8-2011

THERMOELECTRIC PROPERTIES OF NICKEL AND TITANIUM CO-INTERCALATED TITANIUM DISELENIDE

Timothy Holgate
Clemson University, tholgat@clemson.edu

Follow this and additional works at: https://tigerprints.clemson.edu/all_dissertations
Part of the Materials Science and Engineering Commons

Recommended Citation
https://tigerprints.clemson.edu/all_dissertations/810

This Dissertation is brought to you for free and open access by the Dissertations at TigerPrints. It has been accepted for inclusion in All Dissertations by an authorized administrator of TigerPrints. For more information, please contact kokefe@clemson.edu.
THERMOELECTRIC PROPERTIES OF NICKEL AND TITANIUM CO-INTERCALATED TITANIUM DISELENIDE

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
Timothy Charles Holgate
August 2011

Accepted by:
Dr. Terry Tritt, Committee Chair
  Dr. Jian He
  Dr. Jian Luo
  Dr. Eric Skaar
  Dr. Stephen Foulger
Thermoelectric materials are involved in the direct conversion between thermal and electrical energy. They may be used to generate power from a thermal gradient or to pump heat in or out of a system when driven with DC power. Much of the recent advances in thermoelectric research have been in materials whose thermoelectric efficiency has been optimized at temperatures above room temperature where power generation is the main application.

The question that I seek to answer in this dissertation is to use our standard experimental techniques in order to assess the possibility of a class of transition metal dichalcogenides bases on TiSe$_2$ that are suitable candidates for thermoelectric applications. In addition, a further question is to understand the individual roles of intercalating titanium and nickel into the van der Waal planes of these materials and to investigate their effects on the electrical and thermal transport properties as well as the structure (including microstructure) of these materials.

The work presented herein has focused on deriving a thermoelectric material with a maximum ZT in the temperature range between 100 K and room temperature. Some of the niche applications of thermoelectric cooling in this temperature range include high-speed computing, active cooling of detectors, and most importantly, in the region of 100 to 120 K, the viability of superconducting electronic systems without the need of liquefied gasses.
Transition metal dichalcogenides are layered structures with a weakly bonded van der Waals gap between a-b planes. This gap may be intercalated by many different atomic and molecular species, which may significantly affect the structural and transport properties. Intercalation therefore provides a wide-ranging tuning “knob” for optimizing the thermal and electrical transport properties of the host material.

Several compounds chosen from this group of materials were synthesized and intercalated with 3d and 4d transition metals. Thermal and electrical transport properties were measured and the best candidate, TiSe$_2$, was chosen as the host matrix for optimization through co-intercalation with nickel and excess titanium. Additionally, the material was further optimized by the substitution of sulfur on selenium sites. While the maximum thermoelectric efficiency as judge by the dimensionless figure-of-merit ($ZT$) was increased, the temperature of that optimization ($T_{\text{max}}$) was also increased to temperatures near and above room temperature where the state-of-the-art Bi$_2$Te$_3$’s efficiency has been already optimized and is much higher than those of the materials in this work.

Though the goal of developing a material whose $ZT$ is maximized at temperatures below room temperature was not achieved, the overall thermoelectric efficiency of TiSe$_2$ has been increased by the co-intercalation of nickel and titanium, and then further increased by the substitution of selenium with sulfur. The individual roles of each of the intercalants, as well as the substitution of sulfur, in the manipulation and optimization of the thermal and electrical transport properties have been analyzed and understood in terms of fundamental solid-state theory and principles and are explained herein.
DEDICATION

I dedicate this dissertation to the two men who most influenced and inspired me to love science and learning, but certainly not just the learning of science. These men have both done so much to broaden my thinking and understanding of world and the people in it. From them I have learned of history, politics, philosophy, patience, service, charity, and grace. I hope that I have given to them at least a fraction of what I’ve received, or perhaps, as I know would be their wishes, that someday I may give a full measure to those who will come into my life as I did theirs. While serving as two of the greatest mentors I’ve ever known, they have both become dear friends I hope to keep for life: Wynn Mott and Jian He.
ACKNOWLEDGMENTS

First of all, I would like to thank my advisor and friend, Dr. Terry Tritt, who accepted me into his group without hesitation when he was not looking to add to his numbers. Dr. Tritt has given me many wonderful opportunities, more than generous support, and years of friendship and mentorship. Being connected to his name alone has done me a great service. He has played the role of friend, mentor, teacher, and worthy adversary (in pool volleyball). To ask for more in an advisor would be like getting a Ferrari and not liking the color.

To the rest of my committee, I am very appreciative. A heart felt thanks goes out to Dr. Jian Luo, Dr. Stephen Foulger, Dr. Eric Skaar, and Dr. Jian He for giving up their time to serve on my committee. Furthermore, I appreciate the support, encouragement, and many helpful suggestions that brought this work to fruition.

I would also like to thank all of my fellow group members, past and present, who have made my time at Clemson an enjoyable one. To Dr. Jian He, from whom I have learned a great many things; to Dr. Liebenberg, from whom I have received a great deal of encouragement; to Dr. Xiaohua Ji, who gave me my Chinese name; to Brad and Justine Edwards, who made my first two years a whole lot of fun; to Su Zhe, for all the laughs (even when I was the only one laughing); to Dr. Florin Lung, who was my first and most interesting officemate; to Dale Hitchcock, my friend, officemate, occasional landlord, drinking buddy, and there when I needed him; to Jennifer Graff, a great friend
and thermocouple maker; to Song Zhu and his wife Milan, for all the dumplings, and to all the others of the Tritt group, I owe my deepest gratitude.

I like to thank the collaborators, researchers, and technicians outside of Clemson University that have contributed to this work. First and foremost, I would like to thank Dr. Holger Kleinke of the University of Waterloo, with whom I have collaborated for most of my graduate career. Dr. Kleinke has also been a great source of encouragement, knowledge, and friendship. Were Canada not so cold, I would have begged for a postdoctoral position in his group. I would further like to thank Chris Fleisher at the University of Georgia for EPMA data and the tours of the UGA campus, as well as Dr. Ma at the University of South Carolina’s College of Engineering and Computing for the X-ray photoelectron spectroscopy data. My gratitude also goes out to Dr. Yonggao (Jack) Yan at the National Institute of Standards and Technology for assistance with low temperature heat capacity measurements.

Finally, I would like to thank the fellow graduate and undergraduate students in my group who assisted me with sample synthesis (Matthew Hendrix), literature searches and various calculations (Menghan Zhou), low temperature thermal conductivity measurements (Song Zhu), and VSM measurements (Dale Hitchcock and Dr. Jian He). You assistance was invaluable and much appreciated.
TABLE OF CONTENTS

TITLE PAGE ................................................................. i
ABSTRACT ...................................................................... ii
DEDICATION .................................................................... iv
ACKNOWLEDGMENTS .................................................... v
LIST OF TABLES .......................................................... ix
LIST OF FIGURES ......................................................... x

CHAPTER

I. Introduction to Thermoelectrics .............................................. 1
   Thermoelectric Materials .................................................. 1
   Seebeck and Peltier Effects ................................................. 7
   Thermal and Electrical Transport ...................................... 11

II. Material Introduction ....................................................... 27
   Chalcogenides and Thermoelectrics ................................... 27
   Structures of Transition Metal Dichalcogenides .................. 28
   Charge Density Waves .................................................... 30
   Intercalation .................................................................. 31
   The Uniqueness of Titanium Diselenide ............................. 32
   Current Thermoelectric Studies ...................................... 33

III. Measurement Systems and Techniques ................................. 38
   Low Temperature Transport .......................................... 38
      Seebeck and Electrical Resistivity ................................ 38
      Thermal Conductivity .............................................. 41
      Hall Coefficient ...................................................... 45
      Specific Heat Capacity ............................................. 48
   High Temperature Transport ......................................... 50
      Seebeck and Electrical Resistivity ................................ 50
      Thermal Conductivity and Diffusivity ......................... 53
      Differential Scanning Calorimetry ................................. 55
Table of Contents (Continued)

IV. Synthesis and Processing ...........................................................................60
  Sample Synthesis ..................................................................................60
  Processing ..........................................................................................62
  Compositional Analysis .......................................................................73
  Sample Density ..................................................................................74

V. Structural and Compositional Analysis .....................................................67
  Structure Analysis Using X-ray Diffraction .........................................67
  Compositional Analysis .......................................................................73
  Sample Density ..................................................................................74

VI. Thermal Transport Properties ..................................................................83
  Low Temperature Specific Heat Capacity of Ni$_x$Ti$_{1+\delta}$Se$_2$ .............83
  Low Temperature Thermal Conductivity of Ni$_x$Ti$_{1+\delta}$Se$_2$ ...............84
  Low Temperature Thermal Conductivity of Ni$_x$Ti$_{1+\delta}$Se$_{2-y}$S$_y$ .......86

VII. Electronic Transport Properties .............................................................97
  Electrical Resistivity and Seebeck of Ni$_x$Ti$_{1+\delta}$Se$_2$ .......................97
  Low Temperature Electrical Resistivity and Seebeck
  of Ni$_x$Ti$_{1+\delta}$Se$_{2-y}$S$_y$ ..................................................................99

VIII. Conclusion and Final Remarks ............................................................110

APPENDICES ..............................................................................................113
  A: Band Structure and Density of States Calculations .........................113
  B: Magnetic Susceptibility of Ni$_x$Ti$_{1+\delta}$Se$_2$ ..................................116
  C: Complete Sample List ......................................................................121

REFERENCES .............................................................................................123
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Profile of elements used for synthesis</td>
</tr>
<tr>
<td>4.2</td>
<td>Synthesis parameters</td>
</tr>
<tr>
<td>4.3</td>
<td>Samples synthesized</td>
</tr>
<tr>
<td>4.4</td>
<td>Spark plasma sintering (SPS) program parameters</td>
</tr>
<tr>
<td>5.1</td>
<td>X-ray diffraction (XRD) pattern overlay of before and after SPS processing</td>
</tr>
<tr>
<td>5.2</td>
<td>Lattice parameters calculated from high resolution XRD patterns</td>
</tr>
<tr>
<td>5.3</td>
<td>Interplanar spacing of peaks</td>
</tr>
<tr>
<td>5.4</td>
<td>Results of the deconvolution of the (0 0 1) peak in XCh115</td>
</tr>
<tr>
<td>5.5</td>
<td>Nickel concentrations and secondary (0 0 1) peak positions</td>
</tr>
<tr>
<td>5.6</td>
<td>Electron probe microanalysis (EPMA) compositions normalized to two selenium per formula</td>
</tr>
<tr>
<td>5.7</td>
<td>Comparison of measured to theoretical densities of two normalization schemes: one titanium; two selenium</td>
</tr>
<tr>
<td>5.8</td>
<td>Phase fractions used in estimating theoretical density</td>
</tr>
<tr>
<td>5.9</td>
<td>Comparison of measured and estimated densities using two phase scenario</td>
</tr>
<tr>
<td>5.10</td>
<td>Contributed of each phase to the total density</td>
</tr>
<tr>
<td>5.11</td>
<td>Lattice parameters and densities of Ni$<em>x$Ti$</em>{1-x}$Se$_{2-y}$S$_y$</td>
</tr>
<tr>
<td>6.1</td>
<td>Low temperature heat capacity fit parameters</td>
</tr>
<tr>
<td>B-1</td>
<td>Magnetic fit parameters of the magnetic susceptibility</td>
</tr>
<tr>
<td>C-1</td>
<td>Complete sample list</td>
</tr>
<tr>
<td>C-2</td>
<td>Sample list with nominal composition, room temperature transport properties, and SPS conditions</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Thermopower, electrical conductivity, and power factor versus carrier concentration</td>
<td>24</td>
</tr>
<tr>
<td>1.2</td>
<td>Sample band structure plot</td>
<td>24</td>
</tr>
<tr>
<td>1.3</td>
<td>Density of occupied states</td>
<td>25</td>
</tr>
<tr>
<td>1.4</td>
<td>Schematic band structures of metals, semimetals, semiconductors and insulators</td>
<td>25</td>
</tr>
<tr>
<td>1.5</td>
<td>The Seebeck effect from a density of states perspective</td>
<td>26</td>
</tr>
<tr>
<td>1.6</td>
<td>Effect of thermal and electric potential gradients on the Fermi surface</td>
<td>26</td>
</tr>
<tr>
<td>1.7</td>
<td>Two carrier conduction under thermal and electric fields</td>
<td>26</td>
</tr>
<tr>
<td>2.1</td>
<td>1T and 2H polytypes of MX&lt;sub&gt;2&lt;/sub&gt;</td>
<td>34</td>
</tr>
<tr>
<td>2.2</td>
<td>Fermi surface of TiSe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>35</td>
</tr>
<tr>
<td>2.3</td>
<td>TiSe&lt;sub&gt;2&lt;/sub&gt; band structure</td>
<td>36</td>
</tr>
<tr>
<td>2.4</td>
<td>Trigonal unit cell of TiSe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>37</td>
</tr>
<tr>
<td>3.1</td>
<td>Low temperature Seebeck and resistivity mount</td>
<td>56</td>
</tr>
<tr>
<td>3.2</td>
<td>Low temperature thermal conductivity mount</td>
<td>57</td>
</tr>
<tr>
<td>3.3</td>
<td>Hall coefficient measurement configuration</td>
<td>58</td>
</tr>
<tr>
<td>3.4</td>
<td>Thermocouple placement on ZEM-2</td>
<td>59</td>
</tr>
<tr>
<td>3.5</td>
<td>ZEM-2 probe configuration</td>
<td>59</td>
</tr>
<tr>
<td>5.1</td>
<td>Overlay of XRD patterns taken before and after SPS processing</td>
<td>80</td>
</tr>
<tr>
<td>5.2</td>
<td>(0 0 1) peak of XCh115 with one and two peak fits</td>
<td>81</td>
</tr>
<tr>
<td>5.3</td>
<td>Deconvolution of the (0 0 1) peaks of XCh124 and XCh119</td>
<td>82</td>
</tr>
<tr>
<td>6.1</td>
<td>Low temperature heat capacity with Dulong-Petit limit</td>
<td>88</td>
</tr>
<tr>
<td>6.2</td>
<td>Heat capacity below 5 K with c&lt;sub&gt;p&lt;/sub&gt;/T vs. T&lt;sup&gt;2&lt;/sup&gt; inset</td>
<td>89</td>
</tr>
<tr>
<td>6.3</td>
<td>Measure and estimated density versus Debye temperature</td>
<td>90</td>
</tr>
<tr>
<td>6.4</td>
<td>Total thermal conductivity of Ni&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;1+y&lt;/sub&gt;Se&lt;sub&gt;2&lt;/sub&gt;</td>
<td>91</td>
</tr>
<tr>
<td>6.5</td>
<td>Contributions to the measured thermal conductivity</td>
<td>92</td>
</tr>
<tr>
<td>6.6</td>
<td>Lattice thermal conductivity of Ni&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;1+y&lt;/sub&gt;Se&lt;sub&gt;2&lt;/sub&gt;</td>
<td>93</td>
</tr>
<tr>
<td>6.7</td>
<td>Total thermal conductivity of Ni&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;1+y&lt;/sub&gt;Se&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;y&lt;/sub&gt;</td>
<td>94</td>
</tr>
<tr>
<td>6.8</td>
<td>Radiation corrected total thermal conductivity of Ni&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;1+y&lt;/sub&gt;Se&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;y&lt;/sub&gt;</td>
<td>95</td>
</tr>
<tr>
<td>6.9</td>
<td>Radiation corrected lattice thermal conductivity of Ni&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;1+y&lt;/sub&gt;Se&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;y&lt;/sub&gt;</td>
<td>96</td>
</tr>
<tr>
<td>7.1</td>
<td>Low temperature electrical resistivity of Ni&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;1+y&lt;/sub&gt;Se&lt;sub&gt;2&lt;/sub&gt;</td>
<td>101</td>
</tr>
<tr>
<td>7.2</td>
<td>Low and high temperature Seebeck Coefficient of Ni&lt;sub&gt;x&lt;/sub&gt;Ti&lt;sub&gt;1+y&lt;/sub&gt;Se&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;y&lt;/sub&gt; with reference data</td>
<td>102</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>Low temperature Seebeck coefficient of Ni$<em>x$Ti$</em>{1+y}$Se$_{2-y}$S$_y$ with reference data</td>
<td>103</td>
</tr>
<tr>
<td>7.4</td>
<td>Low temperature power factor of Ni$<em>x$Ti$</em>{1+y}$Se$_2$</td>
<td>104</td>
</tr>
<tr>
<td>7.5</td>
<td>Low and high temperature power factor of Ni$<em>x$Ti$</em>{1+y}$Se$_2$</td>
<td>105</td>
</tr>
<tr>
<td>7.6</td>
<td>Effective carrier concentration versus temperature of Ni$<em>x$Ti$</em>{1+y}$Se$_2$</td>
<td>106</td>
</tr>
<tr>
<td>7.7</td>
<td>Low temperature electrical resistivity of Ni$<em>x$Ti$</em>{1+y}$Se$_{2-y}$S$_y$ with reference data</td>
<td>107</td>
</tr>
<tr>
<td>7.8</td>
<td>Low temperature Seebeck coefficient of Ni$<em>x$Ti$</em>{1+y}$Se$_{2-y}$S$_y$ with reference data</td>
<td>108</td>
</tr>
<tr>
<td>7.9</td>
<td>Low temperature power factor of Ni$<em>x$Ti$</em>{1+y}$Se$_{2-y}$S$_y$ with reference data</td>
<td>109</td>
</tr>
<tr>
<td>8.1</td>
<td>Low temperature $ZT$ of Ni$<em>x$Ti$</em>{1+y}$Se$_{2-y}$S$_y$ with reference data</td>
<td>112</td>
</tr>
<tr>
<td>A-1</td>
<td>Density of electronic state (DOS) of TiSe$_2$ and TiSe</td>
<td>114</td>
</tr>
<tr>
<td>A-2</td>
<td>DOS of Ni$_{0.25}$TiSe$<em>2$ and Ti$</em>{1.25}$Se$_2$</td>
<td>115</td>
</tr>
</tbody>
</table>
CHAPTER ONE

INTRODUCTION TO THERMOELECTRICS

Thermoelectric Materials

In the May 1959 issue of Physics Today, George Vineyard wrote a book review in which he began by telling of a report from a news correspondent from Hong Kong that said “a strange device was being exported from Red China, capable of powering a radio by the heat from a kerosene lamp.”\(^1\) Vineyard then pointed out that the book on which he was writing a review contained photos, diagrams, details, and some theoretical descriptions of this device.\(^2\) This book was actually a reprinting of two books written by Abram Ioffe et al. and was published in Russian three years earlier. At this time, thermoelectrics research had been underway for half a century.

In 1929, Ioffe indicated that semiconductors were the best candidates for thermoelectric power generation. This was later reiterated by H. J. Goldsmid and R. W. Douglas in 1954.\(^3\) To understand the attractiveness of semiconductors one must understand how the thermal and electronic transport properties are related to the thermoelectric efficiency of a material. In 1910, Altenkirch first attempted to describe the thermoelectric efficiency.\(^4\) Ioffe later presented the Z parameter from which we get the modern “dimensionless figure-of-merit”, \(ZT\):\(^5\)

\[
ZT = \frac{\alpha^2}{\rho \kappa} T = \frac{\alpha^2 \sigma}{\kappa} T \tag{1.1}
\]
The $Z$ parameter is simply a convenient collection of the material transport parameters ($a$: Seebeck coefficient, $\rho$: electrical resistivity, $\sigma$: electrical conductivity, $\kappa$: thermal conductivity, and $T$: temperature in Kelvin) that are used in the derivation of the overall conversion efficiency defined as the power produced by the power supplied to the system. For thermoelectric power generation, this becomes the electrical power output by the system ($P = EJ$, where $J$ is the current density and $E$ is the electric field that consist of contributions from both Ohm’s law and the Seebeck effect: $E = -\rho J + a\nabla T$) divided by the heat flux (typically in Watts/cm$^2$) into the system ($Q = \alpha TJ + \kappa\nabla T$, in which the first term is the reversible Peltier heat term and the second is the irreversible Fourier heat flow term. Note that this formulation uses the electrical linear power density and linear thermal flux. To obtain the efficiency of the entire thermoelectric element, the $P/Q$ ratio must be integrated over the entire length of the element through a change of variable: $dx = dT / \nabla T$:

$$\eta_{\text{max}} = \int_{x=0}^{L} \frac{P}{Q} \, dx = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \frac{1}{\nabla T} \frac{P}{Q} dT = (\frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}) \left[ \frac{\sqrt{1 + ZT_m}}{\sqrt{1 + ZT_m} + \frac{T_{\text{cold}}}{T_{\text{hot}}}} \right]$$

(1.2)

Here $T_m$ is the temperature at which $ZT$ is a maximum, and the efficiency will therefore be maximized when $T_m$ is the average of $T_{\text{hot}}$ and $T_{\text{cold}}$ ($T_m = (T_{\text{hot}} + T_{\text{cold}}) / 2$). In the limit that $ZT$ is very large the maximum efficiency reaches the Carnot efficiency, which is the first term in parentheses in Eqn. 1.2. It can also be seen here that maximizing the $\Delta T$ maximized both the Carnot efficiency as well as the thermoelectric portion of Eq. 1.2 (this, of course, ignores the fact that $ZT$ is temperature dependent is not
necessarily constant across a materials under a temperature gradient). In the case of Peltier cooling, the overall conversion efficiency, $\phi$, is maximized by minimizing the $\Delta T$. This is consistent with conceptual thinking as one may imagine what happens to a Peltier cooling system just after being switched on: immediately after, as the $\Delta T$ is zero, it is easy to begin “pumping” heat from one side to the other.

$$\phi = \left( \frac{T_{\text{cold}}}{T_{\text{hot}}} \right) \left[ \frac{\sqrt{1 + ZT_m} - \left( \frac{T_{\text{hot}}}{T_{\text{cold}}} \right)}{\sqrt{1 + ZT_m} + 1} \right]$$  \hspace{1cm} (1.3)

From this representation it is clear that a good thermoelectric material will possess a high Seebeck coefficient ($\alpha$), a high electrical thermal conductivity ($\sigma$), and a low total thermal conductivity ($\kappa$). Optimizing these parameters simultaneously has long since proven to be quite difficult as they are interdependent. For reasons explained later in this chapter, the Seebeck coefficient is somewhat less coupled to the thermal conductivity whereas the electrical and thermal conductivities are coupled, since the electrons can carry energy (heat) as well as charge. This fact in addition to $ZT$ being proportional to $\alpha^2$ and only linearly dependent on the electrical conductivity leads one to agree with Ioffe and Goldsmid in that a greater gain in $ZT$ can be achieved in semiconductors (high $\alpha$, moderate $\sigma$) over metals (low $\alpha$, very high $\sigma$).

One way in which the classification of a material as an insulator, semiconductor, or a metal may be determined is by the carrier concentration, $n$. While the electrical conductivity is directly proportional to the carrier concentration, that of the Seebeck coefficient is inversely proportional with different specific dependencies for different regions of the carrier concentration spectrum. By observing a graph of $\alpha^2$ and $\sigma$ plotted
with arbitrary units versus the carrier concentration, an approximate dependence of the thermoelectric power factor (the numerator of Eq. (1.1)—\( PF = \alpha^2 \sigma T \)) on the carrier concentration \( (n) \) may be estimated, as first shown by Ioffe over 50 years ago. The results suggest that the \( PF \) will be maximum when \( n \) is on the order of \( \sim 10^{18}-10^{19} \) cm\(^{-3} \) (Fig. 1.1). The precise \( n \) for which the \( PF \) is maximized is material specific as \( \alpha \) and \( \sigma \) are affected not only by the carrier concentration, but also by the carrier mobilities. One consequence of the relationship between \( \sigma \) and \( n \), however, is that the magnitude and temperature dependence of the electrical conductivity may be used as a rough indicator of a materials classification, but conductivity is not the most fundamental choice.

Strictly speaking, the classification of a material as an insulator, semiconductor, semimetal, or metal is made by investigating the electronic band structure. The kinetic energy states available to electrons in a material (those quantum mechanically allowable when the periodic potentials of the nuclei are considered) as a function of the wave vector \( (k) \) may be calculated along various directions (in reciprocal \( k \)-space) of the crystal. In the simplest case (no thermal or other excitations) the electrons that come with the nuclei will fill the states from the lowest energy states on up while obeying the Pauli-Exclusion principle. The energy of the highest occupied state is known as the Fermi energy \( (E_F = \varepsilon_{highest\ occupied} (T = 0)) \). This construct is known as the band structure of a material; an example is shown in Fig. 1.2.

At finite temperatures it becomes statistically probable that electrons will be excited into higher energy states. As electrons are Fermions, they obey Fermi-Dirac statistics and the number density of electrons with energies of a given interval comes
from integrating the density of occupied states (the product of the temperature dependent Fermi distribution function and the density of allowable energy states) over the interval:

\[ n_{(\Delta E)} = \int_{E}^{E+\Delta E} f(\varepsilon) \cdot g(\varepsilon) \cdot d\varepsilon \quad (1.4)\]

where \( n_{(\Delta E)} \) is the concentration of electrons with energies in the interval \([E, \Delta E]\), \( f(\varepsilon) \) is the Fermi (Fermi-Dirac) distribution function:

\[ f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)k_B T} + 1}, \quad (1.5)\]

and \( g(\varepsilon) \) is the density of electronic states:

\[ g(\varepsilon) \equiv \frac{dN}{d\varepsilon} \text{ (the number of states per unit energy)} \quad (1.6)\]

This is schematically represented for an n-type semiconductor in Fig. 1.3, where it can be seen that the average energy of conduction electrons can be defined and is not necessarily equal to the Fermi level, \( \mu \). Later the charge carrier mobilities will be defined with the same Greek letter \( \mu \), but will carry a subscript.

At absolute zero, the Fermi distribution function is a step function at the Fermi energy with \( f(\varepsilon < E_F) = 1 \) and \( f(\varepsilon > E_F) = 0 \). For non-zero temperatures this step becomes an exponentially sloped function. Since \( f(\varepsilon) \) is a statistical distribution and electrons are fermions, the energy at which \( f(\varepsilon) = 1/2 \) has a particularly significant meaning: a state with this energy has the same probability of being occupied as being unoccupied. Thus, this energy level, known as the Fermi level in semiconductor physics, is equivalent to the chemical potential: \( \mu = \varepsilon_{f=\mu/2} \). Since the total number of fermions must always be conserved, \( \mu \) must change with temperature in a way such that Eq. (1.4)
will be constant when integrated over all energies. For metals, then only the electrons within \( k_B T \) of \( \mu \) contribute to the conduction and they obey Fermi Dirac statistics, however for a semiconductor there are many more allowable states in the conduction band than electrons that could occupy these states, therefore Boltzmann probability statistics can be used for describing both intrinsic and non-degenerate semiconductors.

The construct described above allows for the electronic classification of materials in terms of the Fermi energy and the density of states near the \( E_F \). In the case of semiconductors, there is a region just above or below \( E_F \) where \( g(\epsilon) = 0 \) for given energy interval. This region of forbidden energies is called the band gap, and the bands just below the gap are called the valance band while those above the gap are known as the conduction band. When the bandgap is on the order of ~1 – 100 \( k_B T \)—i.e.: ~0.02 to 2 eV at 300K—thermal excitation of electrons across the gap is probable at finite temperatures. This excitation of electrons across the bandgap and into the conduction band leaves a hole behind in the valence band. This hole may propagate throughout the material as an electron from the valence band of an adjacent atom ‘jumps’ laterally (in terms of energy) to fill it until it is filled by an electron that ‘relaxes’ from a conduction band. Since the population of electrons in the conduction band depends on the size of the bandgap and temperature, the carrier concentration and electrical conductivity of a semiconductor is relatively low and also heavily temperature dependent.

When the bandgap is larger, on the order of several eV, excitation of carriers across the gap is very improbable (at least at temperatures relevant to most any application in the lab or in industry) and the material will be electronically insulating.
Remembering that electronic bands are made up of allowable energy states mapped through reciprocal $k$-space, one can understand a semimetal as the result of overlapping bands near $E_F$. This scenario is referred to as a negative bandgap that can be direct or indirect (overlapping at different $k$-points). While the density of states is non-zero near the Fermi energy, it is still low relative to that of a metal. This results in a carrier concentration and electrical conductivity that is much less than that of a metal, typically by a factor of 1000 or so for the conductivity.

Metals may be uniquely defined as a material that has a well defined Fermi surface, which is defined as a continuous function of constant energy ($E_F$, in particular) that is mapped throughout three-dimensional $k$-space. At $T=0$, all electronic states inside this surface are filled while all states outside are empty. While semimetals and semiconductors may contain regions of $k$-space where ‘pockets’ of a continuous surface exist, only metals have a continuous Fermi surface everywhere.

*Seebeck and Peltier Effects*

Thermoelectricity involves the direct conversion from thermal to electrical energy and a particular way of transporting heat by electronic conduction. The first is achieved by the Seebeck effect while the latter is known as the Peltier effect. In 1821, Thomas Johann Seebeck noticed that upon heating one junction of a loop of two dissimilar metals the needle of a nearby compass was deflected. What Seebeck thought was a thermo-magnetic effect was actually due to magnetic induction arising from a current in the wire.
loop. The current was a result of an electric field produced from what is now known as the Seebeck effect.

The electric field produced in Seebeck’s experiment was actually the result of two competing electric fields. Since only one junction of the loop was heated, each of the two dissimilar metals experienced a thermal gradient. At first, let us consider what is happening in just one of the wires. At the “hot” end of the wire the average energy of the electrons in the conduction bands is shifted towards higher energy due to the increase in thermal energy, and more directly, a change in the electronic distribution function, which is a product of the temperature dependent Fermi-Dirac occupation function (which is universal) and the electron density of states (which is system-dependent) (Fig. 1.4).

A difference in the average energy of the conduction electrons of the two ends of a material will cause the electrons to migrate towards the “cold” end where there are unoccupied states with lower energies relative to the average energy of the “hot” side electrons. As the Fermi-Dirac occupation function at the cold end is shifted upward by the rising electric field produced by the accumulation of electrons, the average energy of the conduction electrons will be uniform across the sample and there will be no more net migration of electrons (Fig. 1.5). A more simplistic explanation, at least in metals, is understood by seeing the conduction electrons as a free flowing gas of electrons, known as a “Fermi-gas”. Heating one end of a material will cause an increase in the thermodynamic chemical potential of the electrons there, and they will therefore diffuse to the cold end until the forces due to coulomb repulsion balance the forces of the thermal diffusion.
In either case, the net flow of electrons towards the cold end of a material due to a thermal difference will result in a potential difference between the two ends. In fact, it is more correct to talk in terms of spatial gradients—a thermal gradient in a material will produce an electric potential gradient. These two are proportional to each other by what is known as the Seebeck coefficient:

\[ \nabla V = -\alpha \cdot \nabla T \]  

(1.7)

One may immediately notice two important properties of the Seebeck coefficient. The first is that it is fundamentally a rank two tensor. In the case that a material is homogeneous, or in the case that one is only concerned about the overall Seebeck coefficient of a composite, one may evaluate the situation just at two spatial points of the system. For instance, by elevating the temperature of one end of a wire while thermally sinking the other, and then measuring the resulting potential difference between the two ends, one can determine the overall Seebeck coefficient of the material:

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

(1.8)

From this notation a second important property is clear—the sign of the Seebeck coefficient will typically indicate whether the dominate carriers are holes or electrons in a semiconductor. It can be a bit more complicated in a metal where a term of \((d\sigma/dE)\) at \(E = E_F\) is involved. In the simpler description, if the material is predominantly n-type, and only electrons are involved in conduction, the end with a higher temperature will have fewer electrons and therefore have a higher, or less negative, potential. This will result in both \(\Delta V\) and \(\Delta T\) being positive, and thus \(\alpha\) being negative. With degenerate
semiconductors and semimetals there is often both hole and electron bands contributing
to electrical transport and the resulting Seebeck coefficient, at any particular temperature,
will take the sign of the dominant carrier at that temperature. Determining the dominant
carrier involves more than just the ratio of electrons to holes. The electron and hole
mobilities and effective masses as well as their temperature dependences must also be
considered.

While the Seebeck effect can be used for generating power from a thermal
gradient, the related Peltier effect uses electrical power to actively heat or cool a system.
In 1834, Jean-Charles Peltier discovered that current flowing through a junction of
dissimilar metals caused the junction’s temperature to either increase or decrease,
depending on the direction of the current. In truth, the Peltier Effect is a result of a
difference in the Fermi levels (or chemical potentials) of the two dissimilar materials,
when brought in contact with each other. As the charge carrier moves through this
junction it will either gain or reject energy through the absorption or rejection of heat.

Since the Fermi level describes the average energy of the most energetic
conduction electrons, an electron driven by an electric field across a junction from a
lower Fermi level to a higher will need to absorb heat from the lattice of the material with
the lower Fermi level. When current is reversed, the electrons (or holes) will dump heat
back to the lattice as they go from a higher Fermi level to a lower. The rate of heat being
absorbed or emitted to the lattice at a junction is proportional to current:

$$\dot{Q} = \Pi \cdot I$$  \hspace{1cm} (1.9)
The Peltier coefficient (\( \Pi \)) is actually defined in terms of a current loop and is defined by the relative coefficient of the two dissimilar materials, which is directly related to the relative Seebeck coefficient of the materials.

\[
\dot{Q} = \Pi_{AB} \cdot I = (\Pi_A - \Pi_B) \cdot I = (\alpha_A - \alpha_B) T \cdot I
\]  

(1.10)

**Thermal and Electrical Transport**

Both thermal (phonons) and electronic (electrons, electron holes) quanta may propagate through a medium when acted upon by driving forces. The motive response is proportional to the driving force by a quantity that is an inherent property of the material. In a sort of \( F = m \cdot a \) construct (more relevantly: \( a = m^{-1} \cdot F \)) the thermal (\( \kappa \)) and electrical (\( \sigma \)) conductivities relate the rate of flow of heat (\( \dot{Q} \)) or charge (\( \dot{J}_e \)) under a thermal (\( \nabla T \)) or potential (\( \nabla V = -\nabla V \)) gradient, respectively.

Thermal: \( \dot{Q} = -\kappa \nabla T \)  

Electrical: \( \dot{J}_e = \sigma \nabla V \)  

(1.11)  

(1.12)

This formulation assumes the steady-state condition where only one driving potential is present and that both the thermal and electrical conductivities are isotropic. The reality of the situation is that there are cross-terms that arise from the interplay between phonons and electrons. Eq. 1.13 is the matrix representation two interdependent fluxes occurring in a system with \( L_{12} \) and \( L_{21} \) being the cross-terms:

\[
\begin{bmatrix}
\dot{J}_e \\
\dot{Q}
\end{bmatrix} =
\begin{bmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{bmatrix}
\begin{bmatrix}
\nabla V \\
-\nabla T
\end{bmatrix}
\]  

(1.13)
Lord Kelvin was the first to address this issue using a pseudo-thermodynamical approach that resulted in the Kelvin relations of thermoelectricity. Later Onsager revisited this problem and showed in general that the cross terms between multiple interdependent, irreversible processes of a system are reciprocal in the absence of magnetic field. H.B. Callen pointed out that “the trick” to obtaining full physical meaning from the parameters from Onsager’s relations depends on picking the correct driving forces for the system. While Eq. (1.13) allows one to easily arrive at $L_{11} = \sigma$ and $L_{22} = \kappa$, the cross-terms do not lead to physically meaningful quantities. Callen showed that by first relating the rate of entropy production to the flow of charge and heat, a more meaningful formulation could be obtained where the driving forces are the gradients of the electrochemical potential and inverse temperature.

$$T \dot{S} = \bar{U} - \mu \bar{J} , \ \nabla_i \cdot \dot{S} = \dot{S} \rightarrow \dot{S} = \nabla_i \cdot \left( \frac{1}{T} \right) \left( \nabla \left( \frac{1}{T} \right) \right) \cdot \bar{J} - \frac{1}{T} \nabla \cdot \mu \cdot \bar{J}$$

(1.14)

In Eq. 1.14 the arrows above a quantity represents a flux density of that quantity. Also, note that here $\bar{J}$ is the particle current density of electrons and not the charge current density—$\bar{J}_e = e\bar{J}$. Since entropy production is a sum of all driving forces multiplied by their resulting flux densities—$\dot{S} = \sum_i \bar{F}_i \cdot \bar{J}_i$, we arrive at the following driving forces:

$$\begin{pmatrix} -J \\ Q \end{pmatrix} = \begin{pmatrix} L_{11} & L_{21} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} T^{-1} \nabla \mu_e \\ \nabla (T^{-1}) \end{pmatrix}$$

(1.15)
By comparing Eq. (1.15) with the steadystate scenario where $\bar{J} = 0$ to the Fourier heat equation ($\bar{Q} = -\kappa \nabla T$) the thermal conductivity may be written as a function of the \( L_{ij} \)'s:

\[
\kappa = \frac{L_{11}L_{22} - L_{12}L_{21}}{T^2 L_{11}} \quad \text{(1.16)}
\]

Since Onsager showed that \( L_{12} = L_{21} \), \( \kappa \) now becomes \( \kappa = (L_{11}L_{22} - L_{12}^2) / (T^2 L_{11}) \), and like Callen, I will collect the terms in the numerator (which is in fact the determinant of \( L_{ij} \)) and call them \( D \):

\[
\kappa = \frac{D}{L_{11} T^2} \quad \text{(1.17)}
\]

In the scenario where the system is isothermal (\( \nabla T = 0 \)) and writing the electrical current density in terms of the electrical conductivity and the gradient of the electrochemical potential (\( \bar{J}_e = e\bar{J} = -\sigma (\nabla \mu_e / e) \)), the electrical conductivity can also be written in terms of \( L_{ij} \):

\[
\sigma = \frac{e^2 L_{11}}{T} \quad \text{(1.18)}
\]

Knowing that the rate of heat flow is related to the rate of entropy flow by temperature (\( \bar{Q} = T \bar{S} \)), solving the first element of Eq. (1.15) (\( \bar{J} \)) for \( \nabla \mu \), substituting it into the second element of Eq. (1.15) (\( \bar{Q} \)), and then dividing by \( T \) gives the rate of entropy flow (Eq. (1.19)). As with solving for \( \kappa \) in the previous paragraph, a change of variable in the gradient was used (\( \nabla x^{-1} = (\partial / \partial x) T^{-1} = (dT / dx)(\partial / \partial T) T^{-1} = -\nabla T / T^2 \)).
\[
\dot{S} = \frac{-L_{22}}{eL_1T} J_e - \frac{D}{L_1T^2} \nabla T
\]  

(1.19)

This formulation is meaningful because it allows for the defining of the entropy flow in terms of parameters that can be macroscopically controlled: the current density and the temperature gradient. The coefficient multiplying the electrical current density is the entropy flow per electron. This is in fact the Seebeck coefficient:

\[
\alpha = \frac{-L_{12}}{eL_1T}
\]  

(1.20)

Now the matrix elements of \( L_{ij} \)—what Callen calls the “kinetic coefficients”—can be written in terms of measurable material properties \( \alpha, \sigma, \) and \( \kappa \):

\[
L_{11} = \frac{\sigma T}{e^2}, \quad L_{12} = L_{21} = -\frac{\alpha \sigma T^2}{e}, \quad \text{and} \quad L_{22} = \alpha^2 \sigma T^3 + \kappa T^2
\]  

(1.21)

The above treatment of the electron and heat fluxes reveals their interdependence through the cross term, \( L_{12} \), as it shows the effect of one driving force on the current density that corresponds to the other driving force. This result was arrived at using quasi-equilibrium thermodynamic quantities and does not take into account the quantum mechanical wave nature of electrons, yet it still leads to meaningful descriptions of thermoelectric phenomena.

From the term \( L_{22} \), which relates the flow of heat to the temperature gradient after the steady-state condition is reached (\( \bar{J} = 0 \)), it is intuitive to expect that electrons will play a roll in the conduction of heat. The total thermal conductivity is therefore comprised of at least two terms: one phononic (lattice) and one electronic.

\[
\kappa_T = \kappa_{ph} + \kappa_{el}
\]  

(1.22)
In insulators the conduction of heat is purely phononic, but in metals the second term dominates. For degenerate semiconductors and semimetals the two terms are on the same order, and now it becomes clear that maximizing \( ZT \) by maximizing \( \sigma \) while simultaneously minimizing \( \kappa_r \) is not necessarily an easy task as the electrical and thermal conductivities are somewhat intertwined, in that the electrons or charge carriers transport both charge and energy as they move through a material.

To more fully understand the relationship between \( \kappa_{el} \) and \( \sigma \) we will first describe the Drude model of electronic transport theory. Shortly after the electron was discovered, Drude wrote a paper on the electronic theory of metals in which he proposed that heat was conducted in metals almost entirely by electrons.\(^{10}\) He erroneously assumed that the heat capacity of an electron was independent of temperature and only proportional to the number of electrons via the equipartition function:

\[
C_{el} = \frac{3}{2} nk_B \quad \text{(for three dimensions)} \quad (1.23)
\]

Drude used this heat capacity in an equation for the electronic thermal conductivity based on kinetic theory where the free electrons are considered to behave collectively as an “electron gas”:\(^{11}\)

\[
\kappa_{el} = \frac{1}{3} \langle v^2 \rangle \tau C_{el} \quad (1.24)
\]

When the average velocity of the electrons (\( \langle v^2 \rangle \)) is taken from the classical kinetic energy due to thermal motion (\( \langle E \rangle = \frac{1}{2} m_e \langle v^2 \rangle \)) being equated to the Maxwell-
Boltzmann statistical value ($E = \frac{3}{2} k_B T$), resulting in $v^2 = 3k_B T / m_e$, the result becomes:

$$\kappa = \frac{1}{3} \frac{3k_B T}{m_e} \tau \frac{3}{2} nk_B = \frac{3}{2} \frac{nk_B^2 \tau T}{m_e}$$  \hspace{1cm} (1.25)

So far we have not discussed anything about the nature and cause of the relaxation time ($\tau$). Simply put, it is the average time between scattering events for the electrons. Since the number of electrons under consideration, $N \gg 1$, the relaxation time is a good average to describe the scattering for all the electrons. A free electron in an electric field will accelerate unimpeded. In a crystal field with periodic potentials from the ions of the lattice, electrons still accelerate but take differently than an electron in a vacuum because the electric field produced by the ions (lattice potentials) must be considered.

The reality of the solid state, however, is one of imperfections and defects. Even the thermal motion of the ions putting them off-center of the lattice points is quite sufficient to disrupt the periodicity of the lattice potentials in a way that interacts with the electron and changes its momentum (of course this may only take place when the resulting changes in the electrons momentum obey conservation of energy and momentum and Fermi-Dirac statistics—for example, there must be quantum mechanically allowable, unoccupied states for the electron to enter). Impurities, crystal defects, and thermal vibrations (phonons) may all cause an electron to change its momentum—this is called scattering the electron. The average time between scattering events (since $N \gg 1$) may be interpreted as the relaxation time and is denoted by $\tau$. 

16
The electrical conductivity should also be proportional to the relaxation time. With the total current density \( \vec{J}_e \) simply being a counting game of the number of electrons \( n \), each with the same charge \( e \), and an average velocity \( \vec{v} \), one can substitute the velocity with the classical momentum divided by the electron mass \( \vec{p}/m_e \) to obtain the following:

\[
\vec{J}_e = -\frac{ne}{m_e} \vec{p}
\] (1.26)

The change in momentum due to an external electric field over an infinitesimal time interval \( \Delta t \), while considering the probability of a scattering event that mitigates the electric fields effect on the momentum of scattered electrons happening during that interval being \( \Delta t/\tau \), will lead to an approximation where the change in momentum over time is equal to the force due to the external field \( \vec{f} = -e\vec{E} \) minus the initial momentum divided by the scattering time:\(^\text{12}\)

\[
\dot{\vec{p}} = \vec{f} - \frac{\vec{p}}{\tau} = -\left(e\vec{E} + \frac{\vec{p}}{\tau}\right)
\] (1.27)

The steady-state definition of the electrical conductivity is the proportionality constant of the current density to the applied electric field:

\[
\vec{J}_e = \sigma \vec{E}
\] (1.28)

Since in the steady-state the net change in momentum is zero, the momentum becomes:

\[
\vec{p} = e\tau \vec{E}
\] (1.29)
Now the substitution of Eqs. (1.28) and (1.29) into Eq. (1.26) gives the relaxation time approximation to the electrical conductivity:

\[ \sigma = \frac{ne^2 \tau}{m_e} \quad (1.30) \]

Here it is necessary to point out that even though the actual rest mass of an electron has been used in both the thermal and electrical conductivities of electrons, present convention is to use an effective mass, \( m^* \), that takes into account the effect of the crystal field on the kinetics of electrons. This is essentially to say that the electrons are not truly free and they ‘feel’ the effects of the crystal field (lattice) potentials.

While Drude got the electronic heat capacity wrong, one major success of his model comes from looking at the ratio of the electronic thermal conductivity to the electrical conductivity (the Wiedemann-Franz relation):

\[ \frac{\kappa}{\sigma} = \frac{3}{2} \frac{k_B^2}{e^2} T = \left( 1.1 \times 10^{-8} \frac{W \Omega}{K^2} \right) T \quad (1.31) \]

This states that the ratio is proportional to the temperature by a constant. This constant is very close to the known value of the Lorenz number (2.45x10^-8 W-\( \Omega/\)K^2)—named after Ludvig Lorenz who first determined the relationship between the ratio of conductivities and temperature. Nearly thirty years later Sommerfield derived a better formulation of the electronic heat capacity that was linearly dependent on temperature (as was experimental data) and lead to a better model for the thermal conductivity, and thus the correct Lorenz number.

The success of Sommerfeld’s approach came from applying the quantum mechanical Fermi-Dirac statistics to electrons rather than the classical Maxwell-
Boltzmann distribution function. This of course led to there only being certain allowable energy states that can only be occupied by two electrons each (one spin up, one spin down) due to the Pauli Exclusion Principle. By filling the allowable energy states from the ground (lowest possible energy) up, a new and important quantity (the Fermi energy, $E_F$) was defined as the energy of the electrons in the highest occupied state (assuming no thermal or other excitation). The resulting formulas for the electronic specific heat and the consequential thermal conductivity (from Eq. (1.24) where $\langle v^2 \rangle$ is replaced by the square of the Fermi velocity, $v_F$, which corresponds to the kinetic energy equal to $E_F$) become:

\[ C_{el} = \frac{1}{2} \frac{n\pi^2 k_B^2}{E_F} T \quad (1.32) \]

\[ \kappa_{el} = \frac{1}{6} \frac{n\pi^2 k_B^2 v_F^2}{E_F} \tau \quad (1.33) \]

Now comparing the Wiedemann-Franz ratio of the electronic thermal, (Eq. (1.33), and electrical, Eq. (1.30), conductivities (and remembering that $E_F = \frac{1}{2} m_v v_F^2$) will result in the correct Lorenz number, which can be used to estimate the electronic contribution to the total thermal conductivity of a material:

\[ \frac{\kappa_{el}}{\sigma_{el}} = \frac{\pi^2 k_B^2}{3e^2} T = L_0 T = \left( 2.45 \times 10^{-8} \frac{W\Omega}{K^2} \right) T \quad (1.34) \]

Indeed, this relationship holds true for many metals at room temperature. A very good explanation of why the Lorenz number in the Wiedemann-Franz relation loses its validity at lower temperatures and for materials other than pure metals has been presented
by John Singleton in his book *Band Theory and the Electronic Properties of Solids*.\textsuperscript{12} Singleton points out that the relaxation time (\(\tau\)) in Eqs. (1.30) and (1.33) are not necessarily the same. The difference comes from the fact that the thermal and electrical conductivities represent the transport of two different quantities by the same carrier—the electron. In terms of electrical conductivity, the electrical relaxation time (\(\tau_e\)) represents the average time between scattering events that cause an electron to lose its forward motion in the crystal (relative to the direction of the electric field that is driving it). The thermal relaxation time (\(\tau_\kappa\)) represents the average time between scattering events that cause the electron to ‘relax’ from its thermally excited state. Uher describes relaxation time as the time scale required for electrons in an excited state (either thermally or electronically) to re-equilibrate.\textsuperscript{15}

Fig. 1.6 shows the shift in the Fermi distribution of electrons due to an external field and the reshaping of the Fermi distribution due to a temperature gradient. In the case of an external electric field, the Fermi distribution is translated along the direction of the electric field (Fig. 1.6a); under a thermal gradient, the exponential tail of the Fermi distribution function is reduced on the “cold” side while it is elongated at the “hot” end (Fig. 1.6b).

The “failure” of the Wiedemann-Franz relationship to determine the electronic contribution to the total thermal conductivity is an important issue in thermoelectrics. Enhancing \(ZT\) is often approached by attempting to lower the thermal conductivity while preserving the electrical conductivity. The obvious route is to independently minimize the lattice thermal conductivity. In order to identify and understand the effects of the
methods employed to do so we must calculate and remove the electronic contribution to
the total thermal conductivity.

At very low temperatures and above the Debye temperature of a material the
Wiedemann-Franz holds and the Lorenz number can be used to subtract the electronic
contribution (see Eqs. (1.22) and (1.34)):

\[ T < 0.1 \theta_D \text{ and } T > \theta_D, \quad \tau_e \approx \tau_\sigma, \quad L \approx L_0 \]  \hspace{1cm} (1.35)

\[ \kappa_{ph} = \kappa_T - L_0 \sigma T \]  \hspace{1cm} (1.36)

At temperatures in the range of \( 0.1 \theta_D < T < \theta_D \), and especially in semiconductors,
the value of \( L \) falls below that of \( L_0 \). For narrow bandgap semiconductors, the value
tends toward 2.0 or \( 2.1 \times 10^{-8} W\Omega K^{-2} \). Though the value may vary a little between
different materials, it is sufficient to use \( L_0 = 2 \times 10^{-8} W\Omega K^{-2} \) when investigating the
trends in the lattice thermal conductivity within a material system where the composition
is only changed by a few percent.

Most narrow bandgap semiconductors and semimetals have both hole and
electron bands near the Fermi energy. At higher temperatures, the interval \( E_F \pm k_BT \)
expands and more minority carriers become involved in electronic conduction. Since the
migration of holes in one direction by default mean the migration of electrons in the
opposite of another, bipolar conduction—the conduction of both holes and electrons—in
an electric field will result in a net migration of electrons in the same direction (for now
we consider only an external electric field; so, \( \nabla_x T = 0 \)). Therefore, holes and electrons
both contribute to electronic conduction (Fig. 1.7a).
\[ \sigma = \sigma_e + \sigma_h \]  

(1.37)

Under a thermal gradient with no external electric field, however, holes and electrons compensate each other as they both migrate to the cold end (Fig. 1.7b). In the case of holes, this can be understood by considering the hole to migrate in a random walk fashion. Since the electrons that neighbor holes at the hot end have more thermal energy, and thus a higher probability of ‘jumping’ to the hole than those of the cold end, holes become ‘frozen’ at the cold end. This results in a net migration of electrons towards the hot end. The promotion (excitation) of minority carriers at high temperatures will inevitably result in a maximum in the Seebeck coefficient as the total Seebeck becomes a sum of each carrier’s Seebeck weighted by its electrical conductivity and normalized by the total electrical conductivity (when \( \nabla_x T = 0 \)).

\[ \alpha = \frac{\alpha_e \sigma_e + \alpha_h \sigma_h}{\sigma_e + \sigma_h} \]  

(1.38)

There is an additional consequence of bipolar conduction that shows up in the form of a rising tail in the total thermal conductivity where a nearly flat \( T^{-1} \) (for high \( T \)) is expected. This tail comes from the electronic contribution, which is no longer just proportional to the total electrical conductivity. The electronic thermal conductivity is not only an addition of the individual carrier conductivities (\( \kappa_{\text{electronic}} = \kappa_e + \kappa_h \)), but an additional term known as the bipolar thermodiffusion effect term becomes significant as Peltier-like heating occurs between different bands.\(^{16}\) This term is proportional to temperature and the square of the difference between \( \alpha_h \) and \( \alpha_e \).
\[ \kappa_{\text{electronic}} = \kappa_e + \kappa_h + \frac{\sigma_h \sigma}{\sigma_e + \sigma_h} \big( \alpha_h - \alpha_e \big)^2 T \]  

(1.39)

While the example has been made for the most extreme case, electrons and holes, the truth is that bipolar conduction and diffusion may occur anytime there is more than one band involved. The bands may only differ in dispersion and therefore effective mass. However, the bipolar thermodiffusion effect will be most noticed in narrow bandgap semiconductors in which valence hole bands and conduction electron bands are both near the Fermi level and where the magnitudes of \( \alpha_e \), \( \alpha_h \), and \( \alpha_h - \alpha_e \) remain high while \( \sigma_e \) and \( \sigma_h \) remain at least moderate.
Figure 1.1: $\alpha$, $\sigma$, and $PF$ plotted versus carrier concentration. 

Figure 1.2: Sample band structure plot. The vertical axis represents the energy of electronic states while the horizontal axis is the $k$-values of the electron momentum.
Figure 1.3: Example of an n-type semiconductor’s density of occupied states.  
*Source: Timothy D. Sands, "Designing Nanocomposite Thermoelectric Materials,"  

Figure 1.4: Simplified electronic band structures of (a) metals, (b) semimetals, (c)  
semiconductors, (d) and insulators. In reality, there are more than just one valence and  
one conduction band. Also, the bands are not necessarily symmetric and parabolic.
**Figure 1.5**: Schematic electronic band representation of the Seebeck Effect. 

**Figure 1.6**: Change in the Fermi-Dirac distribution in the presents of electric (a) and thermal (b) fields. The electrons of (a) may only return to their original state through high angle, horizontal processes whereas those of (b) may also take a small angle, vertical route by returning energy to the lattice.
*Source: Reference 15.*

**1.7**: Two carrier conduction under electric (a) and thermal (b) fields.
CHAPTER TWO

MATERIALS INTRODUCTION

Chalcogenides and Thermoelectrics

The chalcogenide group plays a special role in thermoelectrics. As discussed in the introduction, good thermoelectric materials will be either degenerate semiconductors or semimetals. These classes of materials are best defined by their band structure where a degenerate semiconductor is a material with a small band gap (for thermoelectrics, a rule of thumb is \( E_G = 10k_B T \): \(\sim 0.25\text{eV} \) at room temperature) and contains impurity levels/bands in the gap, whereas semimetals have of an indirect overlapping of conduction and valance bands at different \( k \)-points. These types of materials are often composed of at least one element from the pnictide or chalcogenide groups because it is the difference in electronegativities between constituent elements that gives rise to forbidden states at or near the Fermi energy and thus band gaps. Pnictogens and chalcogens possess sufficient electronegativity values that when combined with metals or semimetals, this criterion is met. Halogens, of course, are so electronegative that they form ionic compounds when combined with most elements and therefore no band structure exists. Intermetallics, on the other hand, have far too many states at and above the Fermi energy, and are thus too metallic for thermoelectric applications.
Structures of Transition Metal Dichalcogenides

Transition metal dichalcogenides form a broad class of materials that contain everything from metals to insulators (when you include oxygen as a chalcogenide). Even in the case of titanium and the specific stoichiometry of TiX₂ (dichalcogenides, where X is a chalcogen), we can find all four classes of materials—insulator: TiO₂, semiconductor: TiS₂, semimetal: TiSe₂, and metal: TiTe₂. Since insulators are of no value to this work we will exclude oxides from further discussions.

Dichalcogenides of group IV and V transition metals form a layered structure that consists of X-M-X layers separated by a van der Waals gap. These structures form several polytypes that depend on the coordination of the chalcogen atoms within the layers and the coordination between the layers themselves. F. R. Gamble put together a very good paper detailing the effects of atomic radii and electronegativities on the resulting structures for these materials.¹⁷

In terms of chalcogen-metal coordination, they may form with octahedral or trigonal prismatic coordination (denoted with prefixes 1T- and 2H-, respectively). Fig. 2.1 shows the difference between the two coordination schemes. In the 1T and in some 2H polytypes (the 2H polytype can form two different ways depending on the interlayer alignment), there are vacancies equidistantly positioned between the Ti atoms along the c-axis. Gamble showed that the 2H structure with trigonal prismatic coordination is preferred and will be adopted when the geometry of the cell due to the relative atomic radii of the metal and chalcogen atoms permits. He further showed that the effective radii of both constituents depend on the fractional ionic character of the bond, and by
definition, their differences in electronegativities. The important consequence of the chalcogen coordination is its effect on the metal $d$ band. For the trigonal prismatic 2H coordination, the $d_{z^2}$ band is separated from the rest of the $d$ bands as it is shifted towards lower energies.\textsuperscript{18,19,20} Hughes and Liang\textsuperscript{19} suggest that it is the filling of this band that determines octahedral or trigonal prismatic coordination. Yoffe\textsuperscript{21} indicated that the $d_{z^2}$ band is just above $E_F$ in the 1T materials but at or just below $E_F$ in 2H compounds. With the $d_{z^2}$ band resulting in a sharp peak in the density of states (DOS) just above $E_F$, the 1T materials will be thermoelectrically advantageous when intercalated as $E_F$ may be raised to where the slope of the DOS is high (remembering $\alpha \propto \partial \rho DOS(E)$).

Fermi surfaces based on electronic structure calculations by Doran\textsuperscript{22} showed the 1T structures to have electron pockets in the shape of a column along the LML direction, while the 2H structures have similar shaped hole pockets along $\Gamma A$ (Fig. 2.2). Wilson et al.\textsuperscript{23} implicate this unique Fermi surface geometry as evidence of the 2D nature of the system as a layered structure. While this leads to anisotropy of the transport properties, it may also prove useful as a mechanism for favorably decoupling the thermal and electrical properties for optimization of the thermoelectric figure-of-merit, $ZT$.

Both titanium diselenide and disulfide form in the 1T polytype. Compared to the other dichalcogenides of group IV transition metals, those of titanium form less X-M-X bonds with a smaller fractional character. This is a result of the small atomic radii of Ti compared to Zr and Hf.\textsuperscript{19} This, in addition to the positioning of the Ti $3d$ bands as a
result of the 1T structure, leads to a very small band gap in the case of both TiSe$_2$ and TiS$_2$. Friend et al.$^{24}$ reported TiS$_2$ to be a narrow bandgap semiconductor with a bandgap of 0.2 – 0.3 eV, and predicted TiSe$_2$ to be a semimetal with a small, indirect overlapping of the Ti-3$d$ and Se-4$p$ bands. Boehm and Isomaki determined the overlap of these bands to be between 0.18 and 0.5 eV with angle-resolved photoemission spectroscopy (ARPES).$^{25}$ Using better angular and energetically resolved ARPES measurements, Andersen et al. determined the overlap of the bands to be less than 0.12 eV while resolving a spin-orbital splitting of the Se-4$p$ orbital, which crosses $E_F$ to give rise to hole carriers.$^{26}$

Charge Density Waves

Several of the groups IV and V dichalcogenides of both 1T and 2H polytypes undergo a periodic lattice distortion due to charge distribution rearrangement below some temperature.$^{23}$ Known as a charge density wave (CDW) state, the adoption of a superlattice is a consequence of the unique Fermi surfaces of the materials that supports the necessary electron-phonon interactions. In the special case of TiSe$_2$, the CDW state is a result of electron-hole pairing (exciton) and the subsequent interactions with the phonons of the lattice (the so-called Overhauser type$^{27}$).$^{28}$ The CDW transition gives rise to a significant peak in the Seebeck coefficient, which makes these materials at least attractive for low temperature thermoelectric studies.$^{43,29}$ On the other hand, the CDW state generally results in a reduction of carrier concentration and, consequently, a
reduction in the electrical conductivity. The hope is to gain more from the increased Seebeck than what is lost in electrical conductivity.

**Intercalation**

Intercalation of transition metal dichalcogenides has been widely studied, but rarely in terms of thermoelectric applications. Yoffe’s paper\textsuperscript{21} reviewed, in general, the effects of intercalating many atomic and molecular species into transition metal dichalcogenides. The paper describes, in general and with some specific examples, the effect of intercalating nitrogen hydrides, organic amines, alkali, and 3\textit{d} transition metals on the electronic properties. There have been a considerable number of efforts in studying the ion conduction properties of Li doped transition metal dichalcogenides where the charge transfer between the intercalants and the host layers is complete (for example\textsuperscript{30,31,32,33}). Many of these studies focused on the use of alkali intercalated transition metal dichalcogenides as ionic conductors. Gamble et al.\textsuperscript{34} showed that by intercalating polymers such as stearamide that the van der Waals gap may be opened widely, resulting in an electronically 2D system where the X-M-X layers are separated by a distance nearly ten times their thickness.

While many 3\textit{d} metal intercalation studies of decades past were focused on finding a route to high T\textsubscript{C} superconductivity, these focused on materials of the 2H and mixed polytypic (i.e. 4H) materials where the density of states at the Fermi surface tend to be higher.\textsuperscript{35} Only recently has superconductivity been found in an octahedrally coordinated structure—the 1T-Cu\textsubscript{x}TiSe\textsubscript{2}.\textsuperscript{36} Pure TiSe\textsubscript{2} has even been found to exhibit a
pressure induced superconductivity state between 2 and 4GPa. These and other recent studies of Cu intercalated TiSe$_2$ have explored the competition between the charge density wave and superconducting states.$^{38,39}$

**The Uniqueness of Titanium Diselenide**

The electronic structure of TiSe$_2$ (Fig 2.3) along with the uncommon Overhauser type CDW transition that arises from it makes this particular transition metal dichalcogenides a unique and interesting material for any electronic transport studies. The small, indirect overlapping of the Ti-3$d$ and Se-4$p$ bands becomes increasingly important when 3$d$ metal intercalants occupy the octahedrally coordinated voids at (0 0 $\frac{1}{2}$) (Fig. 2.4). Since the indirect band overlap of the hole bands of the Se-4$p$ orbitals at $\Gamma$ and the Ti-3$d$ bands at L is small (<120 meV), the ratio of the electron to hole concentration ($n_e/n_h$) is very sensitive to both the concentration of intercalants and the number of valence electrons of the intercalants species. If all intercalants act as electron donors to the host matrix, as Yoffe suggested,$^{21}$ then more electrons per unit cell raises $E_F$ so that fewer holes may be present until the maximum of the Se-4$p$ band is filled. As more recent studies show, the effect of a guest 3$d$ intercalants on the local band structure of the host TiSe$_2$ matrix can be complicated and is species specific. This means the situation becomes more than an electron counting scheme as the 3$d$ orbitals of the intercalants may become hybridized with those of the host Ti atoms (but to a varying degree of hybridization).$^{40}$ The charge transfer may be nearly complete, as is believed to be the case with Cr intercalation,$^{21}$ or the 3$d$ states of the intercalants may be highly
localized, as is the case with Co.\textsuperscript{40} The result is a wide range tuning mechanism for optimizing the band structure of $\text{M}_x\text{TiSe}_2$ in a thermoelectrically favorably way.

\textit{Current Thermoelectric Studies}

Some researchers have made use of the relative band structures of $\text{TiSe}_2$ and $\text{TiS}_2$ to optimize the thermopower (Seebeck) in the ternary $\text{TiSe}_{2-x}\text{S}_x$.\textsuperscript{41,42} As mentioned above, the more negative sulfur renders $\text{TiS}_2$ a narrow bandgap semiconductor. Since the overlap of the bands in $\text{TiSe}_2$ is so small, substitution of only 0.1–0.3 sulfur per formula is enough to open a bandgap in $\text{TiSe}_{2-x}\text{S}_x$ to bring put it in the degenerate semiconductor class in which thermoelectrics are usually found. Only one recent study published in 2009 has focused on $\text{M}_x\text{TiSe}_{2-y}\text{S}_y$ as potential thermoelectric candidate. Hor and Cava\textsuperscript{43} intercalated small amounts of Cu ($x < 4\%$) into $\text{M}_x\text{TiSe}_{2-y}\text{S}_y$ while varying $y$ from 0 to 0.3. This was the first study of this material where both the electronic and thermal properties where measured so that $ZT$ could be calculated. They found a maximum $ZT$ of 0.07 at room temperature in $\text{Cu}_{0.02}\text{TiSe}_{1.7}\text{S}_{0.3}$. The thermal conductivity was not reported for the unintercalated $\text{TiSe}_{2-x}\text{S}_x$, leaving out an understanding of the effect of sulfur substitution on the thermal transport. Additionally, Cu adds a large number of electrons per unit cell, and while this may offset the number of holes favorable, it may shift the Fermi energy past where the peak in the electronic DOS of the Ti-3$d$ bands is positioned. A study of the effects of intercalating other 3$d$ transition metals, or possible a combination of them, on the thermal and electronic transport for thermoelectric applications is of interest by lacking.
Figure 2.1: Examples of 1T (a) and 2H (b and c) polytypes of the transition metal dichalcogenides. Chalcogens are represented by the green, smaller spheres. While the 1T unit cell contains only one X-M-X layer (the z=0 plane cuts through the M layer), the 2H contains two X-M-X layers. The X-M-X bonds are represented by the dashed lines.
Figure 2.2: Columnar hole and electron pockets in the Fermi surfaces of 2H-TaSe$_2$ and 1T-TaS$_2$, respectively.
Figure 2.3: Band structure of 1T-TiSe$_2$. The Se-4$p$ maximum at $\Gamma$ and the Ti3-$d$ minimum at L can both be seen crossing the Fermi energy ($E = 0$).

Figure 2.4: Trigonal unit cell of TiSe$_2$. Full occupation of the vacancy sites at (0 0 $\frac{1}{2}$) give the NiAs structure of TiSe (s.g. P6$_3$/mmc).
CHAPTER THREE

TRANSPORT PROPERTIES MEASUREMENT TECHNIQUES

Low Temperature Transport

Low temperature electrical and thermal transport measurements often provide a great deal of insight into the intrinsic character of a system. Low temperatures mean a reduced phonon population and less thermal excitation of electrons, which, consequently, means less phonon-phonon and phonon-electron interactions. Particularly when temperatures are below about 10% of the Debye temperature ($\theta_D$) of a material, structure and defects (structural, magnetic, impurity, etc.) become the dominant scattering mechanisms for both electrons and phonons.

Seebeck and Electrical Resistivity

Seebeck and electrical resistivity were simultaneously measured using a custom designed system\textsuperscript{44} that employs the differential and traditional four-probe techniques, respectively. Using removable chip mounts (Fig. 3.1), samples were mounted between a copper base thermally sunk to the system and a copper pad with a heater affixed to the transverse side using silver paint. Current input wires were soldered to the two copper pieces while the two voltage leads for resistivity measurements were attached directly to the sample (of length $l$) at about $\frac{1}{3}l$ and $\frac{2}{3}l$. Voltage leads for Seebeck measurements were soldered directly to the copper blocks with the assumption that the very high thermal and electrical conductivities of copper result in no potential or thermal gradients.
within each copper piece. The temperature difference was measured using a differential thermocouple that was embedded into the copper blocks near the sample contact surface.

Measuring both cooling and warming curves between room temperature (~300 K) and 10 K, the system was set to a constant cooling/heating rate of 0.25 K/min and the sample heater was set to maintain a constant temperature difference between the two copper blocks (and assumedly between the two ends of the sample) of about 5 K. The low slew rate of the system allowed for a quasi-steady-state scenario where the change in temperature that occurs during the time to complete the measurements (~1-2 sec) is very small. A high data density was obtained by taking measurements every 120 seconds.

Quantities actually measured were voltages of the system thermocouple, differential sample thermocouple, potential difference between copper blocks, and potential difference between leads affixed to the sample. Tables were used to convert the voltages of the system and differential thermocouples to obtain the system (base) temperature and the $\Delta T$, respectively. The measurement temperature was then taken to be the base temp plus half the $\Delta T$:

$$T_{\text{measure}} = T_{\text{base}} + \frac{1}{2}\Delta T$$  \hspace{1cm} (3.1)

The Seebeck coefficient at a given temperature was simple taken to be the voltage between the copper blocks divided by the temperature difference. Since the copper blocks and the copper wires used to measure the voltages are at different temperatures, this actually creates a two conductor scenario analogous with Seebeck’s wire loop of two dissimilar metals. So, the open circuit voltage measured between the two copper leads gives the sum of the Seebeck voltages of the copper wires and the
The Seebeck voltage of the copper wires was calculated for the measured $\Delta T$ and subtracted:

$$\alpha_{\text{sample}} = \frac{\alpha_{\text{Cu}} \Delta T - V_{\text{measured}}}{\Delta T} = \alpha_{\text{Cu}} - \frac{V_{\text{measured}}}{\Delta T} \quad (3.2)$$

Since a constant $\Delta T$ was maintained across the sample, the voltage between the resistivity leads on the sample also contains a contribution from the Seebeck effect ($V_{\text{measured}} = V_{\text{IR}}(I) + \alpha \Delta T$). By measuring the voltage between the leads with the current on, and then with the current reversed, the thermoelectric voltage may be removed and the resistance of the sample between the leads may be calculated using Eq. (3.3):

$$R = \frac{V_{\text{measured}}(I^+) - V_{\text{measured}}(I^-)}{(I^+ - I^-)} = \frac{[V_{\text{IR}}(I^+) + \alpha \Delta T] - [V_{\text{IR}}(I^-) + \alpha \Delta T]}{(I^+ - I^-)} = \frac{V_{\text{IR}}}{I} \quad (3.3)$$

Here $\Delta T$ is the temperature difference between the two leads, which is unknown. This $\Delta T$ is not to be confused with the one measured between the copper blocks by the differential thermal couple that is used to determine the Seebeck coefficient. Also, $V_{\text{measured}}$ in Eq. (3.3) is measured between leads attached directly to the sample, as opposed to the $V_{\text{measured}}$ in Eq. (3.2), which is measured between the leads attached directly to the copper blocks and is used to measure the Seebeck coefficient.

Since the resistance of the sample should be independent of current and $I^- = -I^+$, we have $V_{\text{IR}}(I^-) = -V_{\text{IR}}(I^+)$. Also, the current is measured by measuring the voltage across a known standard resistor that is in series with sample. With the resistance of the material between the two leads known, the electrical resistivity may be easily determined if the sample geometry is well defined and known. Typically, the largest uncertainty in
determining the sample’s resistivity comes from the measurement of the sample dimensions. Specifically, for a rectangular sample with a uniform cross-section of area, $A$, and length between leads, $l$, the resistivity, $\rho$, is:

$$\rho = \frac{R \cdot A}{l} \quad (3.4)$$

**Thermal Conductivity**

Low temperature thermal conductivity was calculated from thermal conductance data obtained from a custom designed system\(^{45}\) that employs the steady-state power sweeping technique. Sample specimens used for low temperature electrical resistivity and Seebeck measurements were also used for low temperature thermal conductivity measurements so that the uncertainty of the sample’s cross sectional area would cancel out when $ZT$, Eq. (1.1), is calculated. Samples were mounted on commercial pucks designed by Quantum Design for their PPMS® system’s AC Transport option. The pucks were modified for thermal conductivity measurements (Fig. 3.2) and used in a custom built, cryocooler system that measured thermal conductance from 10 to 300 K. The system and technique is described in detail in reference 45.

The following equation was used to calculate the thermal conductivity, $\kappa$, from the thermal conductance, $K$, the cross-sectional area, $A$, and the length, $l$, between the two junctions of a differential thermal couple used to measure the $\Delta T$ between two points of the sample:

$$\kappa = \frac{K \cdot A}{l} \quad (3.5)$$
The thermal conductance of the section of the sample between the two points where $\Delta T$ is measured, $K$, was determined at each temperature by the steady-state equation: $P = K \Delta T$, where $P$ is the heating power input into the sample. By measuring the temperature difference of the differential thermocouple and the heating power input in the sample for a range of heating powers, $K$ may be determined as the slope of $P$ vs $\Delta T$. The base temperature was stabilized to within +/- 30 mK of the set temperature before any data acquisition was taken. This stability of +/- 30 mK was maintained throughout the entire measurement sequence at each temperature set-point. Once a steady-state condition was reached, the current input into the heater was calculated from a measured voltage drop across a standard resistor in series with the heater, and the electrical power input into the heater was calculated from $P = I^2 R$. Since the nominal value of the heater resistance was not nearly precise enough for this calculation, the resistance was determined using Ohm’s law and the voltage drop across the heater was measured for each calculation of the power using a four probe configuration at the sample puck. Since thermal loss through conduction along leads must be minimized, only two leads ran from the heater to the sample puck, and then four wires from the puck to the measurement panel. The small error arising from voltage drops along the two leads from the puck to heater has been determined and is accounted for in calculations of the heater power.

The heating power input into the sample was therefore calculated as the corrected electrical power input into the heater minus any thermal loss terms ($P_{\text{sample}} = I^2 R_{\text{heater}} - P_{\text{loss}}$). The loss terms were minimized by using small diameter (.004") phosphor bronze ($\kappa_{PB} \approx 70$ Wm$^{-1}$K$^{-1}$ at 300 K, compared to $\kappa_{Cu} \approx 400$ Wm$^{-1}$K$^{-1}$) leads to
the heater in order to minimize loss through conduction. The differential thermocouples were made using .001" constantan-chromel-constantan whose small diameter and relatively low thermal conductivity (both: \(\kappa \approx 20 \text{ Wm}^{-1}\text{K}^{-1}\) at 300 K) result in a very low thermal conductance. In order to accurately measure the \(\Delta T\) of sample, two 38 AWG copper wires coated with enamel insulation were affixed to the sample perpendicular to the length at two points using Stycast®. The insulation on outer side of the wires is then removed to expose the copper to which the junctions of the thermocouple are soldered to achieve maximum thermal contact while keeping the thermocouple electrically insulated from the sample.

An additional source of power loss is through radiation from the sample, heater, and wires. This radiative loss term starts to become a concern typically above \(T \approx 200\text{K}\). The rate of radiative heat transfer between an object and its surroundings depends on the surface area and emissivity of the object (sample) and the temperature difference between the object and its surroundings according to the Stefan Boltzmann law (actually the difference in the fourth power of the temperatures). Besides minimizing the heat conduction through the wire leads to minimize the heat available for radiation, a copper cap was placed over the puck in thermal contact with the system base to introduce a surrounding that minimizes the temperature difference. Additionally, the cap was gold plated on the inside to provide a reflective coating to reflect the radiation back to the sample.

Because the surface area should be minimized, the dimensions should be chosen to reduce the surface area relative to thermal conductance (which is directly proportional
to the cross-section). Since the surface area is directly proportional to length while the thermal conductance is inversely proportional to length, a very short, fat sample would be preferred. However, since a thermal gradient must be established and a $\Delta T$ measured between two points whose separation must be measured, a minimum length of at least 4-6 mm is needed. To maximize the cross-sectional area while minimizing the surfaces area for a sample of a given length, the cross-section ought to be square.

Although a short sample with a large cross-section is preferred for thermal conductivity measurements, the opposite is true for electrical resistivity measurements. The length should be maximized to allow for creating a so that the separation between the voltage leads may be maximized since the resistance, and thus the voltage that arises from Ohm’s law, is maximized. This is simply an issue of signal-to-noise ratio. A small cross-section if favorable for two reasons; the first being that the resistance is inversely proportional to the cross-section, and the second is that a uniform current density at and between the resistivity voltage leads is necessary. Tritt suggests placing the leads no closer than the width of the sample (assuming square cross-section) from the ends, where the current is输入.46

Since the Seebeck coefficient is measured simultaneously with electrical resistivity, maximizing the length makes creating a sufficient $\Delta T$ possible within the limitations of the heater power and sample thermal conductivity. A sufficient $\Delta T$ will result in a Seebeck voltage that is large enough to be accurately measured against the inherent signal noise and voltmeter capabilities.
When calculating $ZT$, it is essential to use transport data all measured on the same sample and along the same direction. This will ensure that the $ZT$ is indeed representative of the specimen, as-is, with all defects, texturing, anisotropy, etc. included. Additionally, since the dimensions go into the calculations of both the electrical and thermal conductivities in the same way, the uncertainties in sample cross sectional area will cancel as the ratio becomes a ratio of conductances instead of conductivities in $ZT$. The lengths that are used for resistivity and thermal conductivity are typically not exactly the same so they do not cancel. To balance requirements on the sample dimensions between electrical and thermal transport measurements, samples were cut out of the center of a densified, polycrystalline pellet of about 2 mm thick to be 2 mm wide and 6-8 mm long. Both the voltage leads for resistivity measurements and the copper rails for thermocouple fixing were placed at about 2-2.5 mm from either end.

**Hall Coefficient**

As discussed in the first chapter, the thermoelectric power factor ($PF = \alpha^2 \sigma T$) may be maximized at some carrier concentration. It is therefore useful to determine the carrier concentration via of the Hall Effect.

In 1879, Edwin Hall first made quantitative measurements of the deflection of current due to a magnetic field by driving a current through a rectangular section of gold foil placed in a magnetic field perpendicular to the face of the foil and then measuring the transverse voltage. Because at the time the electron was yet to be discovered, the best that Hall could do in terms of modeling was to not that the voltage produced is directly
proportional to the product of the magnetic field strength and the primary current. In 1904, Henrik Lorentz correctly derived the force, $\vec{F}$, that describes the reaction of a particle with a charge $q$ traveling with a velocity, $\vec{v}$, in a magnetic field, $\vec{B}$:

$$\vec{F} = q\vec{v} \times \vec{B}$$

(3.6)

This magnetic force will be balanced by the electrostatic force ($\vec{F} = e\vec{E}$) that arises from the deflected electrons ‘piling’ up at one of the material. Writing the electric field in terms of the potential difference divided by the distance and the velocity of Eq. (3.6) in terms of the current, $I$, and then equating the two forces gives a result for the voltage that arises due to the Hall effect in terms of the thickness of the material, $d$, and the carrier concentration, $n$:

$$V_H = \frac{IB}{ned} \quad V_H = \frac{IB}{ned}$$

(3.7)

In general one must use and average of 4 voltages [$(+I, +B), (-I, +B), (-I, -B), (+I, -B)$] in order to cancel out all the thermal contributions, such as thermoelectric, Nerst effect and Ettinghausen effect, etc.). We use with the PPMS an ac current and reverse the field and average to get the correct Hall voltage.

Fig. 3.3a schematically shows the Hall effect on a stream of electrons characterized by a current $I$ passing through a thin slab of a material of thickness $d$ in a magnetic field of strength $B$. Eq. (3.7) is only valid when the voltage is measured between two points that fall on a line perpendicular to the flow of current, which must be uniformly distributed through the cross-section of the sample. If the two voltage leads
are not attached perfectly perpendicular to the current, then an additional voltage will arise from Ohm’s law.

The left side of Fig. 3.3b depicts a three probe configuration (five if you include the current leads) where the positive lead for the Hall voltage is replaced by two leads attached at points that are collinear with a line parallel to the flow of current. These two leads are connected to the opposite ends of a high precision potentiometer. The center tap of the potentiometer is then used as the positive lead of the Hall voltage. If the potentiometer is balanced so that the voltage is zero when the magnetic field is zero, regardless of the driving current, then any voltage that arises must be strictly due to the Hall effect.

The Hall coefficient was measured on a few select samples to probe the carrier concentration as a function of nickel concentration in Ni\textsubscript{x}Ti\textsubscript{1+\delta}Se\textsubscript{2}. Using the configuration depicted in Fig. 3.3b, the Hall voltage was measured as the magnetic field was swept from -0.5 Tesla to +0.5 Tesla while the temperature and current remained constant. The slope of \( V_H \) versus \( B \) is then \( 1/(ned) \). The effective carrier concentration was readily obtained from the slope. This was repeated for several temperatures in the range of 100 – 300 K.

It is important to note that this is the effective carrier concentration as it is an average of the hole and electron concentrations (\( p \) and \( n \), respectively) weighted by each carrier’s mobility (\( \mu_p \) and \( \mu_n \)).

\[
n_{\text{eff}} = \frac{2}{n_{\text{eff}}} + \frac{n_{\text{eff}}}{2} = \frac{(p + n\beta)^2}{p - n\beta^2}, \quad \text{where} \quad \beta = \frac{\mu_e}{\mu_h}
\] (3.8)
Specific Heat Capacity

Low temperature specific heat capacity may provide several important pieces of information about a sample. When the data is taken up to room temperature, the shape may indicate that where the Dulong-Petit value of \( c_v \) becomes valid. Above the temperatures where \( c_p \) becomes a linear function of \( T \), the \( c_v \) saturates at the Dulong-Petit limit. So, if the \( c_p \) of a sample is beginning to become linear just below 300 K, it is appropriate to assume that the \( c_v \) has saturated above 100°C (~373 K).

Since both the ions in the lattice and the electrons associated with those ions may store heat, the total heat capacity of a system will have at least two terms. The heat stored in the vibrational modes of the ions (phonons) has been most accurately modeled by Peter Debye.\(^5\) His approach was to associate the vibrational modes of the lattice to phonon wave energies and then to use Bose-Einstein statistics to obtain the total energy of all phonon modes.

\[
U = \frac{9Nk_B T^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x-1} dx
\]  

(3.9)

By differentiating the total energy with respect to temperature, Debye arrived at an equation for the phononic heat capacity that provided a very good fit to the experimental data of insulators over all temperatures:\(^6\)

\[
C_v = \frac{\partial U}{\partial T} = 9Nk_B \left( \frac{T}{\theta_D} \right)^3 \theta_D^{\frac{3}{2}} \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx
\]  

(3.10)

The phononic heat capacity therefore depends on the temperature, \( T \), the total number of atoms, \( N \), and a parameter known as the Debye temperature, \( \theta_D \). The Debye
temperature is a collection of universal and material specific constants, such as Planck’s constant, \( h \), the Boltzmann constant, \( k_B \), the velocity of sound in the material, \( v_s \), and the number of atoms per unit volume, \( N/V \):

\[
\theta_D = \frac{1}{2} \frac{h v_s}{k_B} \left( \frac{6N}{\pi V} \right)^{1/3}
\]  

(3.11)

In the limit of \( T \gg \theta_D \), the integral of Eq. (3.9) may be simplified by the approximation \( e^x \approx 1 + x \). This results in \( C_v = 3Nk_B \)—the classical Dulong-Petit limit.

In the low temperature limit, where \( T \ll \theta_D \), an approximation may be made to the integral in Eq. (3.9) that results in a simplified low temperature phononic heat capacity—Eq. (3.12). The accuracy of Eq. (3.12) to predict the heat capacity of materials below 5 – 8 K was the great success of Debye’s model.

\[
C_v = \frac{12\pi^4 Nk_B}{5\theta_D^3} T^3
\]  

(3.12)

When electrons are no longer localized to an ion core, they may store and transport heat independently of the lattice. From Chapter 1, Eq. (1.32) gives the electronic contribution to the heat capacity and the total heat capacity of conducting materials at low temperatures is:

\[
C_v = \frac{1}{2} \frac{n\pi^2 k_B^2}{E_F} T + \frac{12\pi^4 Nk_B}{5\theta_D^3} T^3
\]  

(3.13)

From Eq. (3.13) it can be seen that low temperature (below 5 K) \( c_p \) data may be fit with a linear plus a cubed term, and the coefficients may be used to determine the Fermi energy and Debye temperature of the system. The fact that \( c_p \) is measured instead of \( c_v \) is
of no consequence as \( c_p \approx c_v \) at low temperatures. Knowing \( E_F \) and \( \theta_D \) can be useful as the latter may be used to calculate the velocity of sound, to which the lattice thermal conductivity is related, and \( E_F \) has much to do with electronic transport.

The specific heat at a constant pressure was measured on a Quantum Design PPMS® system from 1.7 to 300 K at the National Institute for Standards and Technology by Dr. Yonggao Yan. The heat capacity was determined for each sample by the relaxation method\(^{52}\) where heat is input into the sample stage (and sample, when present) for a time and then shut off. The temperature of the platform is measured with a Cernox® thermometer as a function of time and the total heat capacity of the stage and sample (plus any thermal contact media used, such as grease) is determined by the time it required for the temperature to reach the initial temperature. Determining the sample heat capacity therefore involved measuring an addendum of the stage and thermal contact grease. \( E_F \) and \( \theta_D \) were subsequently determined for all samples with \( c_p \)'s measured.

High Temperature Transport

*Seebeck and Electrical Resistivity*

The Seebeck coefficient and resistivity were measure simultaneously with the commercial ZEM-2 system from ULVAC Technologies, Inc. Measurements were taken from 50°C to 300°C. While the sample stability and the capabilities of the ZEM-2 would allow for measurements up to at least 500°C, data was taken only to 300°C because the Seebeck coefficients and thus the \( ZT \)'s of the samples reach a maximum between 200 and
300°C due to bipolar conduction. A high density of data points was not necessary in the temperature range measured as no sharp features were expected in the data. This fact, in addition to data density being proportional to the time required to obtain the data, resulted in data being taken every 50°C.

Like the low temperature systems, the ZEM-2 employs the four-probe technique for measuring electrical resistivity. Unlike the former, the ZEM-2 utilizes mechanical springs to make pressure contacts of the current input posts and the voltage leads. Additionally, the voltage leads themselves are of a different nature. The ZEM-2 uses a method where each lead is actually a thermocouple rather than a single wire. The thermocouple junction is located just outside the end of a two-bore ceramic tube that houses the thermocouple’s leads, and is mechanically pressed to the side of the sample to give good thermal and electrical contact. The advantage of this method is that both the temperature and electric potential may be probed at the point of contact. As two such thermocouple probes are aligned vertically along the sample, the two temperatures ($T_1$ and $T_2$) of their points of contact may be measured to obtain $\Delta T$ while measuring the potential difference between the negative leads of each thermocouple will yield both the Seebeck voltage (when $I=0$) and the voltage due to Ohm’s law (plus Seebeck, when $I \neq 0$)—Fig. 3.4.

The sequence used for measurements involved stabilizing the system at a base temperature and then raising the temperature of the lower arm of the probe to achieve a temperature gradient across the sample. Once the $\Delta T$ is stabilized, the voltages of each probe thermocouple as well as the voltage between the negative leads of each
thermocouple are measured with the current off, and then with the current on. The system will persistently make measurements at an interval of about once every few seconds while tracking the latest three data points. Once the standard deviation of the most recent three measurements is low enough, the average will be recorded and the system moves to a higher $\Delta T$ to repeat stabilization and measurement. The $\Delta T$ set-points used were 5, 10, and 15°C above each base temperature.

The raw data is recorded in a tab delimited text file that must by analyzed by an addition program. The raw data contains one line per each $T+\Delta T$ measured with the following columns: $T$ ($T_{TC1}$, see Fig. 3.4), $\Delta T$ ($T_{TC2}-T_{TC1}$), $\rho$ (sample resistivity at $T+\Delta T$), $\alpha_{wire}$ (tabulated Seebeck of negative lead of thermocouple at $\Delta T$), and $\Delta DC$ ($V_d$). The analysis software will calculate one Seebeck coefficient and resistivity value for each base temperature set (meaning $T+\Delta T=5, 10, 15°C$). Both $T$ and $\rho$ are simply averaged from the set. The Seebeck voltages ($V_d$) must first be corrected by addition of the contribution of the thermocouple leads ($[V_{a+b} = V_a - V_b] \rightarrow V_{\alpha, sample} = V_{\alpha, measured} + \alpha_{wire} \Delta T$). The Seebeck coefficient is then calculated from the slope of the corrected Seebeck voltage versus $\Delta T$:

$$\alpha_{sample} = \text{slope}(V_{\alpha, sample} \text{ vs. } \Delta T)$$ \quad (3.14)$$

Fig. 3.5 schematically shows the ZEM-2 probe configuration. The system temperature is measured by a thermocouple that is inserted into a metal sheath that encloses the parts shown in the figure (base thermocouple and sheath are now shown). This thermocouple is used to measure the base temperature, which is controlled by six halogen lamps at the focal point of six curved reflecting surfaces surrounding the probe.
Once the base temperature is stabilized, the platinum heater located in the lower arm of the probe is used to achieve a temperature difference across the sample. This $\Delta T$ is measured by thermocouples located in upper and lower probe arms, and as such, the actual $\Delta T$ between the sample thermocouples used for measuring Seebeck and resistivity will be lower.

**Thermal Conductivity and Diffusivity**

Due to the high level of radiation loss that comes with high temperature thermal conductance measurements, the thermal conductivity was not measured directly above room temperature. Instead, the total thermal conductivity above room temperature was calculated from the mass density ($\rho_D$), specific heat ($c_v$), and thermal diffusivity ($D$):

$$\kappa = \rho_D c_v D$$

Eq. (3.15) requires the specific heat at a constant volume, which is much more difficult to measure than the specific heat at a constant pressure ($c_p$). In instances where the high temperature thermal conductivity was calculated, the Dulong-Petit limit\textsuperscript{53} ($c_{D,P}$) of the specific heat capacity at a constant volume ($c_v$) was used. The Dulong-Petit law restricts the maximum value of $c_v$ to $3k_B$ per atom.\textsuperscript{54} This results in $c_v = 3aR / f.w.$ where $c_v$ is in units of J·°C/g, $a$ is the number of atoms per formula, $R$ is the ideal gas constant, and $f.w.$ is the formula weight. Unless there is a structural or electronic transition above room
temperature, \( c_v \), ought to approach and saturate at the value of \( c_{D,P} \). As differential scanning calorimetry curves show no such transitions, the Dulong-Petit limit is thought to be valid for high temperature calculations of the thermal conductivity.

A Netzsch *LFA 457 MicroFlash* system was used to measure the thermal diffusivity on a few select samples. This system pulses a laser on the bottom of the sample and then measures the temperature profile of the top as a function of time with an infrared detector. The calculation of the diffusivity of the material comes from measuring the half-time of the rise and saturation of the infrared detector signal. By solving the 1-D heat flow equation using Fourier analysis and the boundary conditions of the sample geometry, the thermal diffusivity may be determined from the half-time of the signal rise, from a relationship known as the Parker equation: \(^{55}\)

\[
D = 0.138785 \frac{L^2}{t_{1/2}}
\]  

(3.16)

Because the initial goal of this project was to probe the low temperature thermoelectric properties, most samples were cut for the low temperature measurements before running high temperature thermal analysis, which requires the whole pellet.

*Differential Scanning Calorimetry*

A very useful tool for thermal analysis of a material is differential scanning calorimetry (DSC). This technique uses the relationship between heat exchange, temperature, and the total heat capacity of a material to probe many types of structural and other transitions that affect the specific heat capacity of a material. Glass transitions,
solid-solid phase transitions, partial or full melting, degassing, etc. may all give signatures in a DSC curve. This may be used to determine melting points, sample purity, decomposition temperature, and when the signal is calibrated using a standard, \( c_p \).

DSC curves were measured on a few select samples on a Netzsch Pegasus 404 C. This system uses a platinum stage that accommodates two small crucibles. The crucibles are platinum with alumina liners and platinum lids. On the underside of the stage, beneath each crucible, one junction of a differential thermocouple is attached. When the two points of contact with the stage (beneath each crucible) are isothermal, the signal from the differential thermocouple leads will be zero. As heat is evenly input into the system at a constant rate, the difference in total thermal capacities of the contents of the two crucibles will result in a difference in their temperatures and thus a DSC signal.

The nature of this method of analysis is so sensitive that differences in the two sides of the stage as well as in the two crucibles must be accounted for. For this reason a baseline is often measured (always in the case of determining \( c_p \)). For determining sample stability (i.e. looking to exclude the occurrence of decomposition or melting up to a particular temperature) a baseline is not necessary as only the shape of the DSC curve is relevant.
Figure 3.1: Removable sample mounts for low temperature resistivity and Seebeck coefficient measurements. Source: See reference 44.
Figure 3.2: Thermal conductivity measurement sample mount. Source: See reference 45.
Figure 3.3a: Deflection of electrons moving in a magnetic field give rise to the Hall voltage, $V_H$.

Figure 3.3b: Hall effect measurement schematic. For a homogeneous sample, the potential at the spatial center between the $+V_A$ and $+V_B$ leads can be found by adjusting a potentiometer in the configuration shown in the figure on the right so that the potential difference between $-V$ and the center tap of the potentiometer is zero when the magnetic field is turned off.
Figure 3.4: ZEM-2 probe sample thermocouple arrangement with signals measured and their interpretations.

Figure 3.5: ZEM-2 probe schematic. The upper and lower arms of the probe are movable in the vertical position and are used to hold the sample. The platinum resistance heater is used to reach the $\Delta T$ set-points as measured by the upper and lower thermocouples. Probe thermocouples in contact with the side of the sample are used for measuring Seebeck and resistivity. The base temperature is measured with an external thermocouple attached to a metal sheath (not shown) that covers the apparatus shown and is supported by the ceramic rails at the top of the image.
Sample Synthesis

All samples were synthesized by mixing raw elemental powders in stoichiometric proportions inside of a quartz tube. Table 4.1 contains the details of the powders used in sample synthesis. Because of the propensity of copper to oxidize, the Cu powders were first etched in dilute HCl and then rinsed with distilled water and then alcohol. The tubes were subsequently evacuated to below 30 mTorr and then sealed using a hydrogen torch. The sealed tubes were placed, upright, into bench-top muffle furnaces with programmable temperature controllers. All samples were synthesized using the same temperature program (Table 4.2), with a reaction temperature of 650°C and a final hold time of 5 days.

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>Purity</th>
<th>Form/Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Alfa Aesar Puratronics</td>
<td>99.996%</td>
<td>Powder -120 Mesh</td>
</tr>
<tr>
<td>Cu</td>
<td>Alfa Aesar</td>
<td>99.5%</td>
<td>Powder -100 Mesh</td>
</tr>
<tr>
<td>Ti</td>
<td>Strem</td>
<td>99.5%</td>
<td>Powder -325 Mesh</td>
</tr>
<tr>
<td>Ta</td>
<td>Alfa Aesar</td>
<td>99.96%</td>
<td>Powder -60 Mesh</td>
</tr>
<tr>
<td>Se</td>
<td>Alfa Aesar</td>
<td>99.9%</td>
<td>Powder -325 Mesh</td>
</tr>
<tr>
<td>S</td>
<td>Alfa Aesar Puratronics</td>
<td>99.999%</td>
<td>Pieces ~2-3 mm</td>
</tr>
</tbody>
</table>

Table 4.1: Elemental suppliers, purities, and sizes.
Based on the work of Hor and Cava\textsuperscript{43} (see Chapter 2) the first samples synthesized were $\text{Cu}_{0.02}\text{TaSe}_{1.8}\text{S}_{0.2}$ (XCh100) and $\text{Ni}_{0.02}\text{TiSe}_{1.8}\text{S}_{0.2}$ (XCh101). The goal with the latter was to switch Cu (one of Hor and Cava’s best samples was $\text{Cu}_{0.02}\text{TiSe}_{1.8}\text{S}_{0.2}$) with Ni to see the effects of other 3d intercalants on electronic transport. Intercalating Cu into sulfur substituted $\text{TaSe}_2$ was more or less a venture of curiosity. Initial transport measurements resulted in the project focusing on $\text{TiSe}_2$-based compounds. Initially, the ratio of Se to S was varies for a constant 2% Ni per formula. While the properties of the Ni intercalated samples (XCh111-114) were improved over Hor and Cava’s Cu doped samples, it was necessary to attempt to understand the role of the nickel intercalant. Therefore, a series of samples with varying amounts of Ni intercalated into $\text{TiSe}_2$ was prepared (XCh115-126). Finally, samples were prepared and processed under different conditions to see the effects of the processing on the structure and transport properties (XCh127-129; XCh130-132 are divisions of the former that were processed at different temperatures).

<table>
<thead>
<tr>
<th>Step</th>
<th>Set Point (°C)</th>
<th>Rate (°C/hour)</th>
<th>Duration (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Ramp</td>
<td>500</td>
<td>125</td>
<td>4</td>
</tr>
<tr>
<td>Preliminary Hold</td>
<td>500</td>
<td>N/A</td>
<td>12</td>
</tr>
<tr>
<td>Final Ramp</td>
<td>650</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>Final Hold</td>
<td>650</td>
<td>N/A</td>
<td>120</td>
</tr>
</tbody>
</table>

*Table 4.2*: Sample synthesis parameters.
Table 4.3: Samples list with nominal compositions. Samples are referred to as XCh[num], where [num] is the sample number. The sample number is sequential and follows chronologically the order of synthesis. The samples are grouped in terms of relevant compositions and investigation goals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>Cu$<em>{0.02}$TaSe$</em>{1.8}$S$_{0.1}$</td>
</tr>
<tr>
<td>100</td>
<td>Cu$<em>{0.02}$TaSe$</em>{1.8}$S$_{0.2}$</td>
</tr>
<tr>
<td>108</td>
<td>Cu$<em>{0.02}$TaSe$</em>{1.7}$S$_{0.3}$</td>
</tr>
<tr>
<td>107</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.9}$S$_{0.06}$</td>
</tr>
<tr>
<td>101</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.9}$S$_{0.1}$</td>
</tr>
<tr>
<td>103</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.8}$S$_{0.2}$</td>
</tr>
<tr>
<td>109</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.7}$S$_{0.3}$</td>
</tr>
<tr>
<td>105</td>
<td>Ta$<em>{0.72}$W$</em>{0.28}$Se$_{2}$</td>
</tr>
<tr>
<td>106</td>
<td>Ta$<em>{0.04}$W$</em>{0.96}$Se$_{2}$</td>
</tr>
<tr>
<td>104</td>
<td>Pb$<em>{0.05}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>110</td>
<td>Pd$<em>{0.05}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>111</td>
<td>TiSe$<em>{1.8}$S$</em>{0.2}$</td>
</tr>
<tr>
<td>112</td>
<td>Ni$<em>{0.01}$TiSe$</em>{1.8}$S$_{0.2}$</td>
</tr>
<tr>
<td>113</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.8}$S$_{0.2}$</td>
</tr>
<tr>
<td>114</td>
<td>Ni$<em>{0.03}$TiSe$</em>{1.8}$S$_{0.2}$</td>
</tr>
<tr>
<td>115</td>
<td>TiSe$_{2}$</td>
</tr>
<tr>
<td>116</td>
<td>Ni$<em>{0.01}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>117</td>
<td>Ni$<em>{0.03}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>118</td>
<td>Ni$<em>{0.05}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>119</td>
<td>Ni$<em>{0.02}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>120</td>
<td>Ni$<em>{0.05}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>121</td>
<td>Ni$<em>{0.04}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>122</td>
<td>Ni$<em>{0.03}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>123</td>
<td>Ni$<em>{0.04}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>124</td>
<td>Ni$<em>{0.06}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>125</td>
<td>Ni$<em>{0.03}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>126</td>
<td>Ni$<em>{0.01}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>127</td>
<td>TiSe$_{2}$</td>
</tr>
<tr>
<td>128</td>
<td>Ni$<em>{0.06}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>129</td>
<td>Ni$<em>{0.10}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>130</td>
<td>TiSe$_{2}$</td>
</tr>
<tr>
<td>131</td>
<td>Ni$<em>{0.05}$TiSe$</em>{2}$</td>
</tr>
<tr>
<td>132</td>
<td>Ni$<em>{0.10}$TiSe$</em>{2}$</td>
</tr>
</tbody>
</table>

Processing

All samples were densified using spark plasma sintering (SPS). Like hot pressing, the SPS process uses uni-axial loading in a high temperature environment to compact powders and induce grain inter-growth to form a solid pellet. The main difference between the two processes is in the source and nature of the heating. In spark plasma sintering, the sample itself is the source of the heat as current driven through the sample causes joule heating at the grain boundaries, which is contrary to a hot press where the sample is externally heated by a large graphite element that surrounds the die and punches that contain the sample.

The current supplied to the sample was rectified into a pulsed direct current. The system, being able to control the output in terms of alternating between on for a number of pulses and then off for a number of pulses in a sort of gating fashion, was set to on for
12 pulses and off for 2 pulses. The reason for using a pulsing direct current instead of a regulated one has to do with maximizing the arcing action that is the signature of the SPS process. The purpose of using an alternating on-off gating action is to allow for the system to have some sort of relaxation time to prevent overheating.

The nature of the heating in spark plasma sintering comes with both advantages and disadvantages. The most obvious advantages of internally heating the sample are higher ramping rates, greater control of the sample temperature, and reduced processing time. The processing time of the SPS is reduced over the hot press (usually $t_{\text{SPS}} \approx 20\% t_{\text{HP}}$) since the entire chamber is not heated in the SPS and therefore the thermal mass of what is actually heated, and then cooled, is much lower. The higher heating rates result in a greater preservation of the microstructure as less time is spent at lower temperatures where surface diffusion dominates over bulk diffusion. Preserving small grain size or unique and complex microstructures is often advantageous for thermoelectrics as they are often effective in suppressing the lattice thermal conductivity in a material. Because of the SPS process’ greater efficiency in initial neck formation by grain boundary pre-wetting and then in promoting densification via crystal diffusion (due to the localized heating), the pressures involved SPS processing are lower than those required for hot pressing—typically, $P_{\text{SPS}} \approx 25\% P_{\text{HP}}$.

One possible consequence of the electric field used in the SPS process is electromigration. This is a result of momentum being transferred from the current carriers to the ions of the conductor, which in the case of SPS, is the sample. This effect is not necessarily a concern to this work because the rate of electromigration
depends on the current density, activation energy of ions. While the current densities used in this work were high (200 – 400 A/cm\(^2\)—not taking pores into account), this is an order of magnitude lower than, for example, those used in the experiments of reference 57. Additionally, the time scale involved with electromigration is generally on the order of days, if not weeks, compared to just minutes for this work. These comparisons considered, the possibility of electromigration in the processing of all samples in this work was ignored.

The processing of all samples began with grinding the precursor powders using an agate mortar and pestle. Each sample was removed from the sealed quartz tube in which it was synthesized, ground, and loaded into a die for SPS processing within a time frame of one to two hours. This was done to minimize any oxidation of the powders. The dies were ½” inside diameter and made out of graphite, as were the punches. A small hole was drilled into the side of each die at half the height and just deep enough so that the distance from the end of the bore to the inside wall of the die was about 1-2 mm. This hole accommodates the thermocouple of the system that is used to monitor the processing temperature.

The processing parameters were initially controlled manually throughout the duration of the sintering process in order to determine the appropriate temperature and force. The force (actually the pressure, which depends on the diameter of the die to which the force is applied) is not as critical for most samples when processing with SPS compared to HP. Generally, 30 to 50 MPa is sufficient, but the only way to know the appropriate force is through trial and error. If the sample does not begin sintering, or
does not sinter enough before the temperature of processing reaches near the decomposition or melting point of the material, then the pressure must be increased. Simply using a very high pressure for all samples is not favorable as the load is not isostatic and therefore a higher pressure means a higher possibility of texturing that would result in anisotropy in the transport and mechanical properties.

While the force is set in the beginning of the process and remains constant, the temperature is actively controlled throughout the process by adjusting the current limiting knob. Monitoring the z-axis position (z) of the rams is key to determining the temperature at which sintering begins and saturates. The initial ramping targets a heating rate of 300 – 400 °C/min, and as the die (sample, die and punches, actually) begins to heat up, the z will first drop as to maintain constant force as it compensates the thermal expansion of the system. Once the temperature reaches roughly 60% of the decomposition or melting limit of the material, the rate was slowed to about 100 – 200 °C/min until the z begins to increase. At this point the temperature is allowed to rise an additional 5-10% and then held constant. The duration of the hold time is determined by the travel of z—once it begins to level off, the process is then deemed to be finished.

The first sample to be densified was XCh100 ($\text{Cu}_{0.02}\text{TaSe}_{1.8}\text{S}_{0.2}$). The force was set to 5.3 kN, which results in ~50 MPa when applied to the ½" (inside) diameter dies that were used for all samples. The temperature was increased as described in the previous paragraph until the z began to increase as the sample began to sinter and compact—near 730 – 750°C. The hold temperature was maintained at 800°C for about 6 – 8 minutes. The second sample, XCh101 ($\text{Ni}_{0.02}\text{TiSe}_{1.8}\text{S}_{0.2}$), was likewise processed
with roughly the same parameters. Both samples came out of the dies as solid pellets without cracks. Even after samples were cut for measurements, they appeared to be macroscopically homogenous and without visible defects. As the processing was assumed to be successful, and to ensure consistency of processing dependent effects between all samples, a temperature program was set for all samples (Table 4.4). Using the programmable temperature controller allowed for further maximization of the initial heating rate.

<table>
<thead>
<tr>
<th>Step</th>
<th>Set Point (°C)</th>
<th>Rate (°C/min)</th>
<th>Duration (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Ramp</td>
<td>600</td>
<td>600</td>
<td>1</td>
</tr>
<tr>
<td>Approach Sintering</td>
<td>750</td>
<td>150</td>
<td>1</td>
</tr>
<tr>
<td>Approach Hold</td>
<td>800</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>Hold</td>
<td>800</td>
<td>0</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 4.4: Automated temperature program used for all samples XCh102 through XCh126, except XCh109.

For reasons explained in the following chapter, samples XCh127 through XCh132 were synthesized with the intention of looking at the effects of different processing temperatures on the final composition, structure, and subsequent transport properties. Samples XCh127-130 were processed with a similar program as described in Table 4.4 with a final hold temperature of 650°C and duration of 6 minutes. Samples XCh131-132 were likewise processed with a final hold temperature of 725°C for 6 minutes.
CHAPTER FIVE
STRUCTURAL AND COMPOSITIONAL ANALYSIS

Structure Analysis Using X-ray Diffraction

The initial phase analysis performed between synthesis and densification was performed with a bench-top X-ray diffractometer (Rigaku MiniFlex). Synthesized powders were ground using an agate mortar and pestle to maximize the random sampling of crystallite orientations. Cu-\(\kappa_a\) radiation was used which included both \(\kappa_{a1}\) and \(\kappa_{a2}\) wavelengths. Using a two-theta goniometer, data was collected in 0.01° steps with a scan rate of 1.0°/min.

These initial XRD scans showed the samples with no Ni to be single phase (TiSe\(_2\), spacegroup \(P\bar{3}m1\)). In all samples that contained Ni, there were peaks indicating a secondary phase of NiSe\(_2\). The relative intensities of these peaks increased with increasing Ni content and the area fraction of the strongest NiSe2 peak to the strongest TiSe\(_2\) peak of XCh118 (~5% Ni) was roughly 4%, suggesting that most of the Ni simply formed NiSe\(_2\) during synthesis rather than going into the TiSe\(_2\) matrix as an intercalant. Since most references indicate that a several step process was necessary for reaching a homogeneous intercalated phase, this should be expected. The surprising result of the SPS process, as shown in Fig. 5.1, is that it removed all observable traces of the secondary phase. A look at the shift in the (002) peak towards higher 2\(\theta\) and the broadening of the (110) peak after SPS indicate that the Ni does go from the secondary phase to the vacancies in the van der Waals gap of the host TiSe\(_2\) matrix.
Table 5.1: Comparison of before and after SPS processing XRD data. The table above contains data for XCh115 while the lower table is of XCh118.

Pieces cut from spark plasma sintered pellets were also ground and sent to the University of Waterloo for high resolution X-ray analysis by Dr. Holger Kleinke’s group. Obtaining high resolution data was necessary for refining the structure parameters. Diffraction patterns were obtained with monochromated Cu-$k_\alpha_1$ radiation using an INEL XRG 3000 diffractometer equipped with a position-sensitive detector. Data was
collected from $2\theta = 8$ to $118^\circ$ with a bin-width of $0.029^\circ$. Since a position sensitive detector collects counts from the full range simultaneously, it is the collection time that contributes the fidelity of the pattern rather than a scan rate—the count time for the high resolution patterns was 18 to 20 hours. While the bin-width of the high resolution data is larger than that of the bench-top Rigaku system, the short sample-to-detector distance of the Rigaku system is roughly half that of the INEL system, and the surface area of the Rigaku detector is also larger than that of the INEL detector. These two differences result in the Rigaku detector being less spatially resolved as it covers a greater portion of the solid angle. Additionally, the combination of the Rigaku’s scan rate and step size results in a count time of 0.6 seconds per step. This is far lower than the 18 to 20 hours of counting for all angles with the INEL system.

The XRD patterns taken with the INEL system were indeed much smoother than those taken with the Rigaku system. The background was easily fitted and removed, and then the peak profiles fitted. Most peaks were easily profiled with the exception of the peak located near $2\theta = 14.5^\circ$ for all samples. In the TiSe$_2$ phase, this peak corresponds to the (001) planes. Figure 5.2a shows the (001) peak of sample XCh115. As seen, the peak profile is not well profiled using just one peak. Using the MDI Jade software package, the peaks were deconvoluted (Table 5.4). Since only the (001) peak is not fitted well with one peak, it is unlikely that a separate phase exist on a macroscopic level—as in separate crystallites. It is more likely that the effect of having both Ni and Ti in the vacancies between $a$-$b$ layers results in an order-disorder scenario where layers may appear ‘corrugated’ or ‘dimpled’. This effect may not be apparent in higher reflections.
across multiple planes because the range of the order-disorder is small enough that it is
lost in the added broadening that naturally comes with higher reflections. That is to say,
that the (002) peak may be a convolution of two peaks which are both broad and centered
closer together so that they can be fit as one peak.

Table 5.2 displays the $c$ and $a$ lattice parameters calculated from the high
resolution XRD patters. The $c$ lattice parameter was calculated by doubling the $d$-spacing
determined from the (002), and also by doubling the difference between (001) and (002).
The latter method is used to negate any possible offset in $2\theta$. In a like manner, the $a$
lattice parameter was calculated from the difference of the (100) and (300) peaks. A
factor of $3/2$ comes from the fact that (300) plane spacing is $1/3$ that of (100) as a result
of being in reciprocal space, and a factor of $2/\sqrt{3} (=1/\sin[60])$ arises from the trigonal
shape of the unit cell. From samples XCh115 to XCh119 both the $c$ and $a$ lattice
parameters increase with both increasing Ni and decreasing Ti. Sample XCh118 does not
necessarily follow this trend, but as it is shown in the later chapters, this sample also
breaks trends in some transport and other physical properties.

The apparent trend itself is somewhat surprising. While studies of Ni
intercalation show a trend of decreasing $c$ with increasing Ni (up to at least $x = .25$),\textsuperscript{61}
quantitative studies of the effect of excess Ti on the lattice parameters are lacking.
However, if all the vacancy sites of the van der Waals gap are filled with Ti, then the
structure becomes TiSe which have the lattice parameters $c = 6.301$ Å and $a = 3.571$ Å.
The TiSe structure preserves the octahedral coordination of the Se and Ti but now forms
a three dimensional structure with no van der Waals gap. The $c$ and $a$ are expanded as
the Ti atoms at \( z = 0 \) are hybridized with those at \( z = 1/2 \) and their covalent radii must be accommodated. Subsequently one should expect the \( c \) lattice parameter to expand with increasing excess Ti. The observed trend does not follow what is expected for either the Ni or the excess Ti. It may be perhaps that Ni + Ti in the van der Waals gap has a unique effect on the lattice at relatively low concentrations, but as the Ni content increases while the excess Ti decreases, the \( c \) parameter will begin to follow the trend of decreasing with the increasing Ni.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( x )</th>
<th>( \delta )</th>
<th>( 2(d_{001} - d_{002}) )</th>
<th>( 2d_{002} )</th>
<th>( (3/\sqrt{3})(d_{100} - d_{300}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>0</td>
<td>0.130</td>
<td>5.993</td>
<td>6.010</td>
<td>3.543</td>
</tr>
<tr>
<td>124</td>
<td>0.009</td>
<td>0.115</td>
<td>6.061</td>
<td>6.012</td>
<td>3.551</td>
</tr>
<tr>
<td>119</td>
<td>0.022</td>
<td>0.109</td>
<td>6.111</td>
<td>6.055</td>
<td>3.585</td>
</tr>
<tr>
<td>118</td>
<td>0.053</td>
<td>0.098</td>
<td>6.085</td>
<td>6.028</td>
<td>3.573</td>
</tr>
</tbody>
</table>

**Table 5.2:** Lattice parameters calculated from high resolution XRD data. The \( c \) parameter was calculated two ways: as double the difference between the \( d \)-spacing of the (001) and (002) peaks, and as double the \( d \)-spacing of the (002) peak. The amount of Ni and excess Titanium were determined from EPMA (see next section: Compositional Analysis).

<table>
<thead>
<tr>
<th>XCh115</th>
<th>XCh118</th>
<th>XCh119</th>
<th>XCh123</th>
<th>XCh118</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>6.0016</td>
<td>6.0365</td>
<td>6.0831</td>
<td>6.0278</td>
</tr>
<tr>
<td>100</td>
<td>3.0683</td>
<td>3.0733</td>
<td>3.0967</td>
<td>3.0721</td>
</tr>
<tr>
<td>002</td>
<td>3.0050</td>
<td>3.0061</td>
<td>3.0274</td>
<td>3.0013</td>
</tr>
</tbody>
</table>

**Table 5.3:** \( d \)-spacing of several peaks for all samples measured. Here the (001) peak has not been deconvoluted so the \( d \)- spacings are a result of the best fit using single peaks.
Table 5.4: Deconvolution of the (001) peak from high resolution XRD data. The separation (in $2\theta$) of deconvoluted peaks increases with Ni concentration.

<table>
<thead>
<tr>
<th></th>
<th>(001) Peak</th>
<th>Height</th>
<th>Relative Area (%)</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2\theta$</td>
<td>$d$ (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XCh115</td>
<td>14.684</td>
<td>6.0277</td>
<td>61102</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>14.752</td>
<td>6.0003</td>
<td>122000</td>
<td>100</td>
</tr>
<tr>
<td>XCh124</td>
<td>14.589</td>
<td>6.0670</td>
<td>68825</td>
<td>56.3</td>
</tr>
<tr>
<td></td>
<td>14.654</td>
<td>6.0398</td>
<td>221203</td>
<td>100</td>
</tr>
<tr>
<td>XCh119</td>
<td>14.407</td>
<td>6.1430</td>
<td>12237</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>14.557</td>
<td>6.0801</td>
<td>138705</td>
<td>100</td>
</tr>
<tr>
<td>XCh118</td>
<td>14.464</td>
<td>6.1190</td>
<td>14645</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>14.610</td>
<td>6.0583</td>
<td>180481</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 5.5: The trend of increasing secondary (001) peak $d$-spacing roughly correlates to both increasing nickel and decreasing excess titanium content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>$\delta$</th>
<th>$d_{001}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>0</td>
<td>0.130</td>
<td>6.0277</td>
</tr>
<tr>
<td>124</td>
<td>0.009</td>
<td>0.115</td>
<td>6.0670</td>
</tr>
<tr>
<td>119</td>
<td>0.022</td>
<td>0.109</td>
<td>6.1430</td>
</tr>
<tr>
<td>118</td>
<td>0.053</td>
<td>0.098</td>
<td>6.1190</td>
</tr>
</tbody>
</table>

Due to sample throughput limitations of the high resolution XRD at the University of Waterloo, only a few samples could be analyzed with high resolution XRD. The samples of the sulfur substituted system (Ni$_x$Ti$_{1+\delta}$Se$_{2+y}$S$_y$, XCh111-114) could only be analyzed by low resolution XRD. The $c$ lattice parameter was calculated using the difference in $d_{001}$ and $d_{002}$ planes, while $a$ was determined from the (100) peak. The results are presented in Table 5.11 and discussed further in the following sections.
**Compositional Analysis**

In order to understand the relationship between the transport properties, structure parameters, and intercalant concentrations of the samples, compositional analysis was required. We decided to use electron micro-probe analysis, EMPA, in order to better determine the composition of the many samples reported herein. This was performed at the University of Georgia’s (UGA) Geology Department by Chris Fleisher. All samples of the two series $Ni_{x}Ti_{1+x}Se_2$ (XCh115 – XCh132) and $Ni_{x}Ti_{1+x}Se_{2-y}S_y$ (XCh111 – XCh114) were set in conducting epoxy and polished with up to 1200 grit metallurgical sand paper.

At UGA, the samples were briefly re-polished in order to freshen the surface and then sputtered with graphite. Using an electron-probe micro analyzer, the system was first optimized with the appropriate standards. Each sample was then spot analyzed in 4 to 6 random locations, making sure to sample any areas of contrast that showed up on the scanning electron image. The resulting data points were averaged and converted from weight percent to atomic percent to determine the stoichiometry of each sample.

The EPMA data revealed that all samples had a Ti:(Se,S) ratio greater than 1:2, with the exception of XCh114 ($Ni_{0.037}Ti_{0.996}Se_{1.815}S_{0.185}$). It was then necessary to determine whether the off-stoichiometry was due to chalcogen vacancies or excess Ti. Woo et al.\(^{58}\) have shown that $Ti_{1+x}Se_2$ crystals may be synthesized with $x$ being as high as 0.2. Additionally, the samples were synthesized at 650°C and processed at 800°C. DiSalvo et al. showed that synthesis temperatures higher than 700°C (but possibly even lower) resulted in an amount of excess titanium in the van der Waals gap proportional to the
synthesis temperature.\textsuperscript{59} While the higher processing temperature of the spark plasma sintering used to pelletize the powders proved effective in removing secondary phases, it appears to have also removed some selenium from the system, therefore resulting in excess titanium. The density studies described in the next session provide additional proof that this is indeed the case.

### Table 5.6: Sample compositions normalized to 2 chalcogens per formula.

<table>
<thead>
<tr>
<th>ID</th>
<th>Nom. %Ni</th>
<th>EPMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>0</td>
<td>Ti\textsubscript{1.13}Se\textsubscript{2}</td>
</tr>
<tr>
<td>125</td>
<td>0.3</td>
<td>Ni\textsubscript{0.003}Ti\textsubscript{1.096}Se\textsubscript{2}</td>
</tr>
<tr>
<td>124</td>
<td>0.7</td>
<td>Ni\textsubscript{0.009}Ti\textsubscript{1.115}Se\textsubscript{2}</td>
</tr>
<tr>
<td>126</td>
<td>1</td>
<td>Ni\textsubscript{0.012}Ti\textsubscript{1.099}Se\textsubscript{2}</td>
</tr>
<tr>
<td>119</td>
<td>2</td>
<td>Ni\textsubscript{0.022}Ti\textsubscript{1.109}Se\textsubscript{2}</td>
</tr>
<tr>
<td>123</td>
<td>4</td>
<td>Ni\textsubscript{0.045}Ti\textsubscript{1.085}Se\textsubscript{2}</td>
</tr>
<tr>
<td>118</td>
<td>5</td>
<td>Ni\textsubscript{0.053}Ti\textsubscript{1.098}Se\textsubscript{2}</td>
</tr>
<tr>
<td>111</td>
<td>0</td>
<td>Ti\textsubscript{1.041}Se\textsubscript{1.787}S\textsubscript{0.213}</td>
</tr>
<tr>
<td>112</td>
<td>1</td>
<td>Ni\textsubscript{0.011}Ti\textsubscript{1.036}Se\textsubscript{1.780}S\textsubscript{0.220}</td>
</tr>
<tr>
<td>113</td>
<td>2</td>
<td>Ni\textsubscript{0.015}Ti\textsubscript{1.038}Se\textsubscript{1.795}S\textsubscript{0.205}</td>
</tr>
<tr>
<td>114</td>
<td>3</td>
<td>Ni\textsubscript{0.037}Ti\textsubscript{0.996}Se\textsubscript{1.815}S\textsubscript{0.185}</td>
</tr>
</tbody>
</table>

**Sample Density**

The density of each sample was measured using Archimedes’ method with water as the medium. Each sample was measured twice to confirm the results. In order to confirm whether the off-stoichiometry is due to excess Ti or Se vacancies, the theoretical density was calculated for composition of both scenarios. The unit cell used in these calculations was determined from the experimental lattice parameters.
Table 5.7 presents the calculated and measured densities with the percent differences. A negative percent difference means the calculated density is lower than the experimental. The Se normalized theoretical densities are much closer to the measured than the Ti normalized densities, which are 10 to 15% lower than the measured. The mechanical properties of dilutely intercalated ‘3d’$_x$TiSe$_2$ results in high relative densities even for cold pressed samples—even up to 99%. It is then expected that samples processed with SPS will be very close to theoretical density. Therefore, the Ti normalized theoretical densities being significantly lower than the measured indicate that the compositional model doesn’t fit.

Table 5.7: Comparison of measured densities to theoretical densities for both normalization scenarios.
While the Se normalized theoretical densities are much closer than those of the Ti normalized to experimental values, the percent difference is still a little high. This difference comes partly from the uncertainty involved with the density measurement, which is on the order of 1 – 2%. An additional source of error is in the determined lattice parameters. While the XRD data indicates a single phase, the peaks used to determine the lattice are a bit complex in terms of their width and shape. This is due to the effects of two different intercalant species being dispersed throughout the van der Waals gap, with each expected to have different effects on the lattice constant (especially the $c$ parameter).

An additional attempt was made to determine the theoretical density of the densified samples by considering the intercalated bulk to be made up of several pure phases with known structural parameters—TiSe (note: the formula of the whole unit cell is Ti$_2$Se$_2$) and Ni$_x$TiSe$_2$. The lattice parameters used for cell volume calculations of TiSe were taken from the literature.$^{60}$ The lattice parameters used for Ni$_x$TiSe$_2$ were calculated using Vegard’s Rule with data obtained from Arnaud et al.$^{61}$ The total density was then estimated to be the atomic masses of the elements of each phase summed according to stoichiometry, divided by the unit cell volume, and then apportioned by the phase fractions.

$$\rho_{\text{est.}} = \frac{Xm_{\text{Ni}} + (1-\delta)(m_{\text{Ti}} + 2m_{\text{Se}}) + 2\delta(m_{\text{Ni}} + m_{\text{Se}})}{V_{\text{TiSe}}^\text{Ni,TiSe, Vegard’s Law}} \frac{V_{\text{TiSe}}}{V_{\text{TiSe}}} \quad (5.1)$$

Table 5.8 reveals the details of this calculation while Table 5.9 displays the resulting theoretical densities, which agree quite well (at least within the limit of the
uncertainty of the density measurements) with experimental data. It must be mentioned that the measured densities do not vary much from sample to sample (less than 3% between most and less dense), and the spread of the estimated densities is even less (~1%). In Table 5.10 the contribution to the total estimated density from each phase is shown. From the EPMA data, it appears that the amount of excess Ti is roughly inversely related to the amount of Ni. This trend is followed by the phase contributions of TiSe and Ni$_x$TiSe$_2$, and the result is only a weak spread in the estimated densities. The measured densities follow this trend much more than the theoretical densities obtained from experimental lattice parameters of the system. As discussed in earlier in this chapter, the peaks of the XRD patterns appear to be complex and defining a single value for the peak position from which the lattice parameters were determined may not be valid. These results suggest that the Ni and Ti intercalants do not randomly mix in the van der Waals gap, but due to their opposite effects on $c$, they create separate regions of Ti and Ni intercalation.
Table 5.8: Constituent phase cell parameters, volume, and fraction. Literature values were used for constituent lattice parameters and thus cell volumes. Theoretical densities were determined by summing the constituents’ densities scaled by their phase fractions.

<table>
<thead>
<tr>
<th>Ni$<em>x$Ti$</em>{1+\delta}$Se$_2$</th>
<th>Phase</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_x$TiSe$_2$</td>
<td>=1-(\delta)</td>
<td></td>
</tr>
<tr>
<td>TiSe</td>
<td>=(\delta)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XCh115</th>
<th>c</th>
<th>a</th>
<th>Cell Volume</th>
<th>Phase Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSe$_2$</td>
<td>6.008</td>
<td>3.640</td>
<td>65.203</td>
<td>0.870</td>
</tr>
<tr>
<td>TiSe</td>
<td>6.301</td>
<td>3.571</td>
<td>69.586</td>
<td>0.130</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XCh124</th>
<th>c</th>
<th>a</th>
<th>Cell Volume</th>
<th>Phase Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_{0.009}$TiSe$_2$</td>
<td>6.005</td>
<td>3.539</td>
<td>65.124</td>
<td>0.885</td>
</tr>
<tr>
<td>TiSe</td>
<td>6.301</td>
<td>3.571</td>
<td>69.586</td>
<td>0.115</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XCh126</th>
<th>c</th>
<th>a</th>
<th>Cell Volume</th>
<th>Phase Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_{0.012}$TiSe$_2$</td>
<td>6.003</td>
<td>3.539</td>
<td>65.116</td>
<td>0.901</td>
</tr>
<tr>
<td>TiSe</td>
<td>6.301</td>
<td>3.571</td>
<td>69.586</td>
<td>0.099</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XCh119</th>
<th>c</th>
<th>a</th>
<th>Cell Volume</th>
<th>Phase Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_{0.022}$TiSe$_2$</td>
<td>5.999</td>
<td>3.539</td>
<td>65.088</td>
<td>0.891</td>
</tr>
<tr>
<td>TiSe</td>
<td>6.301</td>
<td>3.571</td>
<td>69.586</td>
<td>0.109</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XCh123</th>
<th>c</th>
<th>a</th>
<th>Cell Volume</th>
<th>Phase Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_{0.045}$TiSe$_2$</td>
<td>5.990</td>
<td>3.640</td>
<td>65.024</td>
<td>0.915</td>
</tr>
<tr>
<td>TiSe</td>
<td>6.301</td>
<td>3.571</td>
<td>69.586</td>
<td>0.085</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XCh118</th>
<th>c</th>
<th>a</th>
<th>Cell Volume</th>
<th>Phase Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_{0.063}$TiSe$_2$</td>
<td>5.987</td>
<td>3.541</td>
<td>65.002</td>
<td>0.902</td>
</tr>
<tr>
<td>TiSe</td>
<td>6.301</td>
<td>3.571</td>
<td>69.586</td>
<td>0.098</td>
</tr>
</tbody>
</table>
Table 5.9: Comparison of the measured densities and the densities calculated from volume fractions of constituent phases.

| Sample Name | EMPA Composition | Measured by Archimedes (g/cc) | Estimation from Constituents (g/cc) | Percent Difference (Est.-Meas./Avg.,%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>XCh115</td>
<td>Ti₁,₁₂₀Se₂</td>
<td>5.364</td>
<td>5.346</td>
<td>-0.32%</td>
</tr>
<tr>
<td>XCh124</td>
<td>Ni₀,₀₀₀Ti₁,₁₁₉Se₂</td>
<td>5.317</td>
<td>5.353</td>
<td>0.68%</td>
</tr>
<tr>
<td>XCh126</td>
<td>Ni₀,₀₁₂Ti₁,₀₀₉Se₂</td>
<td>5.353</td>
<td>5.345</td>
<td>-0.14%</td>
</tr>
<tr>
<td>XCh119</td>
<td>Ni₀,₀₂₂Ti₁,₁₀₉Se₂</td>
<td>5.321</td>
<td>5.371</td>
<td>0.92%</td>
</tr>
<tr>
<td>XCh123</td>
<td>Ni₀,₀₄₅Ti₁,₀₈₅Se₂</td>
<td>5.372</td>
<td>5.390</td>
<td>0.34%</td>
</tr>
<tr>
<td>XCh118</td>
<td>Ni₀,₀₅₃Ti₁,₀₉₈Se₂</td>
<td>5.470</td>
<td>5.402</td>
<td>-1.24%</td>
</tr>
</tbody>
</table>

Table 5.10: The individual contributions of the TiSe and NiₓTiSe₂ phases to the total estimated densities. Excess titanium appears to be inversely proportional to the amount of intercalated nickel, though the trend is loosely correlated. The result is that the phase contributions follow the same trend, and the total estimated density is roughly independent of composition within the series.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>EMPA Composition</th>
<th>Excess Titanium</th>
<th>Intercalated Nickel</th>
<th>Contribution of TiSe</th>
<th>Contribution of NiₓTiSe₂</th>
<th>Total Est. Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>XCh115</td>
<td>Ti₁,₁₂₀Se₂</td>
<td>0.130</td>
<td>0.000</td>
<td>0.787</td>
<td>4.560</td>
<td>5.346</td>
</tr>
<tr>
<td>XCh124</td>
<td>Ni₀,₀₀₀Ti₁,₁₁₉Se₂</td>
<td>0.115</td>
<td>0.009</td>
<td>0.696</td>
<td>4.656</td>
<td>5.353</td>
</tr>
<tr>
<td>XCh126</td>
<td>Ni₀,₀₁₂Ti₁,₀₀₉Se₂</td>
<td>0.099</td>
<td>0.012</td>
<td>0.599</td>
<td>4.744</td>
<td>5.346</td>
</tr>
<tr>
<td>XCh119</td>
<td>Ni₀,₀₂₂Ti₁,₁₀₉Se₂</td>
<td>0.109</td>
<td>0.022</td>
<td>0.660</td>
<td>4.707</td>
<td>5.371</td>
</tr>
<tr>
<td>XCh123</td>
<td>Ni₀,₀₄₅Ti₁,₀₈₅Se₂</td>
<td>0.085</td>
<td>0.045</td>
<td>0.515</td>
<td>4.870</td>
<td>5.390</td>
</tr>
<tr>
<td>XCh118</td>
<td>Ni₀,₀₅₃Ti₁,₀₉₈Se₂</td>
<td>0.098</td>
<td>0.063</td>
<td>0.593</td>
<td>4.814</td>
<td>5.402</td>
</tr>
</tbody>
</table>

Table 5.11: The lattice parameters from which the density of the sulfur substituted samples was calculated were determined from low resolution XRD data. The theoretical densities increase with increasing Ni as expected. The measured densities follow the opposite trend and decrease with increasing Ni.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Composition</th>
<th>c</th>
<th>a</th>
<th>Theoretical (g/cm)</th>
<th>Measured (g/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XCh111</td>
<td>Ti₁,₀₄₁Se₁,₀₇₈S₀,₀₂₃₃</td>
<td>6.036</td>
<td>3.548</td>
<td>4.990</td>
<td>4.874</td>
</tr>
<tr>
<td>XCh112</td>
<td>Ni₀,₀₁₁Ti₁,₀₅₆Se₁,₀₇₈S₀,₀₂₂₀</td>
<td>6.031</td>
<td>3.548</td>
<td>4.997</td>
<td>4.793</td>
</tr>
<tr>
<td>XCh113</td>
<td>Ni₀,₀₁₅Ti₁,₀₃₈Se₁,₀₇₉S₀,₀₂₀₅</td>
<td>5.963</td>
<td>3.537</td>
<td>5.112</td>
<td>4.716</td>
</tr>
<tr>
<td>XCh114</td>
<td>Ni₀,₀₃₇Ti₀,₀₉₉₀S₁,₈₁₅S₀,₁₈₅</td>
<td>5.955</td>
<td>3.54</td>
<td>5.115</td>
<td>4.663</td>
</tr>
</tbody>
</table>
Figure 5.1: Comparison of pre- and post-SPS. While the $c$ lattice parameter calculated by the (001) peak was calculated to have expanded, the shift in the (002) peak indicates the van der Waals gap to have decreased slightly.
Figure 5.2a: The (001) peak of all samples could not be easily profiled using single peaks. This is the best possible fit obtained for XCh115.

Figure 5.2b: The (001) peak of XCh115 is a convolution of two peaks.
Figure 5.3: Deconvolution of the (001) peaks of XCh124 and XCh119. The area fraction of a second peak required to fit the peak becomes less as the Ni and excess Ti increase.
CHAPTER SIX
THERMAL TRANSPORT PROPERTIES

Low Temperature Specific Heat Capacity of Ni\textsubscript{1-x}Ti\textsubscript{1+x}Se\textsubscript{2}

Eq. (3.13) gives the electronic and phononic contributions to the specific heat capacity as a function of temperature. Dividing the heat capacity by the temperature and collecting constants results in the temperature (and of course molar) specific heat capacity to be written as a function of a constant, $\gamma$, and a $T^2$ term multiplied by $\beta$. The first constant represents the electronic contribution to the specific heat capacity and $\beta$ represents the phononic (lattice) contribution. Plotting $c_p T^{-1}$ versus $T^2$ allows for easy linear fitting, which will yield the constants of interest.

$$\frac{c_p}{T} = \gamma + \beta T^2 \quad (5.2)$$

The results of the fitting are presented in Table 6.1. The Debye temperature remains nearly constant as the Ni is increased up to sample XCH118 (Ni\textsubscript{0.053}Ti\textsubscript{1.098}Se\textsubscript{2}), of which $\theta_D$ is increased. Eq. (3.11) defines the Debye temperature and shows its dependence on the velocity of sounds in the material and density of atoms per unit volume. The trend in density from Table 5.9 appears to correlate to the trend in $\theta_D$, and a plot of both measured and theoretical densities versus Debye temperature is shown in Fig. 6.3.
Table 6.1: Results of low temperature ($T < 5K$) fitting of the specific heat. The Debye temperature ($\theta_D$) and the Fermi energy ($E_F$) were determined from $\beta$ and $\gamma$, respectively, using Eqs. (3.13) and (5.2).

<table>
<thead>
<tr>
<th></th>
<th>XCh115 Ti$_{1.13}$Se$_2$</th>
<th>XCh124 Ni$<em>{0.006}$Ti$</em>{1.115}$Se$_2$</th>
<th>XCh119 Ni$<em>{0.022}$Ti$</em>{1.109}$Se$_2$</th>
<th>XCh118 Ni$<em>{0.053}$Ti$</em>{1.099}$Se$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>2.07E-03</td>
<td>1.93E-03</td>
<td>2.29E-03</td>
<td>3.61E-03</td>
</tr>
<tr>
<td>$\beta$</td>
<td>3.50E-04</td>
<td>3.52E-04</td>
<td>3.49E-04</td>
<td>3.30E-04</td>
</tr>
<tr>
<td>$\theta_D$ (K)</td>
<td>259</td>
<td>259</td>
<td>259</td>
<td>264</td>
</tr>
<tr>
<td>$E_F$ (eV)</td>
<td>1.7</td>
<td>1.8</td>
<td>1.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Low Temperature Thermal Conductivity of Ni$_x$Ti$_{1+x\delta}$Se$_2$

The intercalation of Ni into Ti$_{1+x\delta}$Se$_2$ appears to lower the low temperature crystalline peak that is expected in an ordered crystal with only a few defects/impurities at the temperature where phonon-phonon scattering compensates the decreasing effect of defect scattering. This indicates, as may be corroborated by Fig. 5.1, that the Ni adds to the disorder of the system, and the thermal conductivity below 100 K decreases with increasing Ni. Towards room temperature, however, the electronic contribution to the total thermal conductivity comes into play and the higher electrical conductivity of the samples with more Ni results in an increase in total thermal conductivity of the Ni intercalated samples over the samples that were not intercalated.

Fig. 6.4 shows the low temperature total thermal conductivity of the Ni$_x$Ti$_{1+x\delta}$Se$_2$ system. Due to the nature of the measurement technique, the radiative loss must be corrected for at high temperatures. In order to correct for the radiation that increases with temperature, the electronic contribution was first calculated using the Wiedemann-Franz relation shown in Eq. (1.34) with a Lorenz number appropriate for degenerate semiconductors and semimetals—$2.1\times10^{-8}$ W·Ω/K$^2$. The electronic contribution was
then subtracted and the remaining thermal conductivity attributed to the lattice, $\kappa_{ph}$, and radiation contributions. The $\kappa_{ph}$ vs. temperature curve was then analyzed. At higher temperatures, above the peak temperature, $\kappa_{ph}$ should show a $1/T$ dependence due to phonon-phonon interactions. The higher temperature data for $\kappa_{ph}$ was fit with a three term formula accounting for (1) a constant term that indicates the minimum value at which the $\kappa_{ph}$ will saturate, (2) the $T^{-1}$ dependence of $\kappa_{ph}$, and (3) a $T^3$ radiation term:

$$\text{fit}(\kappa_{ph}) = A + B \frac{T}{T} + CT^3$$

(5.3)

This model fit the data above 225 K very well and the total and lattice thermal conductivities were corrected for radiative losses. Fig. 6.5 shows all the contributions to the uncorrected total thermal conductivity of XCh118. At room temperature, the correction is only on the order of 10 to 12%. This was essentially the same for all samples since sample geometries were very similar. Fig. 6.6 compares the corrected lattice thermal conductivities of Ni$_x$Ti$_{1+\delta}$Se$_2$. Now that the electronic contributions have been subtracted, there is a clear trend of decreasing lattice thermal conductivity with increasing Ni for all the samples shown. The lattice thermal conductivity is proportional to the cube of the Debye temperature divided by the square of the Grüneisen parameter, $(\kappa_{ph} \propto \theta_D^3 / \gamma_G^2)$, and it can be seen from Table 6.1 that the Debye temp of XCh115 (Ti$_{1.130}$Se$_2$) and XCh119 (Ni$_{0.022}$Ti$_{1.109}$Se$_2$) are nearly the same. The reduction in thermal conductivity must be due to an increase in $\gamma_G$, which is proportional to the thermal expansion coefficient and inversely proportional to the density ($\gamma_G \propto \alpha_v / \rho_v$). The measured and estimated theoretical densities of are nearly the same (Table 5.9). All of
this at least suggest that the decrease in lattice thermal conductivity is due to an increase in the thermal expansion coefficient, $\alpha_t$. While this was not measured, it certainly is possible as the increase of Ni and the disorder it adds to the lattice of the system may increase the anharmonicity of the phonon modes. While this same argument may suggest that $\alpha_t$ should also be higher for XCh118 (Ni$_{0.033}$Ti$_{1.098}$Se$_2$), the reduction in the Debye temperature indicates a reduction in available phonon modes. The likely case is that both a reduction of the phonon density of states as well as an increase in the anharmonicity of the system is the result for further reduction of the lattice thermal conductivity.

*Low Temperature Thermal Conductivity of Ni$_x$Ti$_{1+\delta}$Se$_{2-y}$S$_y*$

The sulfur substituted system exhibited a lower total thermal conductivity than the Ni$_x$Ti$_{1+\delta}$Se$_2$ system. As compared to Cu$_x$TiSe$_{2-y}$S$_y$ data from Hor and Cava, the thermal conductivities of the Ni$_x$Ti$_{1+\delta}$Se$_{2-y}$S$_y$ system are still lower, and show more of an amorphous behavior (Fig. 6.7). The total and lattice thermal conductivities of the sulfur-substituted samples were also corrected for radiation loss, and the results are shown in Figs. 6.8 and 6.9, respectively. It is observed from the data that the lattice thermal conductivity is not monotonically related to the Ni concentration.

Sample XCh114 (Ni$_{0.037}$Ti$_{0.996}$Se$_{1.815}$S$_{0.185}$) is the only sample of either series to not have excess Ti. The small deficiency of Ti may be due to Ni substitution on Ti sites made energetically favorable by the distortions of the lattice from the sulfur substitutions, or the deficiency may be false—resulting from the uncertainty of the EPMA data. In either case, it is interesting to compare samples XCh111 (Ti$_{1.041}$Se$_{1.787}$S$_{0.213}$) and XCh114.
Both samples have only one atomic species in the van der Waals gap. As a result, the intercalants may order themselves within the gap to increase the crystallinity. The two samples with both Ni and Ti in the gap exhibit more of an amorphous behavior.

All samples of the $\text{Ni}_x\text{Ti}_{1+y}\text{Se}_2$, $\text{Ni}_x\text{Ti}_{1+y}\text{S}_2$, series exhibit both lower total and lattice thermal conductivity values versus those of the $\text{Ni}_x\text{Ti}_{1+y}\text{Se}_2$ series. This is mostly most likely due to the lower densities of the sulfur-substituted samples (between 4.66 and 4.87 g/cm$^3$ versus 5.32 to 5.47 g/cm$^3$ for the system without sulfur). An additional source of the reduction in the lattice thermal conductivity may come from the added disorder that the sulfur creates in the structure of the $a$-$b$ planes, as well as from the effects of mass fluctuation on phonon scattering. Perhaps a useful future study would be the effect of sulfur substitution on the phonon dispersion relation and consequential phonon density of states.
Figure 6.1: Specific heat with Dulong-Petit limit of $c_v$ in the inset.
Figure 6.2: Specific heat of $Ni_{x}Ti_{1+x}\delta Se_{2}$ below 5 K. The inset is $c_{p}T^{-1}$ plotted versus $T^{2}$ with linear fit lines.
Figure 6.3: Measured and estimated theoretical densities versus the Debye temperatures calculated from low temperature $c_p$ data.
Figure 6.4: Total thermal conductivity of \( \text{Ni}_{x} \text{Ti}_{1-x} \text{Se}_2 \) after radiation correction. Inset shows the uncorrected data as measured.
Figure 6.5: Radiation correction to the thermal conductivity of $Ni_{0.053}Ti_{1.098}Se_{2}$. The relative magnitudes of the corrections were comparable between samples.
Figure 6.6: Lattice thermal conductivity of $Ni_xTi_{1+y}Se_2$ after radiation correction. The unexpected plateau feature between 75 and 150 K in $Ni_{0.022}Ti_{1.109}Se_2$ is probably a result of the charge density wave transition. This feature may also be present in $Ti_{1.130}Se_2$ but may weaker or be hidden in the higher crystalline peak.
Figure 6.7: Total thermal conductivity of \( \text{Ni}_{x} \text{Ti}_{1+x} \text{Se}_{2+y} \text{S}_{y} \) before radiation correction. Thermal conductivity of similar Cu intercalated compounds from Hor and Cava.\(^{43}\)
Figure 6.8: Radiation corrected total thermal conductivity of $Ni_{x}Ti_{1+x}Se_{2-y}S_{y}$. 
Figure 6.9: Radiation corrected lattice thermal conductivity of $Ni_{x}Ti_{1+\delta}Se_{2-y}$. 
CHAPTER SEVEN

ELECTRONIC TRANSPORT PROPERTIES

*Electrical Resistivity and Seebeck of Ni$_x$Ti$_{1+y\delta}$Se$_2*

The electronic transport measurements of the Ni$_x$Ti$_{1+y\delta}$Se$_2$ system are sensitive to both the sample species and amount of intercalants. The electronic structure of the semimetal TiSe$_2$ has special implications for the transport properties when it comes to doping and alloying. With both holes and electron bands meeting at the Fermi energy at different $k$-points, just a few percent of intercalants can significantly affect the number and sign of the carriers as well as the density of states at the Fermi energy. Appendix A gives electronic density of states diagrams for several relevant compounds to show the effects of Ni and excess Ti in the van der Waals gap.

From Fig. 7.1 it can be seen that the intercalation suppresses the magnitude of the charge density wave (CDW) anomaly as observed from the resistivity versus temperature curves shown for the Ni$_x$Ti$_{1+y\delta}$Se$_2$ system. The onset temperature of the anomaly is also systematically shifted towards lower temperatures. This is a further indication of Ni inducing disorder in the lattice. In the sample with the most Ni, XCh118 ($Ni_{0.053}Ti_{1.098}Se_2$), there is no evidence of a CDW transition that can be observed.

The low and high temperature Seebeck coefficient (thermopower) values are compared to the low temperature data of TiSe$_2$ (Disalvo et al.)$^{59}$ in Fig. 7.2. In sample XCh115 ($Ti_{1.130}Se_2$), the CDW peak is considerably suppressed but still at roughly the same temperature that of pristine TiSe$_2$. The magnitude and temperature dependence of
the thermopower above 150 K are, however, very different. The thermopower of TiSe$_2$
rapidly goes to zero and changes sign by room temperature. In XCh115, the
thermopower remains below -50 $\mu$V/K up to 575 K with a gently sloping region between
200 and 400 K. By comparing the DOS of TiSe$_2$ in Fig. A-1 with that of Ti$_{1.25}$Se$_2$ in Fig.
A-2, the addition of Ti into the vacancies of the van der Waals gap results in extra Ti-3d
states just above $E_F$. These bands most likely add electron states and along with itinerate
3d electrons to compensate the hole concentration that must increase with temperature in
the TiSe$_2$ host. This picture is corroborated by the effective carrier concentrations
calculated from the Hall resistivity as shown in (Fig. 7.6).

The addition of Ni into the van der Waals gap further suppresses the charge
density wave anomalies at low temperatures but increases the temperature at which the
maximum thermopower is reached. This temperature, having to do with bipolar
conduction, is related to the ratio of holes to electrons. The trends in the temperature
dependencies of the effective carrier concentrations at room temperature correlate to the
high temperature thermopower data—showing a more negative slope as it approaches the
temperature regime above room temperature as the maximum temperature for the
thermopower is shifted upwards.

The power factor was calculated from the electrical resistivity and the
thermopower ($PF = \alpha^2 T / \rho$). The linear, metallic behavior of the three samples with the
most nickel (XCh119, XCh123, and XCh124) results in a quadratic trend in their power
factors. Due to the curvature of the thermopower in the samples with less nickel, the PF
exhibits a down turn above ~100 K. The high and full temperature range for the power
factors are shown in Fig. 7.4. The high temperature turnover in the power factors of all samples comes from the bipolar conduction induced turnovers in the thermopower. XCh123 and XCh118, having the highest thermopower maximum temperature, exhibit the highest power factors at the highest temperatures.

Low Temperature Electrical Resistivity and Seebeck of Ni$_x$Ti$_{1+\delta}$Se$_{2-y}$S$_y$

The low temperature transport properties of Ni$_x$Ti$_{1+\delta}$Se$_{2-y}$S$_y$ were measured and are compared with those of the Cu intercalated Cu$_x$TiSe$_{2-y}$S$_y$. The electrical resistivity versus temperature curves displayed in Fig. 7.7 shows all the nickel intercalated, sulfur substituted samples to be metallic with the magnitude of the most resistive sample remaining under 1 mΩ-cm at room temperature. A clear correlation between the resistivity and the Ni, excess Ti, or Se:S trends independently. The expected trends are that the resistivity should increase with increasing Ni and excess Ti, whereas they should decrease with increasing sulfur. Observing the three samples with Ni, the excess Ti and the sulfur concentrations decrease with increasing Ni. Additionally, the packing densities of the samples also decrease with increasing Ni. Unfortunately, there are too many variables in the system to make a clear correlation of these data with either the Ni or Ti intercalants. However it is clear that these samples are all considerably lower than those of the Cu intercalated samples in the reference.

As is typical in thermoelectrics research, the gains in electrical conductivity were offset with losses in the Seebeck coefficients. Fig. 7.8 presents the low temperature Seebeck coefficient data of Ni$_x$Ti$_{1+\delta}$Se$_{2-y}$S$_y$ and selected samples from the reference. The
charge density wave anomaly is unobservable in all $Ni_xTi_{1+y}Se_{2-z}S_y$ samples with the
exception of XCh112 ($Ni_{0.011}Ti_{1.036}Se_{1.780}S_{0.220}$). However, in XCh12, the anomaly is very
small—much smaller than that of XCh115 ($Ti_{1.130}Se_2$) and all the Cu intercalated samples
shown. This indicates that the excess Ti (which is about three times less in all sulfur
substituted samples than in the unsubstituted samples) in conjunction with the
substitution of sulfur is enough to suppress the formation of excitons (hole-electron
pairing), or at least prevent exciton-phonon interactions that result in a CDW. Note that
the Seebeck coefficient of $TiSe_{1.8}S_{0.2}$ of the reference exhibits quite a large CDW
anomaly.

The power factors of the sulfur substituted samples are plotted with reference data
in Fig. 7.9. Due to the absence of a CDW, all sulfur substituted samples of this work
exhibit a $T^2$ dependence, with the exception of XCh112, which happens to be near linear
above 100 K due to the small presence of the CDW anomaly in the Seebeck coefficient.
This results in XCh112 having the highest power factor at room temperature of about 3.3
Wm$^{-1}$K$^{-1}$. The temperature dependencies of the Ni intercalated samples suggests that
their power factor values above room temperature will be higher than the best samples
from Hor and Cava’s work.
Figure 7.1: Low temperature electrical resistivity of $Ni_xTi_{1+\delta}Se_2$. 

Lower $T_{\text{ONSET}}$ with increasing Ni.
Figure 7.2: Low and high temperature Seebeck coefficients of $Ni_xTi_{1+x}Se_2$ with reference data of pristine $TiSe_2$ from DiSalvo et al.\textsuperscript{59}
Figure 7.3: Low temperature Seebeck coefficients of $Ni_xTi_{1+x}Se_2$ with reference data of pristine $TiSe_2$ from DiSalvo et al.\textsuperscript{59}
Figure 7.4: Low and temperature power factor of $Ni_xTi_{1+y}Se_2$. 

Change in sign of the curvature of PF
Figure 7.5: Low and high temperature power factor of $Ni,Ti_{1+x}\delta Se_2$. 
Figure 7.6: Effective carrier concentration as a function of temperature.
Figure 7.7: Low temperature electrical resistivity of $Ni_{x}Ti_{1+y}Se_{2-x}S_{y}$. 
Figure 7.8: Low temperature Seebeck coefficients of $Ni_xTi_{1+y}Se_{2+y}S_y$. 
Figure 7.9: Low temperature power factors of $Ni_xTi_{1+y}Se_{2-y}S_y$. 

- Ti$_{1.041}$Se$_{1.787}$S$_{0.213}$
- Ni$_{0.011}$Ti$_{1.038}$Se$_{1.780}$S$_{0.220}$
- Ni$_{0.015}$Ti$_{1.038}$Se$_{1.795}$S$_{0.205}$
- Ni$_{0.037}$Ti$_{1.036}$Se$_{1.815}$S$_{0.185}$
- Hor & Cava (2009) TiSe$_{1.8}S_{0.2}$
- Hor & Cava (2009) Cu$_{0.01}$TiSe$_{1.8}S_{0.2}$
- Hor & Cava (2009) Cu$_{0.02}$TiSe$_{1.8}S_{0.2}$
CHAPTER 8
CONCLUSION AND FINAL REMARKS

The goal of this study was to see if a viable, cheap, and relatively environmentally safe thermoelectric material can be made from a system that is traditionally hasn’t been sought after for thermoelectric studies. Despite exhibiting a charge density wave transition—which competes with thermoelectricity for the Fermi surface—TiSe$_2$ was chosen to be a good candidate. This is due to its structural and electronic versatility in terms of the large number of atoms—both in variety and quantity—that it may host in between its layers, and its unique band structure that is in the “grey area” between a metal and semiconductor, and also between a majority hole carrier and majority electron carrier system.

The structural, thermal, and electronic properties of Ni and Ti co-intercalation do not follow the conventional trends of the single 3$d$ intercalated TiSe$_2$ systems, including Ni$_x$TiSe$_2$. The synergetic combination of two intercalants has provided a new way to improve the thermoelectric properties of this system. The effects of the intercalants have been explained and understood in terms of their independent and collaborated effects on the disorder of the crystal structure, independent effects on the density of electronic states at the Fermi energy, contribution of carriers to the system, and their effects on the phononic transport of the system.

The additional parameter of sulfur substitution on the selenium sites has also been studied and compared to similar recent studies of other, single intercalant systems. The
co-intercalation of both Ni and Ti into the mixed system \( Ti(Se,S)_2 \) has resulted in an enhanced ZT for this system. To date very little complete thermoelectric data has been published on 3d-intercalated \( TiSe_2 \), and Hor and Cava’s work, published in 2009, represent the current state of the thermoelectric studies of this material. Fig. 8.1 displays the ZT of \( Ni_xTi_{1+y}Se_{2-y}S_y \) with that of Hor and Cava’s best sample.

While a ZT of \(~0.09\) has been realized in sample XCh112 at room temperature, this is well below the ZT\(~1 - 2\) range that the state-of-the-art materials possess. Therefore, titanium and nickel co-intercalated titanium diselenide, even with sulfur substitution, are not viable thermoelectrics. Still, these materials are rich in interesting electrical transport phenomena and have proved to be an ideal system for the investigation and understanding of the effects on intercalation on the electronic structure and resulting electronic transport properties.
Figure 8.1: Low temperature ZT of $Ni_xTi_{1+y}Se_{2-y}S_y$. The maximum ZT in Hor and Cava’s $Cu_xTiSe_{2-y}S_y$ system was found for $x=0.02$, $y=0.3$ with ZT~0.07 at 300 K, over which sample XCh112 ($Ni_{0.011}Ti_{1.036}Se_{1.780}S_{0.220}$) shows nearly a 30% increase.
APPENDICES

Appendix A

Band Structure and Density of States Calculations

The electronic band structures of several compounds were calculated using the Stuttgart TB-LMTO software package. This program employs the linear muffin tin orbital (LMTO) and the atomic spheres approximation. Calculations were performed with 16 points along each \( k \)-vector. In the case of intercalated supercells, the lattice parameters used were multiples of \( c \) and \( a \) parameters determined by Vegard’s rule.
The extra layer of Ti atoms located in the van der Waals gap at (0 0 ½) result in added states at $E_F$. As shown in Fig. A-2, even just 25% excess Ti results in these added states.
Figure A-2: Density of States for $\text{TiSe}_2$ with 25% Ni and 25% Ti in the van der Waals gap vacancies.
Appendix B

*Magnetic Susceptibility of Ni\textsubscript{5}Ti\textsubscript{1+x+δ}Se\textsubscript{2}*

Thermoelectric phenomena by nature pertain to the lattice and charge degrees of freedom, and the magnetic properties that originate from the spin degree of freedom are usually not of interest in thermoelectric materials research. However, the magnetic susceptibility at low temperatures may provide some useful information about the structural and electronic states of the system. The susceptibility is defined as the moment, $M$, of a material in an external magnetic field of strength, $B$.

$$\chi = \frac{M}{B}$$  \hspace{1cm} (5.4)

Conduction electrons are paramagnetic in terms of their response to an external magnetic field (actually, the susceptibility of conduction electrons contains both a paramagnetic term and a weaker, negative diamagnetic term that arises from the Lorentz force and is equal to one-third the contribution from Pauli paramagnetism). While their susceptibility ($\chi$) should follow a $T^{-1}$ Curie dependence, the fact that only those electrons within $k_B T$ of $E_F$ are available to the conduction bands results in their $\chi$ being temperature independent. The paramagnetic susceptibility of conduction electrons is therefore:

$$\chi_p \propto \frac{1}{k_B T} \cdot \frac{k_B \chi}{E_F} \rightarrow \chi_p = \frac{3\mu^2}{2E_F}$$  \hspace{1cm} (5.5)

The ion cores of the lattice may also exhibit paramagnetic behavior, but with the total population participating, the $T^{-1}$ behavior is observed. However, the ion cores may exhibit the tendency to ferromagnetically (or antiferromagnetically) order themselves by way of an exchange field, $B_E$, that must be added to the applied field when evaluating the
magnetic susceptibility. In the temperature regime where there is enough thermal energy prevent the ions from actually achieving the ferromagnetic ordering, the result is a paramagnetic susceptibility that follows the Curie-Weiss Law:

\[
\chi_{C-W} = \frac{C}{T-\theta} \tag{5.6}
\]

The parameter \(\theta\) is related to the strength of the exchange field, and in ferromagnets, \(\theta\) is the Curie temperature \((T_C)\)—the temperature at which thermal energy overcomes the exchange field and the material goes from ferromagnetic to paramagnetic. This value may be negative, which indicates that there nearest neighbor interactions of the exchange field are of the antiferromagnetic type. The Curie constant \((C)\) is related to the effective moment of the paramagnetic ions by the gyromagnetic ratio \((g)\) and the spin angular momentum \((S)\):

\[
C = \frac{g^2 S(S+1)\mu_B^2}{3k_B} = \frac{g^2 \mu_B^2}{3k_B} \tag{5.7}
\]

There have been a few studies of the effects of 3d metal intercalation on the magnetic properties of \(M_xTiSe_2\). At low concentrations of magnetic intercalants, many of these are paramagnetic with a Curie-Weiss ‘tail’ above 5 K. As with many of the materials in the references, the magnetic susceptibilities of all samples measured in this study were fit over the entire temperature regime (~7 – 300 K) with a constant term that contains all diamagnetic and Pauli free-spin contributions and a Curie-Weiss term:

\[
\chi = \chi_0 + \chi_{C-W} = \chi_0 + \frac{C}{T-\theta} \tag{5.8}
\]
From Eq. (5.7) the effective moment may be deduced. Comparing the effective moments of the intercalants (Ti and Se ions have no magnetic moments) with the corresponding value for a free ion will give an indication of the degree to which the orbitals of the intercalants are hybridized with the Ti-3\textit{d} and Se-4\textit{p} orbitals of the host.\textsuperscript{65} The effective moment ought to also correlate to the change in the \textit{c} lattice parameter as the bonding of the intercalants to the layers of the TiSe\textsubscript{2} host matrix will effect the separation between layers.\textsuperscript{64,65} If the diamagnetic contribution to $\chi_0$ can be calculated, then the Pauli free-spin term may be calculated and $E_F$ estimated from Eq. (5.5).

The magnetic moment versus temperature was measured for a selection of samples from the $\text{Ni}_x\text{Ti}_{1+\delta}\text{Se}_2$ set using a vibrating sample magnetometer (VSM) option of a Quantum Design PPMS®. Sample pieces weighing between 25 and 50 mg were cut from the same pellets from which the bar samples for thermal and electrical transport measurements were cut. The samples were each placed at the center of a quartz paddle about 3 inches long, and held in place by heat shrink tubing that covered the whole length of the paddle. Measurements were taken from 7 K to room temperature under a field of 1 – 2 Tesla.

The magnetic moment was measured on the same selection of samples for which the heat capacity and high resolution XRD were measured. All samples show a Curie-Weiss behavior indicating the samples to be paramagnetic. The data was fit to extract the Pauli paramagnetic contribution from the carrier free spins and the effective moments of the ions. As with the Debye temperature and other properties, the effective moment of the localized ions increases with increasing Ni content until sample XCh118. This may
indicate that the Ni atoms in sample XCh118 are more strongly bonded to the layers, which would be supported by the metallic behavior of its resistivity and Seebeck.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Ni</th>
<th>$\chi_0$ (emu/Oe·g)</th>
<th>$\chi_P$ (emu/Oe·g)</th>
<th>$\theta$ (K)</th>
<th>$P$ ($K^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XCh115</td>
<td>0.0%</td>
<td>-3.34E-09</td>
<td>5.17E-07</td>
<td>-1.24</td>
<td>5.19E-13</td>
</tr>
<tr>
<td>XCh124</td>
<td>0.9%</td>
<td>1.06E-08</td>
<td>5.31E-07</td>
<td>-2.01</td>
<td>1.80E-12</td>
</tr>
<tr>
<td>XCh119</td>
<td>2.2%</td>
<td>3.15E-08</td>
<td>5.51E-07</td>
<td>-1.60</td>
<td>9.22E-14</td>
</tr>
<tr>
<td>XCh118</td>
<td>5.3%</td>
<td>5.65E-08</td>
<td>5.76E-07</td>
<td>-1.13</td>
<td>2.20E-13</td>
</tr>
<tr>
<td>Baranov</td>
<td>10.0%</td>
<td>1.20E-07</td>
<td>6.40E-07</td>
<td>-1.30</td>
<td>4.55E-13</td>
</tr>
</tbody>
</table>

Table B-1: The magnetic parameters of $Ni_xTi_{1+x}Se_2$ determined by VSM. The diamagnetic contribution was assumed to be a constant and taken from Baranov et al.\textsuperscript{64.}\textsuperscript{Error! Bookmark not defined.} The data of Baranov et al. is listed here for comparison. In their work, the nickel concentration was nominal and the possibility of excess Ti was not investigated.
Figure B-1: Curie-Weiss behavior of the localized magnetic moments of the ions in Ni$_x$Ti$_{1+\delta}$Se$_2$. 

\[ \chi \text{ (emu/[Oe-g]}) \]

\[ \text{Temperature (K)} \]

- Ni$_{0.022}$Ti$_{1.109}$Se$_2$
- Ni$_{0.009}$Ti$_{1.115}$Se$_2$
- Ti$_{1.130}$Se$_2$
Appendix C

Complete Sample List

Though the scope of this work focuses on the effects of Ni and Ti co-intercalation in TiSe$_2$ and TiSe$_{1.8}$S$_{0.2}$, many other samples were synthesized and the low temperature electronic transport properties measured. The initial samples (XCh100 – XCh110) were chosen for thermoelectric investigations based on recent literature reports of similar compounds (XCh101, -103, -107, and -109), which would become the bases for the work of this dissertation. Some were selected based on preliminary band structure calculations (XCh104 – 106, -110), while others were selected purely out of curiosity—note that these were some of the early samples that, while they showed interesting charge density wave behavior, they were not potential thermoelectrics (XCh100, -102, and -108). The samples XCh127 – XCh132 were prepared for the purpose of investigating the effect of synthesis temperature on the amount of excess Ti, which is discussed in Appendix D.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Formula</th>
<th>Sample No.</th>
<th>Formula</th>
<th>Sample No.</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>Cu$<em>{0.02}$TaSe$</em>{1.8}$S$_{0.1}$</td>
<td>111</td>
<td>TiSe$<em>{1.8}$S$</em>{0.2}$</td>
<td>115</td>
<td>TiSe$_2$</td>
</tr>
<tr>
<td>100</td>
<td>Cu$<em>{0.02}$TaSe$</em>{1.8}$S$_{0.2}$</td>
<td>112</td>
<td>Ni$<em>{0.01}$TiSe$</em>{1.8}$S$_{0.2}$</td>
<td>125</td>
<td>Ni$_{0.03}$TiSe$_2$</td>
</tr>
<tr>
<td>108</td>
<td>Cu$<em>{0.02}$TaSe$</em>{1.7}$S$_{0.3}$</td>
<td>113</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.8}$S$_{0.2}$</td>
<td>120</td>
<td>Ni$_{0.06}$TiSe$_2$</td>
</tr>
<tr>
<td>107</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.8}$S$_{0.05}$</td>
<td>114</td>
<td>Ni$<em>{0.03}$TiSe$</em>{1.8}$S$_{0.2}$</td>
<td>124</td>
<td>Ni$_{0.03}$TiSe$_2$</td>
</tr>
<tr>
<td>101</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.9}$S$_{0.1}$</td>
<td>116</td>
<td>Ni$_{0.01}$TiSe$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>103</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.8}$S$_{0.2}$</td>
<td>127</td>
<td>TiSe$_2$</td>
<td>126</td>
<td>Ni$_{0.01}$TiSe$_2$</td>
</tr>
<tr>
<td>109</td>
<td>Ni$<em>{0.02}$TiSe$</em>{1.7}$S$_{0.3}$</td>
<td>128</td>
<td>Ni$_{0.05}$TiSe$_2$</td>
<td>119</td>
<td>Ni$_{0.02}$TiSe$_2$</td>
</tr>
<tr>
<td>105</td>
<td>Ta$<em>{0.75}$W$</em>{0.25}$Se$_2$</td>
<td>129</td>
<td>Ni$_{0.10}$TiSe$_2$</td>
<td>117</td>
<td>Ni$_{0.03}$TiSe$_2$</td>
</tr>
<tr>
<td>106</td>
<td>Te$<em>{0.9}$W$</em>{0.1}$Se$_2$</td>
<td>130</td>
<td>TiSe$_2$</td>
<td>122</td>
<td>Ni$_{0.03}$TiSe$_2$</td>
</tr>
<tr>
<td>104</td>
<td>Pb$_{0.02}$TiSe$_2$</td>
<td>131</td>
<td>Ni$_{0.05}$TiSe$_2$</td>
<td>123</td>
<td>Ni$_{0.04}$TiSe$_2$</td>
</tr>
<tr>
<td>110</td>
<td>Pd$_{0.02}$TiSe$_2$</td>
<td>132</td>
<td>Ni$_{0.10}$TiSe$_2$</td>
<td>118</td>
<td>Ni$_{0.05}$TiSe$_2$</td>
</tr>
</tbody>
</table>

Table C-1: Complete list of samples synthesized grouped by relevant compositions. The sample number ID follows chronological order of synthesis.
| Sample ID | Nominal Composition | SPS T (°C) | SPS t (min) | RT α (µV/K) | RT ρ (mΩ-cm) | RT PF (Wm⁻¹K⁻¹) | RT κ (Wm⁻¹K⁻¹) | RT ZT |}
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>Cu₉₀₂TaSe₁₈S₀₁</td>
<td>800</td>
<td>6</td>
<td>-2.9</td>
<td>0.644</td>
<td>3.9E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>Cu₉₀₂TaSe₁₈S₀₂</td>
<td>VAR</td>
<td>VAR</td>
<td>-1</td>
<td>0.956</td>
<td>2.0E-05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>108</td>
<td>Cu₉₀₂TaSe₁₈S₀₃</td>
<td>800</td>
<td>6</td>
<td>-2.8</td>
<td>0.669</td>
<td>3.6E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>Ni₀₀₂TiSe₁₈S₀₅</td>
<td>800</td>
<td>6</td>
<td>-75.3</td>
<td>0.640</td>
<td>0.265</td>
<td></td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>Ni₀₀₂TiSe₁₈S₀₅</td>
<td>VAR</td>
<td>VAR</td>
<td>-74.5</td>
<td>15.506</td>
<td>0.011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>103</td>
<td>Ni₀₀₂TiSe₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-59.9</td>
<td>1.283</td>
<td>0.083</td>
<td></td>
<td></td>
</tr>
<tr>
<td>109</td>
<td>Ni₀₀₂TiSe₁₈S₀₃</td>
<td>800</td>
<td>6</td>
<td>-54.7</td>
<td>0.629</td>
<td>0.142</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>Ta₀₃₉₃W₀₇₇₅Se₂</td>
<td>800</td>
<td>6</td>
<td>-3.0</td>
<td>0.814</td>
<td>3.2E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>106</td>
<td>Ta₀₃₉₃W₀₇₇₅Se₂</td>
<td>950</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>104</td>
<td>Pb₀₂TiSe₂</td>
<td>800</td>
<td>6</td>
<td>-69.7</td>
<td>0.934</td>
<td>0.156</td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>Pb₀₂TiSe₂</td>
<td>800</td>
<td>6</td>
<td>-37.3</td>
<td>0.973</td>
<td>0.042</td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>TiSe₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-68.6</td>
<td>0.617</td>
<td>0.229</td>
<td>3.82</td>
<td>0.06</td>
</tr>
<tr>
<td>112</td>
<td>Ni₁₀TiSe₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-84.5</td>
<td>0.647</td>
<td>0.331</td>
<td>3.60</td>
<td>0.09</td>
</tr>
<tr>
<td>113</td>
<td>Ni₀₀₂TiSe₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-70.8</td>
<td>0.859</td>
<td>0.174</td>
<td>3.34</td>
<td>0.05</td>
</tr>
<tr>
<td>114</td>
<td>Ni₀₀₂TiSe₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-61.3</td>
<td>0.558</td>
<td>0.200</td>
<td>3.32</td>
<td>0.06</td>
</tr>
<tr>
<td>115</td>
<td>TiSe₂</td>
<td>800</td>
<td>6</td>
<td>-73.0</td>
<td>0.740</td>
<td>0.216</td>
<td>4.29</td>
<td>0.05</td>
</tr>
<tr>
<td>125</td>
<td>Ni₀₀₃₉₉₀₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-77.9</td>
<td>0.691</td>
<td>0.261</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>Ni₀₀₉₉₀₉₉₀₂</td>
<td>800</td>
<td>6</td>
<td>-84.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>Ni₀₀₇₉₉₀₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-74.6</td>
<td>0.718</td>
<td>0.231</td>
<td></td>
<td></td>
</tr>
<tr>
<td>116</td>
<td>Ni₁₀₀₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-77.5</td>
<td>0.775</td>
<td>0.232</td>
<td></td>
<td></td>
</tr>
<tr>
<td>126</td>
<td>Ni₁₀₀₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-72.7</td>
<td>0.626</td>
<td>0.253</td>
<td></td>
<td></td>
</tr>
<tr>
<td>119</td>
<td>Ni₀₀₉₉₀₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-70.2</td>
<td>0.634</td>
<td>0.233</td>
<td>4.51</td>
<td>0.05</td>
</tr>
<tr>
<td>117</td>
<td>Ni₁₀₀₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-62.6</td>
<td>0.710</td>
<td>0.166</td>
<td></td>
<td></td>
</tr>
<tr>
<td>122</td>
<td>Ni₀₀₉₉₀₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-67.5</td>
<td>0.635</td>
<td>0.214</td>
<td></td>
<td></td>
</tr>
<tr>
<td>123</td>
<td>Ni₀₀₉₉₀₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-56.7</td>
<td>0.514</td>
<td>0.186</td>
<td></td>
<td></td>
</tr>
<tr>
<td>118</td>
<td>Ni₀₀₉₉₀₁₈S₀₂</td>
<td>800</td>
<td>6</td>
<td>-45.5</td>
<td>0.516</td>
<td>0.121</td>
<td>4.32</td>
<td>0.03</td>
</tr>
<tr>
<td>127</td>
<td>TiSe₂</td>
<td>650</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>Ni₀₀₉₉₀₁₈S₀₂</td>
<td>650</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>129</td>
<td>Ni₁₀₀₁₈S₀₂</td>
<td>650</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>TiSe₂</td>
<td>725</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>131</td>
<td>Ni₀₀₉₉₀₁₈S₀₂</td>
<td>725</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>132</td>
<td>Ni₁₀₀₁₈S₀₂</td>
<td>725</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table C-2: Nominal compositions, processing conditions, and room temperature transport properties of all samples.
REFERENCES

8 L Onsager, *Phys. Rev.* **37** (1931) 405; **38** (1931)


