad (42)
\]

Eq. (42) is true because the function \( \left( \frac{E - \mu}{k_B T} \right) \) inside the integral is an odd function of \( (E - \mu) \). As well, it is integrated over an even domain with respect to is symmetry axis \( E = \mu \). The next order function is:

\[
\int_{-\infty}^{\infty} \left( \frac{E - \mu}{k_B T} \right)^2 \left( -\frac{\partial f}{\partial E} \right) dE = \frac{\pi^2}{3} \quad (43)
\]

Combining Eqs. (37), (38), (41), (42), and (43), we can reproduce the Bethe-Sommerfeld expansion and the Mott relation for degenerate statistics:
\[
\alpha = \frac{\pi^2 k_B}{3 e k_B T} \left[ \frac{d \sigma_E(E)}{dE} \right]_{E=\mu} 
\]  

(34)

We arrived at the result of Eq. (34).

Two important approximations were made to get to Eq. (34). First, only the first order derivative is used in Eq. (40). Second, in Eq.(42) and (43), the integration is taken from \(-\infty\) to \(\infty\). If the lower integration bound was not extended to \(-\infty\), Eq. (42) will no longer hold. In fact, we know that the lower bound of this integration should be at the band edge, e.g. \(E = 0\) in our definition. The reason that Eq.(42) is a justifiable approximation is because when \(\frac{E-\mu}{k_B T} \gg 1\), \(-\frac{\partial f}{\partial E}\) is sufficiently small for \(E < 0\) (see Figure 46), and can be set arbitrarily at any finite value without affecting the result of the integration in Eq. (36). However, we know that \(\frac{E-\mu}{k_B T} \gg 1\) does not always hold for semiconducting thermoelectric materials. Therefore Eq. (42) may not hold, and it will in turn affect the validity of Eq. (34). In the following, we will develop a higher-order approximation that more accurately calculate the Mott Relation.
Mathematical Preparation

To have a higher order Bethe-Sommerfeld Expansion, we need the following mathematical tools.

Define:

\[ G_n(x) \overset{\text{def}}{=} \frac{1}{n!} \int_x^\infty \frac{z^n \exp(-z)}{[1 + \exp(-z)]^2} \, dz \tag{44} \]

Then we can integrate functions that have the form of \( x^n \left( -\frac{\partial f}{\partial x} \right) \) over any range.

\[ \int_{x_1}^{x_2} x^n \left( -\frac{\partial f}{\partial x} \right) \, dx = n! \cdot [G_n(x_1) - G_n(x_2)] \tag{45} \]

For any function that can be expanded around \( x = 0 \) by the Taylor expansion:

\[ h(x) = \sum_{n=0}^\infty \frac{h^{(n)}(x)}{n!} \bigg|_{x=0} \]

\( h^{(n)}(x) \) denotes the \( n \)-th derivative of \( h(x) \). We can write the following:

\[ \int_{x_1}^{x_2} h(x) \left( -\frac{\partial f}{\partial x} \right) \, dx = \sum_{n=0}^\infty h^{(n)}(x) \bigg|_{x=0} G_n(x_1) \tag{46} \]

More generally:

\[ \int_{x_1}^{x_2} h(x)x^m \left( -\frac{\partial f}{\partial x} \right) \, dx = \sum_{n=0}^\infty h^{(n)}(x) \bigg|_{x=0} \frac{(n + m)!}{n!} G_{n+m}(x_1) \tag{47} \]
The function of $G_n(x)$ has the following mathematical properties:

1. $G_n(x)$ decreases monotonically when $x \geq 0$.
2. $\lim_{x \to \infty} G_n(x) = 0$.
3. $G_n(0) < 1$.
4. $G_n(0) = \left(1 - \frac{1}{2^{n-1}}\right)\xi(n)$, when $n > 1$, where $\xi$ is the Riemann Zeta function.
5. $G_n(-x) = \frac{\pi^n (2^{n-2})}{n!} (-1)^{n+1} B_n - (-1)^n G_n(x)$, for $(x > 0)$, where $B_n$ is the Bernoulli number; see Table 6 below.
6. For $n = 0$ and $n = 1$, $G_n(x)$ are analytical functions:
   
   $G_0(x) = \frac{1}{1 + \exp(x)}$
   
   $G_1(x) = \frac{x}{1 + \exp(x)} + \ln[1 + \exp(x)]$

7. For $n > 1$, $G_n(x)$ can be written as expansions:
   
   $G_n(x) = -\sum_{k=0}^{n} \frac{x^k}{k!} Li_{n-k}(-e^{-x})$ for $(x > 0)$

where $Li_s(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^s}$ is the polylogarithmic function, (also known as the Jonquière's function)

Table 6. First 9 Bernoulli numbers.

<table>
<thead>
<tr>
<th>$n$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_n$</td>
<td>1</td>
<td>-1/2</td>
<td>1/6</td>
<td>0</td>
<td>-1/30</td>
<td>0</td>
<td>1/42</td>
<td>0</td>
<td>-1/30</td>
</tr>
</tbody>
</table>
The following shows useful analytical approximations for $G_n(x)$

\[
G_0(-x) = \frac{1}{1 + \exp(-x)} \\
G_1(-x) \approx \ln 2 \frac{2 + x}{1 + \exp(x)} \\
G_2(-x) \approx 2 \times \frac{\pi^2}{12} - \frac{\pi^2}{12} \frac{2 + x + \frac{x^2}{2}}{1 + \exp(x)} \\
G_3(-x) \approx \frac{3}{4} \text{Zeta}(3) \frac{2 + x + \frac{x^2}{2} + \frac{x^3}{3!}}{1 + \exp(x)} \\
\]

\[
G_{2n}(-x) \approx \frac{\pi^{2n}}{(2n)!} \frac{(2^{2n-1} - 1)}{(-1)^n} B_{2n} \cdot \left[ 2 - \frac{1 + \sum_{k=0}^{2n} \frac{x^k}{k!}}{1 + \exp(x)} \right] \\
G_{2n+1}(-x) \approx \left( 1 - \frac{1}{2^{2n}} \right) \text{Zeta}(2n + 1) \cdot \left[ 2 - \frac{1 + \sum_{k=0}^{2n+1} \frac{x^k}{k!}}{1 + \exp(x)} \right]
\]
Second Order Beth-Sommerfeld Expansion

With the previous mathematical preparation, we can derive a better approximation for the Mott Relation. First, we normalize the variables:

\[
    x = \frac{E - \mu}{k_B T}
    \]
\[
    x_\mu = \frac{\mu}{k_B T}
    \]
\[
    f(x) = \frac{1}{1 + \exp(x)}
    \tag{49}
\]

Substituting Eq. (49) in Eq. (36), the \( L_n \) integrals become:

\[
    L_n = \int_{E=0}^{\infty} \sigma_E(E) \cdot \left( \frac{E-\mu}{k_B T} \right)^n \cdot \left( -\frac{\partial f}{\partial E} \right) dE = \sigma_E(\mu) \sum_{n=0}^{\infty} \int_{x=-x_\mu}^{\infty} \sigma_E(x) \cdot x^n \cdot \left( -\frac{\partial f}{\partial x} \right) dx'
\]

To list the first few:

\[
    L_0 = \sigma_E(\mu) \left[ G_0(-x_\mu) + k_B T \frac{\sigma_E'}{\sigma_E} G_1(-x_\mu) \right]
\]
\[
    L_1 = \sigma_E(\mu) \left[ G_1(-x_\mu) + 2k_B T \frac{\sigma_E'}{\sigma_E} G_2(-x_\mu) \right]
\]
\[
    L_2 = \sigma_E(\mu) \left[ 2G_2(-x_\mu) + 3k_B T \frac{\sigma_E'}{\sigma_E} G_3(-x_\mu) \right]
    \tag{50}
\]

From a first order Taylor expansion of \( \sigma_E(E) \) around \( \mu \), we can derive:

\[
    \sigma_E(E) \approx \sigma_E(\mu) + \left[ \frac{d \sigma_E(E)}{dE} \right]_{E=\mu} (E - \mu)
\]
\[
    \approx \sigma_E(\mu) + \sigma_E'(\mu)(E - \mu)
\]
\[
    \approx \sigma_E(\mu) \left( 1 + k_B T \frac{\sigma_E'}{\sigma_E} x \right)
    \tag{51}
\]
Similarly one can derive for thermopower:

\[
\alpha = -\frac{\pi^2}{3} \frac{k_B}{e} \left( \frac{\sigma'}{\sigma} k_B T \right) \left[ 1 - \frac{1}{4} (2x_\mu + x_\mu^2) \exp(-x_\mu) \right] + \ln 2 (2 + x_\mu) \exp(-x_\mu)
\]

\[
1 + \frac{\pi^2}{3} \left( \frac{\sigma'}{\sigma} k_B T \right) (\ln 2) (2 + x_\mu) \exp(-x_\mu)
\]

Figure 47. Comparison of Thermopower calculation in a single parabolic band. The empty circles are accurate numerical integration. The red dashed line corresponds to Eq. (34), and the blue solid curve corresponds to Eq. (52).

Although Equation (52) looks more complicated than Eq. (34), it is still an analytical formula valid when \( \mu \) is 0.5\( k_B T \) into the gap. For demonstration, a comparison between the two equations and the accurate full numerical integral for a parabolic band is shown in Figure 47. It demonstrates that Eq. (52) has a better convergence where the Fermi level is a few \( k_B T \) into the band edge. This is the region into which most semiconducting thermoelectric material fall.
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