

A Search for Novel Low Temperature Thermoelectric Materials
by
Christopher G. HolmesParker

A PROJECT
submitted to
Oregon State University
University Honors College

in partial fulfillment of
the requirements for the
degree of

Honors Baccalaureate of Science in Chemical Physics (Honors Associate)

Presented June 04, 2009
Commencement June 2009

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AN ABSTRACT OF THE THESIS OF

Christopher G. HolmesParker for the degree of Honors Baccalaureate of Science in Chemical Physics presented on June 04, 2009. Title: A Search for Novel Low Temperature Thermoelectric Materials.

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Research was conducted to determine the thermoelectric behavior of Co_9S_8 , Co_9Se_8 , CoSe , CoTe_2 , $\text{CoSbSe}_x\text{S}_{1-x}$ ($x=0, 0.25, 0.50, 0.75, 1.0$), CoSbTe , AuTe_2 , $\text{AuTe}_{1.90}\text{Sb}_{0.10}$, $\text{Au}_{0.95}\text{Pt}_{0.05}\text{Te}_2$, $\text{Au}_{0.95}\text{Ag}_{0.05}\text{Te}_2$, MnTe_2 , $\text{MnTe}_{1.95}\text{Sb}_{0.05}$, $\text{MnTe}_{1.90}\text{Sb}_{0.10}$, CoSb_2 , and $\text{Co}_{0.95}\text{Fe}_{0.05}\text{Sb}_2$. Recently discovered sodium cobalt oxide compounds have been found to have large Seebeck coefficients coupled with favorable thermal and electrical resistivity, making them promising candidates for future thermoelectric device applications. Research suggests that this behavior in the sodium cobalt oxides is due to the 4^+ oxidation state of cobalt atoms within these materials. Cobalt compounds can in some cases retain large amounts of entropy until low temperature magnetic ordering of electrons occurs within the compound. The electrical resistivity and thermal resistivity of these cobalt compounds become more favorable at these lower temperatures. In these compounds, a consistently high Seebeck coefficient is maintained until the rapid low temperature magnetic ordering occurs. Additional non-cobalt-containing compounds were also tested based upon their promise as future thermoelectric materials. The Seebeck coefficient, magnetic susceptibility, electrical resistivity, and structural properties of selected compounds were observed and recorded.

Key Words: Thermoelectric, Cobalt, Manganese, Conductivity, Resistivity, Seebeck
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I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes the release of my project to any reader upon request.

Christopher G. HolmesParker

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This thesis is dedicated to Martin and Luana Parker, who have believed in me and provided me with unwavering support throughout all my endeavors.

A Search for Novel Low Temperature Thermoelectric Materials

INTRODUCTION

Problem Definition

Modern technologies are reaching the physical limits of materials used within the devices. In the future, advancements in technologies will be limited to the rate of progress within the field of materials science. Currently, materials science research is one of the fastest growing fields in the world. One of the much needed material advancements and discoveries comes in the field of thermoelectric materials research. The United States Air Force put out a proposal for Low Temperature Thermoelectric Materials Research. This proposal was aimed at the development of thermoelectric materials which can be used and in fact perform at their peak in cold environments. The development of these materials is the primary concern of this research.

The History and Discovery of Thermoelectric Materials

The thermoelectric effect was accidentally discovered in 1823 by Thomas Johann Seebeck. This discovery occurred when Seebeck observed a compass needle deflecting in the presence of two dissimilar metals joined together at a junction in which a thermal gradient was present. Seebeck did not realize that the deflection was due to a current induced between the metals, he instead hypothesized that a magnetic phenomenon occurred between the two materials. [1]. Seebeck investigated numerous materials,

arranging them in order of the product of their electrical conductivity, α , and Seebeck coefficient, σ . If Seebeck had created a thermocouple with the first and last materials in his data series, he would have created a thermoelectric generator with 3% efficiency, comparable to the most efficient steam engine of that time. [1].

In 1834, French physicist Jean Charles Athanase Peltier described thermal effects at the junction between two dissimilar conductors when an electric current flowed between the materials. [3]. Peltier did not realize at the time that there was a link between the absorption and generation of thermal energy in each of the materials relative to the direction of current flow through the junction. The discovery of the link between absorption and generation of thermal energy was attributed to Lenz in 1883. Lenz concluded that the heat generated or absorbed at a junction between two dissimilar materials is dependent upon the direction of the current flow through the junction. [4].

Between 1906 and 1911 Altenkirch observed that good thermoelectric materials possessed large Seebeck coefficients (σ), high electrical conductivity (α), and low thermal conductivity (λ). [5],[6]. A high electrical conductivity is needed in order to minimize Joule heating. Low thermal conductivity allows the thermal gradient between the hot and cold sides of the junction to be maintained. The relationship between these properties was later used to determine a material's Z factor or figure-of-merit. The figure-of-merit is a function of temperature so a more useful dimensionless figure-of-merit can be defined as ZT.

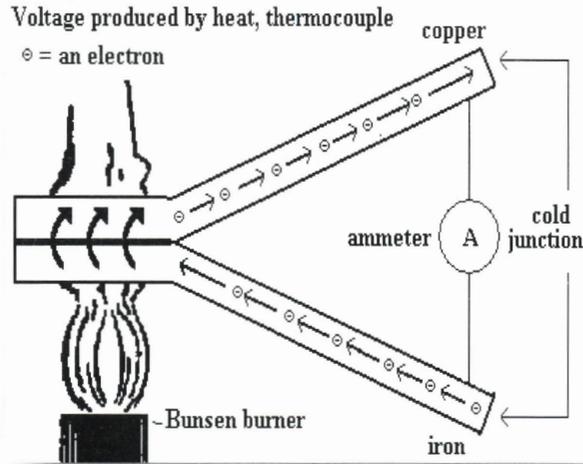
$$Z = \frac{\alpha\sigma^2}{\lambda} \quad (1)$$

Where T is the temperature and Z is the figure of merit. It is impossible to maximize all of the thermoelectric factors simultaneously due to the interdependence of each variable on the other two. Instead, scientists have concentrated on methods of optimizing conflicting properties in order to provide a maximum figure of merit ZT . Typical properties of good thermoelectric materials can be found in Table 1. Now we will discuss each of the thermoelectric properties contributing to the ZT figure-of-merit.

The Thermoelectric Effect

The **thermoelectric effect** is the generation of an electric potential due to the temperature gradient between hot and cold ends of certain materials, or the creation of a temperature difference due to an applied electric potential. The thermoelectric effect will generate a temperature difference when a voltage is applied across the ends of a given material. It should be pointed out that the thermoelectric effect is not responsible for the potential difference between two materials placed into contact at thermal equilibrium. A temperature gradient is required in order for the thermoelectric effect to be present. The thermoelectric effect does not contribute to the potential difference generated by the junction of two dissimilar materials at thermal equilibrium [1].

Figure 1: Thermocouple Diagram (Seebeck Effect)



As a thermal gradient is introduced at the junction between two dissimilar materials such as copper and iron in a thermocouple, a voltage difference is created and current flows. Often times, the current generated as a function of temperature between two common

metals such as iron and copper are known. In these cases, the current is measured in order to determine the temperature at the junction. Figure was obtained from source [7].

Table 1: Typical values of key thermoelectric factors

Thermoelectric Property	Typical Range
Seebeck coefficient (σ)	$ \sigma \geq 100 \frac{\mu V}{K}$
Electrical Conductivity (α)	$2 \cdot 10^{-5} \Omega \cdot m \leq \alpha \leq 3 \cdot 10^{-3} \Omega \cdot m$
Thermal Conductivity (λ)	$1 - 3 \frac{W}{K \cdot m}$

The Seebeck Coefficient

The Seebeck coefficient, also called the thermopower, is defined as the open circuit voltage produced between two points on a conductor, where a uniform temperature difference of 1 Kelvin exists between those points.[2]. Stated in simpler terms, the Seebeck effect is the creation of a voltage potential across a junction in which a thermal gradient is present. The Seebeck coefficient is typically low in metallic compounds, high in insulators, and intermediate values are found in semiconductors. A mathematical description of the Seebeck coefficient would show the reliance upon the negative partial derivative of the change in potential, $V(T)$, across a material at with respect to temperature, T , at constant pressure. Typically in solids, the constant pressure portion of the mathematical definition is irrelevant, and indeed it is usually referred to as a derivative (Equation 2).

$$\sigma = -\frac{dV(T)}{dT} \quad (2)$$

At a basic level, the Seebeck effect is caused by charge separation and charge build-up within a material. A potential difference is created as negative charge diffuses to one side of a material, leaving the other side with a net positive charge. This separation of charge generates an electric field. By convention the electric field lines point antiparallel to the flow of electrons. The strength of this electric field grows as the total charge separation present within the material increases. The potential created between the hot and cold ends of a material enables charge carriers to flow throughout the material. The main carrier

type (p or n type) in a given compound determines the direction of the flow of charge within that compound. In an n-type compound, the major charge carriers are electrons, while in a p-type compound the major charge carriers are holes. Entropy is the measure of disorder within a system. In p-type materials the electric field and temperature gradient point in the same direction, this gives rise to a positive change in entropy and the system goes to more disorder. The reason for this increased disorder lies in the fact that in p-type materials, electrons travel counter intuitively away from the cold end and towards the hot end. In the case of n-type materials, the electric field and temperature gradient point in opposite directions and the electrons flow from the hot side of the material towards the cold side. In the case of an n-type material the entropy is less than zero and the system goes to a more ordered state.

$$\sigma = \frac{E}{|\nabla T|} \quad (3)$$

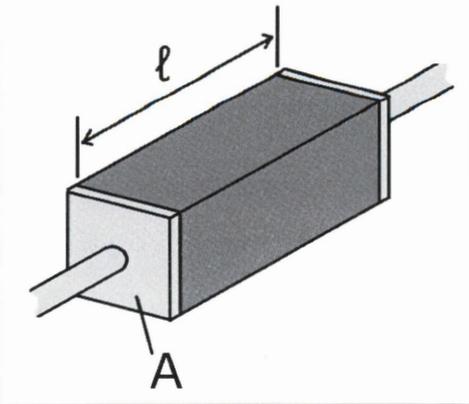
The Seebeck coefficient, σ , is dependent upon the materials temperature and crystal structure. Typically metallic compounds have very low Seebeck coefficients and insulators have very high Seebeck coefficients. Metallic compounds have low Seebeck coefficients due to their half-filled valence band. In metals the valence band and conduction band overlap. This allows for mobile charge carriers such as electrons to flow easily throughout the material. In metallic compounds there is nearly equal flow of positive and negative charge carriers, this effectively equal and opposite flow of charge carriers diminishes the Seebeck coefficient of the material. It reduces the value of the Seebeck coefficient because nearly equal amounts of p-type and n-type carriers are

moving in opposite directions. When this occurs only a small potential difference is created. Metallic compounds typically have the smallest Seebeck coefficients, highest electrical conductivity, and high thermal conductivity.

Electrical Resistivity

The **electrical resistivity** is a measure of how much a material resists the flow of electric current. Metallic compounds typically exhibit low electrical resistivity, insulators exhibit high electrical resistivity, and semiconductors fall somewhere in between. A relationship between the electrical resistivity and resistance of a material is given by Equation 4.

Figure 2: Electrical Resistivity Parameters



$$\rho = \frac{A}{l} \cdot R \quad (4)$$

The electrical resistivity, ρ , is measured in Ohm-meters ($\Omega\cdot m$). The resistance R is measured in Ohms, Ω . A is the cross sectional area of the material in square meters, m^2 , and l is the length of the material measured in meters, m .

Metals, insulators, and semiconductors all have different electrical properties. In metallic compounds the electrical resistivity generally increases as temperature increases. The electrical resistivity decreases as temperature increases for semiconductor materials. Insulators have high electrical resistivity compared to all other materials. In insulators, the electrical resistivity generally increases as a function of temperature.

In metallic compounds, the resistivity increases with temperature due to electron-phonon and electron-structure interactions. A good first order approximation of electrons moving throughout a conducting material is to consider a free electron gas. This is a good approximation because the nuclei of the atoms occupy a small fraction of the space taken up by a given compound. The electron cloud of a compound occupies a much greater volume of space than the nucleus. As the materials are heated, the vibrations of the atomic nuclei increase and they cover a broader area making it harder for electrons to flow. Thus, as the temperature within a metal increases, the number of paths for the free electrons to take becomes increasingly limited.

Thermal Conductivity

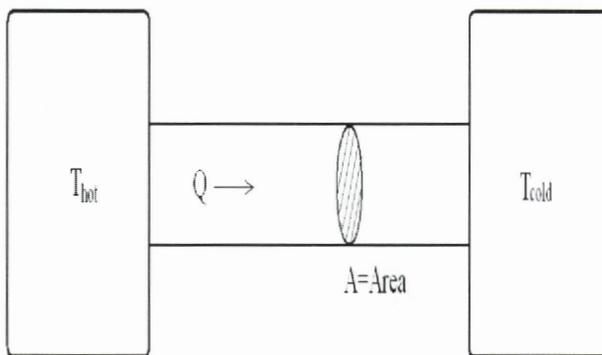
Thermal conductivity is a thermodynamic quantity used to quantify and describe the amount of heat that flows through a cross sectional area of a material per unit of time.

The thermal conductivity can be described by the following equation:

$$\lambda = \frac{\Delta Q}{\Delta T} \cdot \frac{1}{A} \cdot \frac{x}{\Delta T} \quad (5)$$

The quantity of heat being transferred is ΔQ , the total elapsed time during the transfer of heat is Δt , x is the length of the path the heat travelled through the material perpendicular to the cross-sectional area A , and the temperature difference between the hot and cold sides of the material is ΔT .

Figure 3: Thermal Conductivity



$$Q = \text{heat [Joules]}$$

$$\Delta T = T_{\text{hot}} - T_{\text{cold}}$$

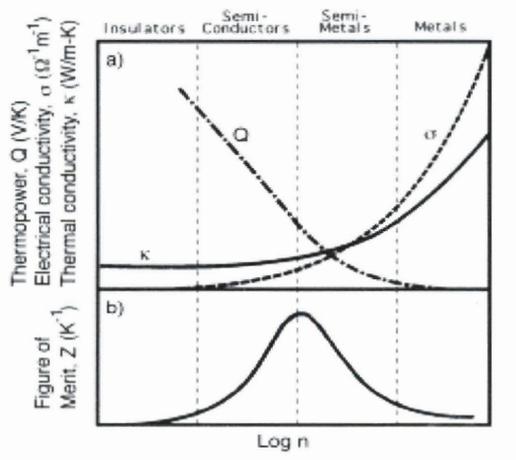
This is a schematic of heat transfer between a hot and cold reservoir. The heat is transferred from the hot side to the cold side over a certain period of time, distance, and through a certain cross sectional area of material. This schematic provides a physical representation of the parameters in Equation 5.

The Figure of Merit - ZT

The Seebeck coefficient, electrical resistivity, and thermal conductivity all contribute to a materials Figure-of-Merit. This is the way scientists and engineers rate a materials ability to perform a thermoelectric device application. Due to the interdependence of these properties, it is impossible to simply maximize each quantity and obtain the best possible

figure-of-merit (ZT). The thermoelectric factors compete, as one changes for the better, one changes for the worse. A good example of two competing factors in a thermoelectric compound are the electrical conductivity and thermal conductivity, as one increases, the other must also increase. Equation 1 shows that the thermal conductivity needs to decrease as the electrical conductivity increases in order to increase the Seebeck coefficient. The case where both factors increase together will not allow for a good thermoelectric material because these two factors become competing factors, non-complementary to one another and result in cancelling each other out.

Figure 4: Figure of Merit (ZT)



The behavior of insulators, semiconductors, semimetals, and metals are shown in Figure 5, as are their thermoelectric properties. The bell-curve shape in the bottom of the graph shows where the thermoelectric figure of merit ZT is maximized. It is maximized at the transition boundary between semiconductors and semimetals.

Thermoelectric Properties by Material Type

In the broad field of materials science research, almost all solid state materials can be classified into one of the following groups: Insulators, metals, metalloids, semimetals, and semiconductors. These classifications are a way of describing a materials general properties without going into specifics. The general properties of each group will be discussed briefly.

Insulators have enormous Seebeck coefficients. Unfortunately, they also have extremely low carrier concentrations, low thermal conductivity, and high electrical resistivity which cripple their potential as thermoelectric materials. This is due to the large band gap between the valence and conduction band in insulating materials, this large band gap makes it difficult for electrons to get promoted from the valence band into the conduction band where charge flow occurs.

In semiconductor materials the disparity between the amount of positive and negative charge carriers allows a much larger potential difference to be created and thus a much larger Seebeck coefficient than is allowed in metallic compounds. In these materials it is possible to have a large excess of carriers of a particular type (p-type or n-type). The creation of a dominant carrier type within these semiconductor compounds comes primarily from doping the material with excess electrons or holes (n-type or p-type doping). These sizable Seebeck coefficients are one of the properties that make semiconductor materials attractive for thermoelectric device applications. Semiconductor materials take on a broad range of intermediate characteristics which are between those

of typical metallic and insulator compounds. It is this quality of semiconductor materials that makes them the most promising prospect for future thermoelectric materials.

The reason semiconductor materials have been so successful in thermoelectric device applications is their intermediate band gap. The energy gap between the valence band and conduction band in a semiconductor is large enough for the compound to have a sizable Seebeck coefficient and small enough for charge carriers to become excited and charge to be induced within the compounds. In semiconductor materials the electrical conductivity and thermal conductivity take on intermediate values. Enough charge is allowed to flow that the material has an acceptable charge carrier density. In addition, semiconductor materials are easily doped with extra electrons or holes which add a large amount of either n-type or p-type charge carriers.

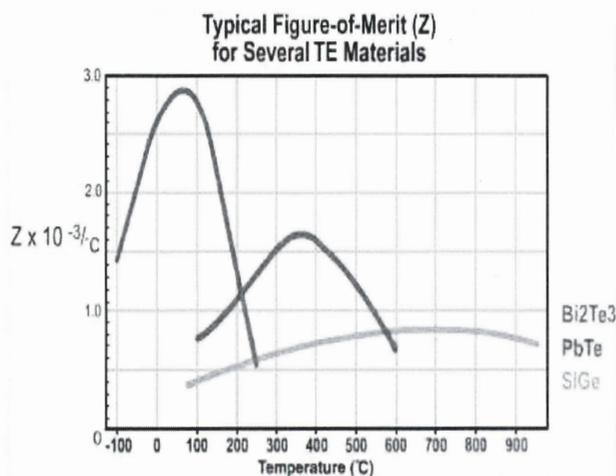
Metallic compounds are at the opposite end of the spectrum and tend to exhibit the highest thermal and electrical conductivities and the lowest Seebeck coefficients. In metals, the small Seebeck coefficient is due to the lack of a dominant charge carrier. In metallic compounds, there are essentially equal amounts of positive and negative charge carriers; this makes it difficult to build up a potential difference and charge separation in these materials. Metallic compounds conduct extremely well due to the overlap in the valence and conduction bands. This makes it very easy for charge to flow throughout these materials. This small and overlapping band gap also makes it possible for electrons to be excited through thermal agitation of the compounds.

A special case of compounds with a Seebeck coefficient of zero are superconductors, in which the charge carriers carry no entropy. In these compounds it is impossible to have any potential difference, which is proved by Ohm's law ($V=IR$). If the resistance is zero, which it is in a superconductor whose carriers have zero entropy, then the potential difference (voltage) must also be zero.

In order for a material to be a good thermoelectric compound it must exhibit a mixture of each of these specific properties. Figure 4 (Page 8) shows a graph comparing typical behavior of each thermoelectric quality as a function of the transition between material types including insulators, semiconductors, semimetals, and metals.

Current Thermoelectric Materials

Figure 5: Current Thermoelectric Materials



Thermoelectric behavior is temperature dependent. As seen, BiTe₃ is the dominant thermoelectric material at low temperatures, and then PbTe for moderate temperatures and for high temperature device applications SiGe has superior thermoelectric properties.

The best and most widely used thermoelectric materials to date include bismuth telluride (Bi_2Te_3), lead telluride (PbTe), and silicon/germanium alloys (SiGe). Each of these materials has different applications dependent on the temperature range in which they are most efficient. As seen in Figure 5, bismuth telluride has by far the highest maximum ZT value out of the compounds listed, and silicon/germanium alloys have the lowest maximum ZT value. The difference between the two is the environment in which they can serve as functional thermoelectric devices. The bismuth telluride compound has the highest ZT values below operating temperatures of 350K. After 350K, the effectiveness of bismuth telluride as a thermoelectric material rapidly diminishes. The lead telluride compound exhibits the most favorable ZT factor over a temperature region ranging from approximately 450K up to 850K. Devices operating above 850K are most efficient when a silicon/germanium alloy is used. This goes to show the need for a wide range of thermoelectric materials, these devices are not simply one size fits all.

Bismuth telluride compounds are used most commonly in refrigeration units. These materials have application in low temperature devices at or below 350K. These devices became popular when the chlorofluorocarbons were found to damage the atmosphere. These devices offered a convenient alternative to environmentally conscious manufacturers and consumers.

Applications of Thermoelectric Materials

Thermoelectric devices have served many purposes over the last century. These devices have applications including power generation and cooling. As a method of generating power, thermoelectric devices are not very efficient, however they are highly reliable. Thermoelectric power sources have some of the highest Technical Readiness Level (TRL) ratings by NASA and have been used in space missions dating back to the Saturn and Voyager launches.

Modern refrigeration and cooling units use thermoelectric materials which has helped shift the dependence off of less safe alternatives such as chlorofluorocarbons. When a potential difference applied in the opposite direction of current flow for a thermoelectric device, heat actually travels from the cold end towards the hot end. This results in a decrease in the entropy of the cold side of the system and an increase in entropy for the hot side.

In the generation of power, two dissimilar thermoelectric materials are placed in thermal contact at one end and an “open circuit” exists at the other end. A temperature difference is generated between the hot and cold ends of the device giving rise to a potential difference between ends and flow of current. Two examples of this application were the Saturn and Voyager missions. The spacecraft were too far away from the sun to harness solar power during their mission so instead thermoelectric power generating devices were used. A radioactive heat source was placed at one end of these devices serving as the hot side of the material; the other end was exposed to the cold space surrounding the

spacecraft. This was a reliable method of providing power to the spacecraft throughout its mission, even when very distant from the sun.

These devices can also be used to salvage wasted heat energy from exhaust systems at power plants and in vehicles. In order to increase the overall efficiency and reduce the amount of power wasted, these low efficiency devices salvage waste energy due from excess heat given off. Currently scientists and engineers are developing a thermogenerator for automobiles which could potentially replace a vehicles alternator. These devices would rely upon the induced voltage and current created when a thermal gradient exists between the hot and cold ends of a material junction. Through developing more efficient thermoelectric materials, the amount of waste energy that can be salvaged will increase, resulting in a reduced need of resources for energy production.

Thermocouples are devices in which the known thermoelectric properties of the materials are so well established that any variance in the potential, power output, or current of the device can be directly traced back to an exact change in temperature. The potential difference and current flow through a two compound junction created by a temperature difference between the hot and cold ends of the device are measured and the temperature at the junction can then be mathematically deduced using the laws of thermodynamics.

EXPERIMENTAL DESIGN

Experimental Background Section

Recently it was discovered that sodium cobalt oxide Na_xCoO_2 , where $x=0.90, 0.95, 1.0$, has a large positive Seebeck coefficient on the order of a few hundred $\mu\text{V}/\text{K}$. There has been much speculation as to why this occurs in this compound. One possible explanation involves the idea that when the compound is made with $x = 1.0$ all the cobalt atoms on the cobalt sites have an oxidation state of 3^+ . When the cobalt atoms are in this arrangement and carry a 3^+ charge, there is no magnetic moment, and the cobalt atoms have octahedral coordination. As holes are placed on the sodium sites a small fraction of the cobalt 3^+ atoms convert into the cobalt 4^+ oxidation state. In the 4^+ oxidation state, the cobalt atoms have 5 electrons in the 5d electron shell. It is speculated that perhaps due to a peculiarity in the cobalt, where there would theoretically be one unpaired d-electron in the 5d shell, all five of the electrons are unpaired and in a high spin arrangement. This possible explanation concludes that the difference in having all five of these electrons unpaired and in the spin up state drastically changes the magnetic entropy in comparison to the one unpaired electron case. In this case, the charge carriers would be holes, and as they moved through the lattice structure they would carry with them large amounts of entropy.

Co_9S_8 , Co_9Se_8 , CoSe , CoTe_2 , $\text{CoSbSe}_x\text{S}_{1-x}$ ($x=0, 0.25, 0.50, 0.75, 1.0$), CoSbTe , CoSb_2 , and $\text{Co}_{0.95}\text{Fe}_{0.05}\text{Sb}_2$ were synthesized and tested in order to see if they undergo the same sort of magnetic ordering and charge ordering as the sodium cobalt oxide compounds.

Cobalt oxides are not typically compatible with non-oxide thermoelectric materials. Intermetallics are close to metals, whereas oxides definitely do not portray the characteristic behaviors of metallic acting compounds. Oxides have high thermal conductivity which negates their thermoelectric potential even though they have a high Seebeck coefficient.

The gold telluride compounds were selected because of their mass density. Thermal conductivity is generally related to the mass in such a way that the heavier the atoms, the higher the thermal conductivity. This takes place due to phonon trapping and rattling cages present in these heavier structure types. The phonons within these compounds affect the lattice structure much less because they are absorbed by the rattling cages and they don't impede the flow of electrons as they would in a lighter material type. In less dense materials the absorption of phonons can cause major lattice vibrations which make it difficult for charge carriers to move through the lattice. In heavier compounds the phonons don't carry as much effect on lattice vibrations, resulting in more efficient flow of charge carriers.

Experimental Methods & Techniques

The experimental methods and techniques used throughout these experiments are described in this section.

Preparation and Synthesis

The compounds of the Co_9S_8 structure type were prepared using the methods described below. These compounds include Co_9S_8 , Co_9Se_8 , Co_8NiS_8 , and Co_8FeS_8 . Stoichiometric amounts of the elements were weighed out. The samples were then ground into a uniform powder for 15 minutes, placed into a quartz tube, flushed with argon, vacuumed, and sealed. The quartz ampoules were then baked at 390°C for 5-days. The powders were then removed from the tubes, re-ground, pressed into pellets, placed into a quartz tube, flushed with argon, vacuumed, and sealed. The pellets inside the quartz ampoules were then baked at 350°C for 4-days. The pellets were then crushed and placed into quartz ampoules via the method described above. They were then baked at 390°C for 5 additional days.

CoTe_2 , CoSb_2 , $\text{Co}_{0.95}\text{Fe}_{0.05}\text{Sb}_2$, and $\text{CoSb}_{1.90}\text{Sn}_{0.10}$ were synthesized using the same methods described below. Each compound was weighed out using stoichiometric amounts of the elements. They were then ground into a fine uniform powder and sealed into evacuated quartz ampoules and placed into an oven at 650°C for 5-days. They were then removed from the oven, re-ground, pressed into pellets, placed in quartz ampoules, and returned to the oven at 650°C for 4 days. Then they were ground up again, pressed into pellets, and placed into the oven at 700°C .

The AuTe_2 , $\text{Au}_{0.95}\text{Pt}_{0.05}\text{Te}_2$, $\text{Au}_{0.95}\text{Ag}_{0.05}\text{Te}_2$, and $\text{AuTe}_{1.90}\text{Sb}_{0.10}$ samples were prepared using the same methods. Each element in the compound was weighed out in stoichiometric amounts and placed into a sealed and evacuated quartz ampoule. The

samples were then placed in an oven at 500°C and heated for 5-days. Then the samples were taken out, re-ground, pressed into pellets, sealed into evacuated quartz ampoules placed in the oven at 400°C. Finally they were re-ground, pressed to pellets, sealed in an evacuated quartz ampoule and placed into an oven at 450°C for 4-days.

The MnTe_2 , $\text{MnTe}_{1.95}\text{Sb}_{0.05}$, and $\text{MnTe}_{1.90}\text{Sb}_{0.10}$ samples were prepared using stoichiometric amounts of the elements. The samples were ground into a fine uniform powder and placed into an alumina crucible inside of a sealed and evacuated quartz ampoule. They were then fired at 650°C for 5-days. The samples were re-ground, pressed into pellets, placed in alumina crucibles inside of evacuated quartz ampoules and returned to the oven at 500°C for 5-days. It is important to note that the use of alumina crucibles was crucial here because manganese reacts with the quartz tube.

Compounds of the $\text{CoSbSe}_x\text{S}_{1-x}$ ($x=0, 0.25, 0.50, 0.75, 1.0$) system were synthesized using the same techniques. Stoichiometric amounts of the elements were weighed out for each compound. These powders were then ground and mixed into a fine uniform powder, placed in a quartz ampoule, evacuated, and sealed under vacuum. The compounds were then placed into an oven at 600°C for 4-days. They were re-ground, placed into evacuated quartz ampoules and then placed into an oven at 400°C for 4-days.

CoSbTe was synthesized from stoichiometric amounts of the elements. The elements were ground together into a fine uniform powder, placed into an evacuated quartz tube

and baked at 800°C for 4-days. The sample was then re-ground, pressed into a pellet, placed into an evacuated quartz tube, and placed into an oven at 800°C for 4 days.

Re_2Te_5 and $\text{Re}_2\text{Te}_{4.5}\text{Sb}_{0.50}$ were synthesized using stoichiometric amounts of the elements. The elements were mixed together into a fine and uniform powder, placed into evacuated quartz ampoules, and placed into the oven at 700°C for 5-days. The samples were then re-ground, pressed into pellets, sealed into evacuated quartz ampoules and baked for 5-days at 700°C.

Measurement Equipment

The Seebeck coefficient was determined using the Seebeck Effect Measuring System (SEMS) from MMR Technologies Inc. In practice it is rarely the case that the absolute Seebeck coefficient of a material is measured directly. This is because in order to measure the Seebeck coefficient electrodes attached to a voltmeter need to be attached to the material in order to measure its thermoelectric potential. The problem with this system lies in the thermal contact of the electrodes with the material. The temperature gradient across the probes induces a thermoelectric potential which is measured in addition to the thermoelectric potential of the material being tested. Since the results of both materials are included in the result they must be decoupled. As a function of both Seebeck coefficients from the two contributing materials, the result could be written as follows:

$$\sigma_{AB} = \frac{\Delta V_B}{\Delta T} - \frac{\Delta V_A}{\Delta T} = \sigma_B - \sigma_A \quad (6)$$

Where T is the temperature in Kelvin and V is the potential difference measured in micro-volts per degree Kelvin, $\frac{\mu V}{K}$. There are other approaches to determining the Seebeck coefficient or thermopower of a material; however they were not used in this set of experiments so they will not be discussed. Information on the Seebeck Effect Measuring System can be found in the appendices.

The Quantum Design Physical Properties Measurement System (QD-PPMS) is an open architecture, variable temperature-field system, designed to perform a variety of automated measurements.[10]. This device was used to measure the magnetic susceptibility of samples. Detailed information about this device can be found in the appendices, or online (See Reference 11).

RESULTS

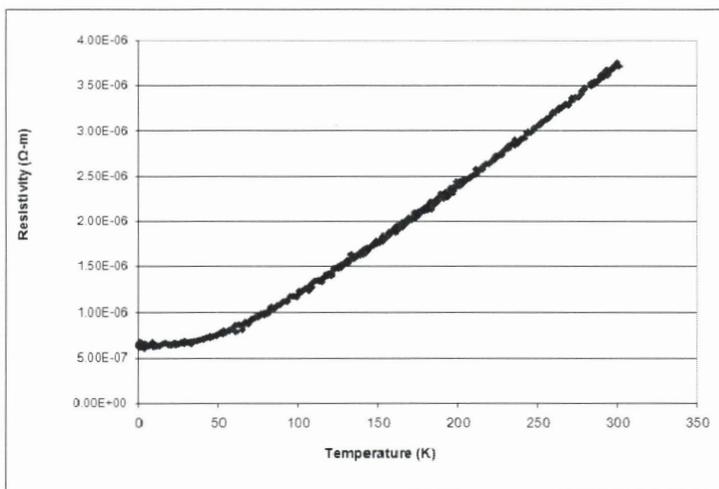
X-ray diffraction was used to determine the official structure type of each compound created. This paper will not provide an in depth discussion on the materials structure type unless it is believed to pertain to the thermoelectric properties of the compound. Synthesis information for each compound can be found in the preparations and synthesis portion of this report.

Co₉S₈-Co₉Se₈ Systems

The Co₉S₈ compound had a small p-type Seebeck coefficient which grew more negative as the temperature increased (Figure 7). The Seebeck coefficient of Co₉S₈ reached a maximum of approximately 22 μ VK⁻¹ around 300K. The magnetic susceptibility of the Co₉S₈ compound was obtained in order to determine whether the compound would be superconducting. Although the resistivity does drop to an extremely low value at low temperatures around 2 Kelvin, the compound was not determined to be superconducting. No special magnetic ordering behavior was observed for this compound. The resistivity was measured and it was determined that the compound acted metallic with resistivity increasing with temperature. Although the Seebeck coefficient was not relatively small for the Co₉S₈ compound, the resistivity at low temperatures was extremely low. This merited additional research of this compound and a thermoelectric power calculation was performed (Figure 9). Determining the compounds thermopower provided insight as to the thermoelectric nature of the compound, more specifically its figure of merit. The thermopower was calculated because the compound exhibited extremely low resistivity.

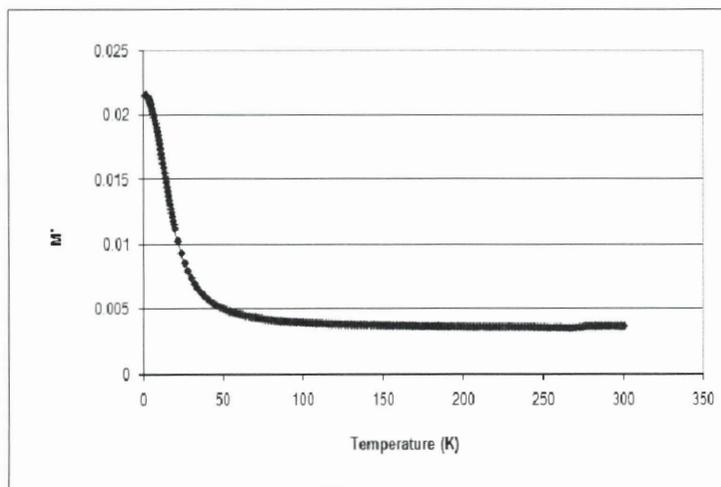
It was determined that the thermopower of the compound was too low to be of use for thermoelectric device applications and no further research of the compound was conducted.

Figure 7: Co_9S_8 Resistivity Data



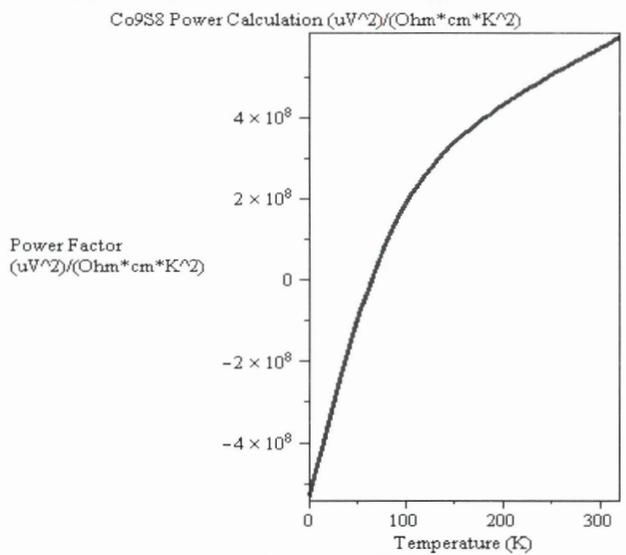
Co_9S_8 behaved as a metal. The resistivity of this compound increased with temperature.

Figure 8: Co_9S_8 Magnetic Susceptibility



As seen here, Co_9S_8 had a sharp decrease in magnetic susceptibility below 50K.

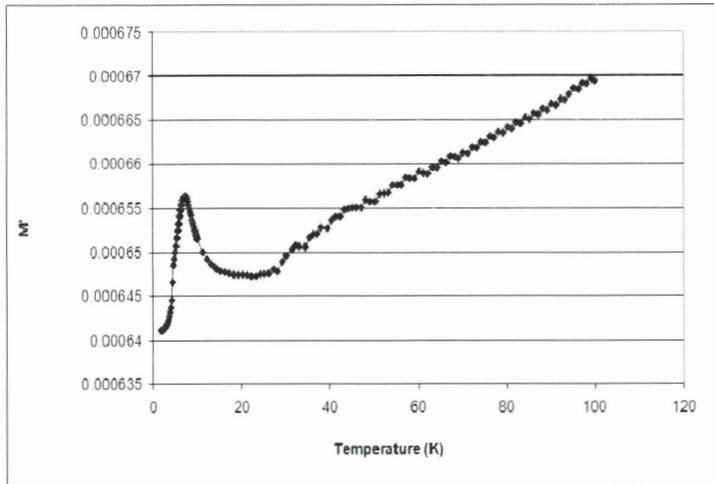
Figure 9: Co_9S_8 Thermopower



The thermopower of Co_9S_8 was calculated. It was determined that the material did not have a high enough thermopower to merit further research on its thermoelectric properties. A good thermopower would be at two orders of magnitude higher than the $2.0 \times 10^8 \mu\text{V}^2 / \Omega \cdot \text{cm} \cdot \text{K}^2$ value that was calculated at 50K.

A mixed phase solid state solution of Co_9Se_8 - CoSe was created. The compound Co_9Se_8 was not formed single phase. The M' measurement of the Co_9Se_8 - CoSe solid state solution was measured and it was observed that the compound undergoes a large magnetic ordering at around 8K. Due to the odd behavior and extremely low resistivity of Co_9S_8 the Co_9Se_8 - CoSe solid state solutions resistivity measurement was taken in order to check for low temperature superconductivity. It was not determined to be a superconductor.

Figure 10: $\text{Co}_9\text{Se}_8\text{-CoSe}$ M' Data Plot

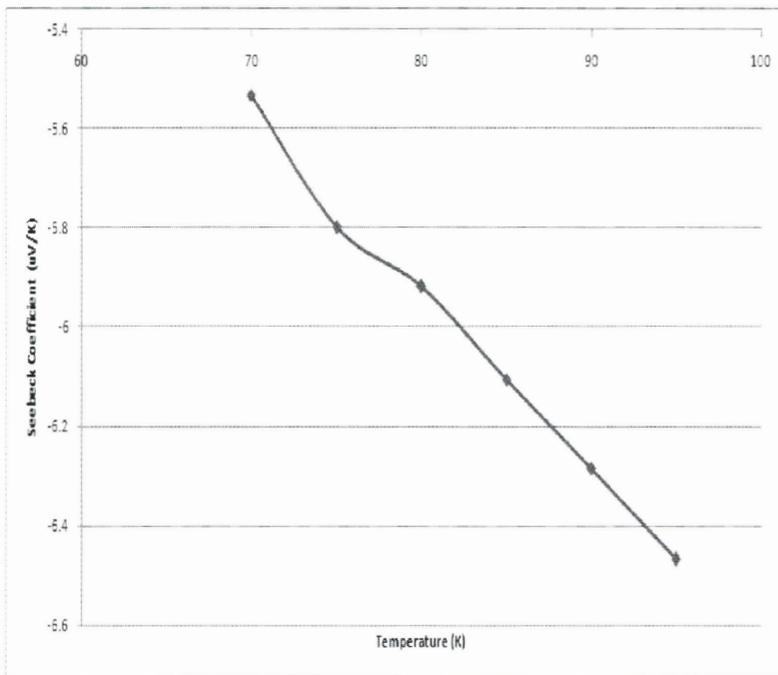


The $\text{Co}_9\text{Se}_8\text{-CoSe}$ solid solution exhibited a large magnetic ordering around 8 Kelvin as seen in the figure to the left in the behavior of its magnetic susceptibility.

CoTe₂ Structure Type

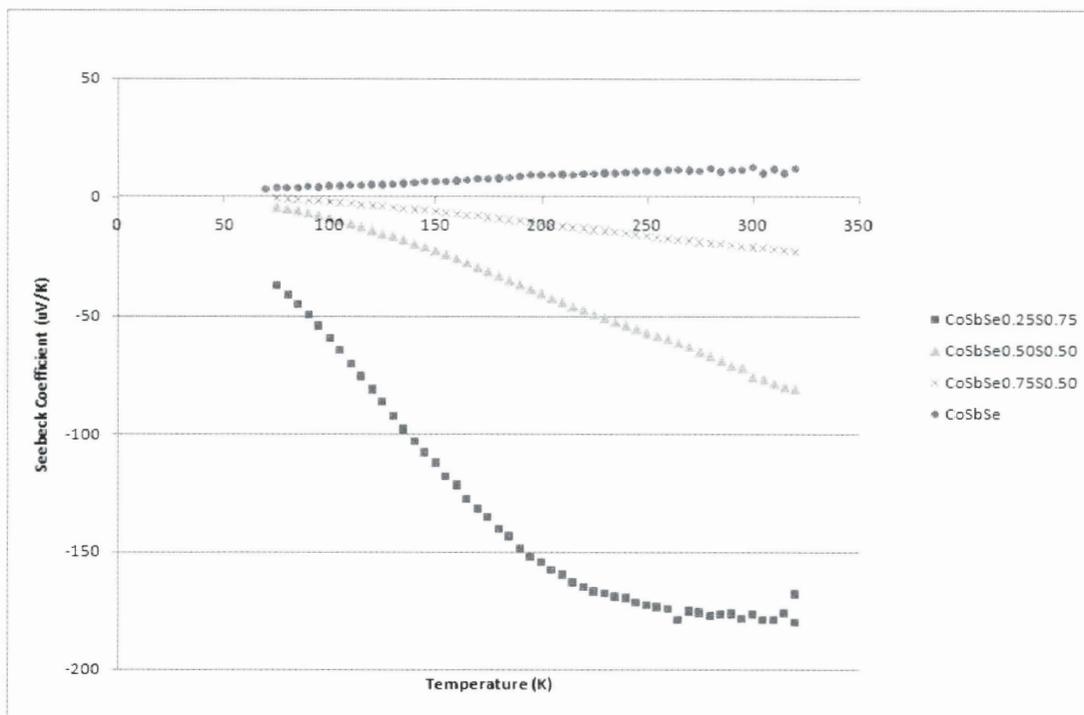
The CoTe_2 compound did not exhibit behavior favorable in thermoelectric compounds. Once it was synthesized and a sintered pellet was created the Seebeck coefficient was measured. The compound was n-type and the Seebeck coefficient was approximately $-6.5\mu\text{VK}^{-1}$ at 95K. There were no additional experiments performed on this compound due to its low Seebeck coefficient.

Figure 11: CoTe_2 Seebeck coefficient



This compound exhibited a very low Seebeck coefficient and seemed to be a metal. Due to its extremely low Seebeck coefficient, further research on the thermal and electrical conductivity of this compound was not conducted.

Figure 12: $\text{CoSbSe}_x\text{S}_{1-x}$ System Seebeck coefficient Data



The $\text{CoSbSe}_x\text{S}_{1-x}$ System starts out as a slightly p-type metal and as it is doped with sulfur on the selenium site becomes an increasingly n-type semiconductor. There is a structural transition between the CoSbSe and CoSbS structure types that occurs during the doping process.

$\text{CoSbSe}_x\text{S}_{1-x}$ System

The CoSbSe compound exhibited p-type behavior with a Seebeck coefficient of less than $13\mu\text{VK}^{-1}$. The resistance of the CoSbSe compound measured at room temperature was low enough to reach the limitations of the digital multi-meter being used and in order to obtain its true value needed to have additional experiments performed. The room

temperature resistance measured for a small, approximately 4mm x 1.5mm x 2mm, piece of a sintered powder pellet was less than one Ohm. The Seebeck coefficient of this material was not high enough to merit an electrical resistivity measurement and power factor calculation.

It wasn't until the CoSbS compound was observed that the CoSbSe-CoSbS system became of interest. The CoSbSe compound exhibited characteristics typical of a p-type semiconductor with a low Seebeck coefficient. Substituting sulfur atoms onto all of the selenium sites to yield CoSbS, the compound exhibited behavior characteristic of an n-type insulator. The CoSbS compound itself was too resistive for the Seebeck Effect Measuring System from MMR Technologies Inc. to measure the value. The room temperature resistance of a small piece of sintered CoSbS powder with approximate dimensions of 4mm x 1.5mm x 2mm was just over 1.5k Ω .

Initially the compounds CoSbSe and CoSbS were investigated for their thermoelectric properties. However, upon further analysis it was determined that CoSbSe was a good conductor while CoSbS exhibited properties of an insulator. Crossovers between these compounds were discovered in order to see where the change in structure and properties occurred for the system. The concentration of selenium and antimony were changed according to CoSbSe_xS_{1-x} (x=0, 0.25, 0.50, 0.75, 1.0). A simple digital multi-meter showed that the resistance across the CoSbSe pellet was approximately 1 Ω while the resistance across the CoSbS pellet was close to 1500 Ω . With just a 25% substitution of

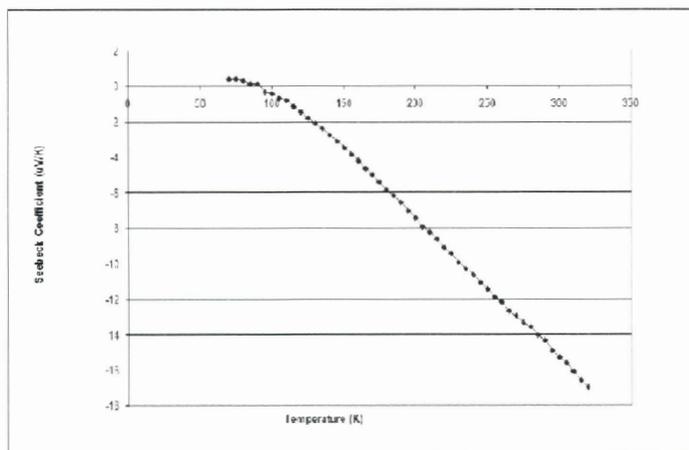
selenium on the sulfur site, the resistance of the $\text{CoSbSe}_{0.25}\text{S}_{0.75}$ sample was only 200Ω , approximately seven times less than that of the CoSbS compound.

As the compounds transitioned from CoSbSe towards CoSbS with increasing amounts of sulfur on the selenium site the compound transitioned from the FeS_2 (CoSbSe) to the NiAs_2 (CoSbS) structure type. Often time's transitions from a metallic compound to an insulator often result in an intermediate superconducting phase. This is currently being studied for this system. The difference between the behavior of the CoSbSe and CoSbS compounds can be primarily attributed to structural differences and coordination of the atoms involved.

CoSbTe Structure Type

The CoSbTe compound exhibited n-type behavior with a small Seebeck coefficient of approximately $-17\mu\text{VK}^{-1}$ at a temperature of 320K. No additional experiments were performed on this compound. The small Seebeck coefficient made it an unlikely candidate for an efficient thermoelectric material.

Figure 13: CoSbTe Seebeck coefficient

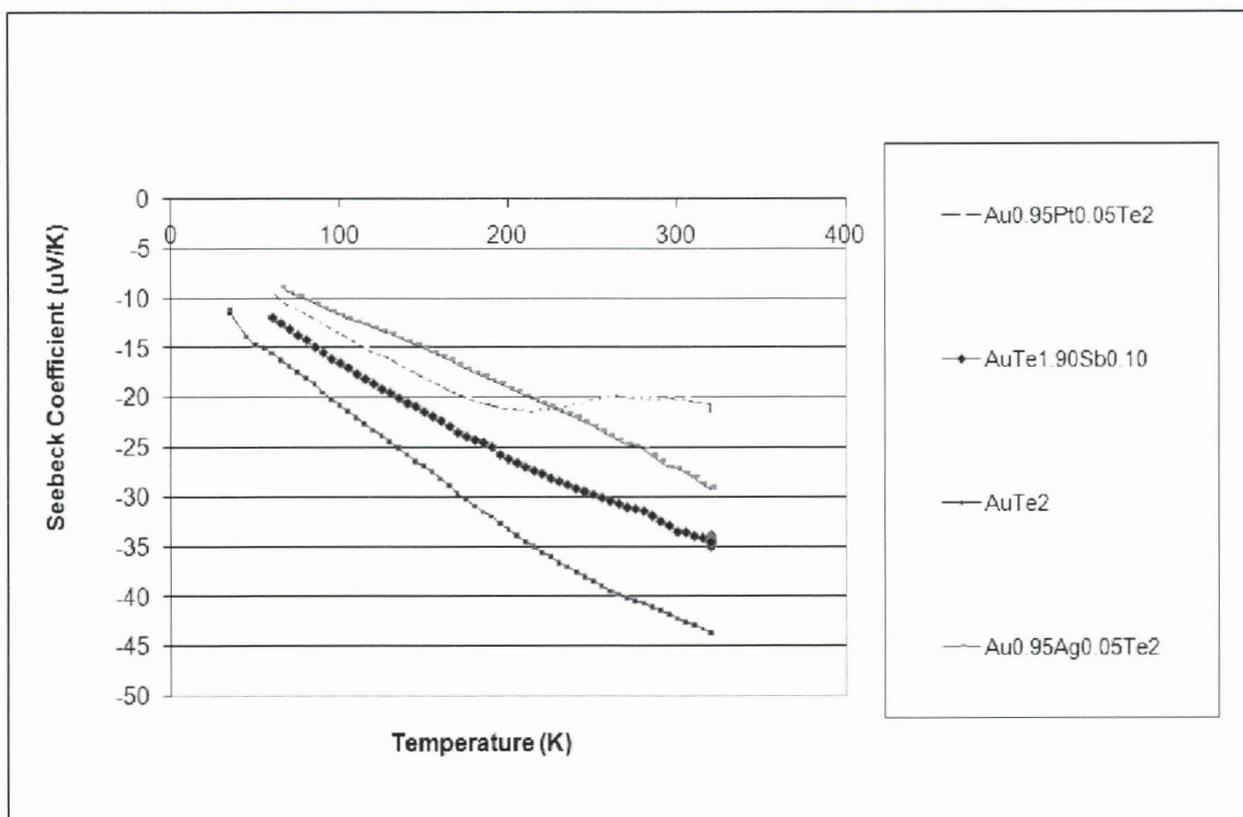


CoSbTe has a low n-type Seebeck coefficient. This means that the compound is most likely metallic, has a low electrical resistivity, and a high thermal conductivity.

AuTe₂ Structure Type

The compounds AuTe₂, Au_{0.95}Pt_{0.05}Te₂, Au_{0.95}Ag_{0.05}Te₂, AuTe_{1.90}Sb_{0.10} were synthesized and had their Seebeck coefficients measured. The Au_{0.95}Pt_{0.05}Te₂ compound exhibited peculiar behavior over the 200K-320K temperature range. This was most likely due to an impurity within the sample. Solid platinum shot was used and may not have been entirely homogenized throughout the sample. This non-homogeneity within the sample was not enough to interfere with the X-ray diffraction pattern, but may have been enough to offset the Seebeck measurement. Gold-telluride exhibited a Seebeck coefficient of approximately -44μV/K. The doped samples took on intermediate values which can be seen in Figure 14.

Figure 14: $AuTe_2$ System Seebeck coefficients

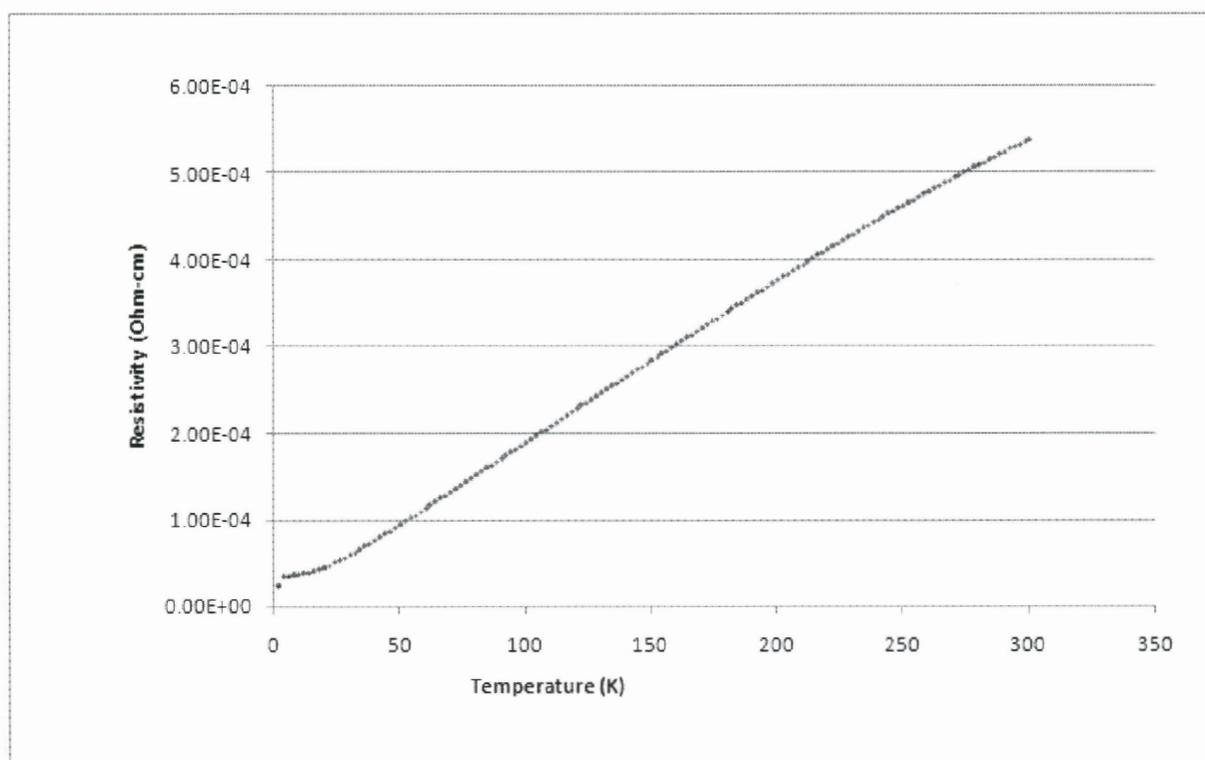


$AuTe_2$ has a sizable negative Seebeck coefficient. Several versions of p-type doping were performed on this material and the results of the doping can be viewed above. The jumpiness in the $Au_{0.95}Pt_{0.05}Te_2$ sample was likely due to impurities within the sample. Platinum shot was used in this sample and the shot may not have reacted in the furnace.

The resistivity behavior of $AuTe_2$ can be found in Figure 15. The compound exhibits resistivity behavior characteristic of metallic compounds. Resistivity increases as temperature increases. This compound did not show promise for low temperature thermoelectric device applications so additional research was not conducted. Perhaps doping this compound n-type would produce a more valuable result, however the

elements required to perform n-type doping on this compound are very hazardous and were not used in the laboratory.

Figure 15: $AuTe_2$ Resistivity Data



Gold-Telluride ($AuTe_2$) acted as a metal with its resistivity increasing almost linearly with temperatures above 50 Kelvin. A power factor calculation was performed for this compound due to its low resistivity and relatively high Seebeck coefficient.

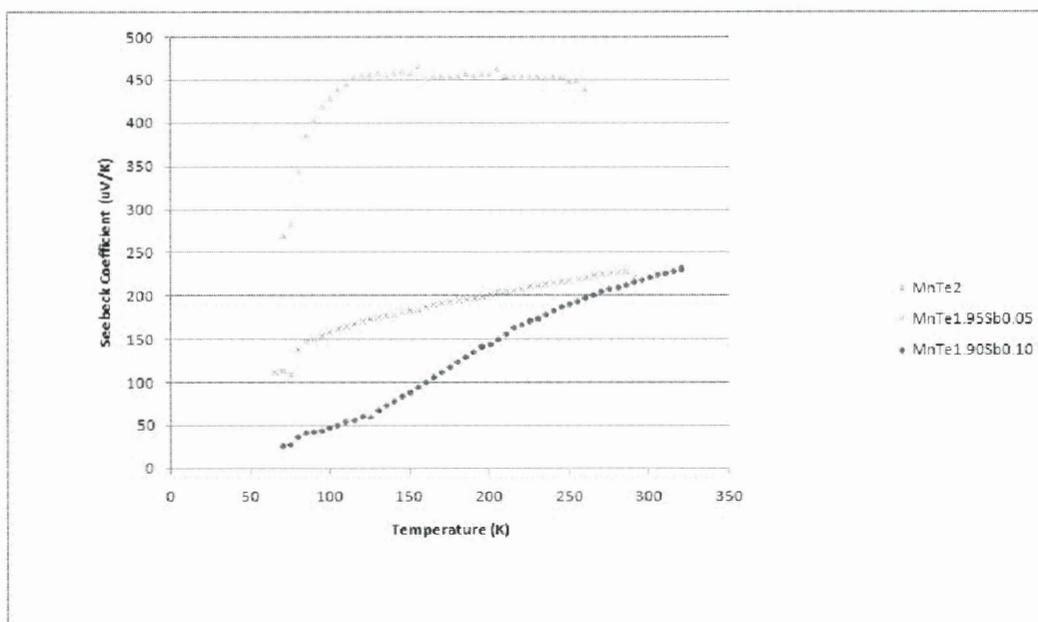
MnTe₂ Structure Type

The $MnTe_2$ system had some of the most promising material properties found in these experiments. The compound $MnTe_2$ exhibited a very large Seebeck coefficient and a high resistivity. The antimony doped versions of this compound exhibited very interesting

characteristics. They had high Seebeck coefficient's on the order of $200\mu\text{V}/\text{K}$ at room temperature, but the resistivity dropped drastically in comparison to the case of undoped MnTe_2 . The decreases in resistivity between doped and undoped samples was likely due to the increased carrier concentration within doped compounds. All of these compounds seemed to undergo some sort of magnetic ordering. The magnetic ordering in the MnTe_2 compound was most distinct and resulted in a $200\mu\text{V}/\text{K}$ drop in the Seebeck coefficient as the temperature decreased from 100K down to around 70K.

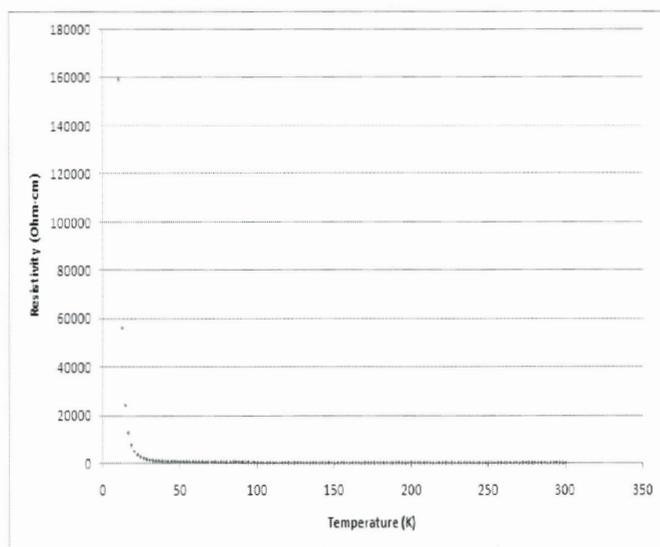
The resistivity of MnTe_2 increased drastically at low temperatures and at room temperature it was still too high to be useful as a thermoelectric material. The resistivity of the antimony doped samples was a great deal lower than that of the un-doped MnTe_2 compound. The standard, approximately 4mm x 1.5mm x 2mm piece of material used for the resistivity measurement had a room temperature resistance as measured by a digital multi-meter that was on the order of $1.5\text{k}\Omega$ for MnTe_2 . The 5% antimony doped sample showed a room temperature resistance of approximately 150Ω and the 10% antimony doped sample had a room temperature resistance of less than 10Ω .

Figure 16: $MnTe_2$ System Seebeck coefficients



Un-doped $MnTe_2$ had a Seebeck coefficient of around $450 \mu V/K$ at temperatures above 100 Kelvin. Once temperatures dropped below 100 Kelvin, rapid magnetic ordering occurred within the compound and the Seebeck coefficient dropped down to $250 \mu V/K$ by the time the temperature reached 70 Kelvin. This prompted additional research and the compound was doped with 5% and 10% antimony in separate trials. The results can be seen above, the doping reduced the Seebeck coefficient but it still maintained a value of well over $200 \mu V/K$ at temperatures around 300 Kelvin. The resistivity in these compounds dropped significantly for the doped compounds.

Figure 17: $MnTe_2$ Resistivity



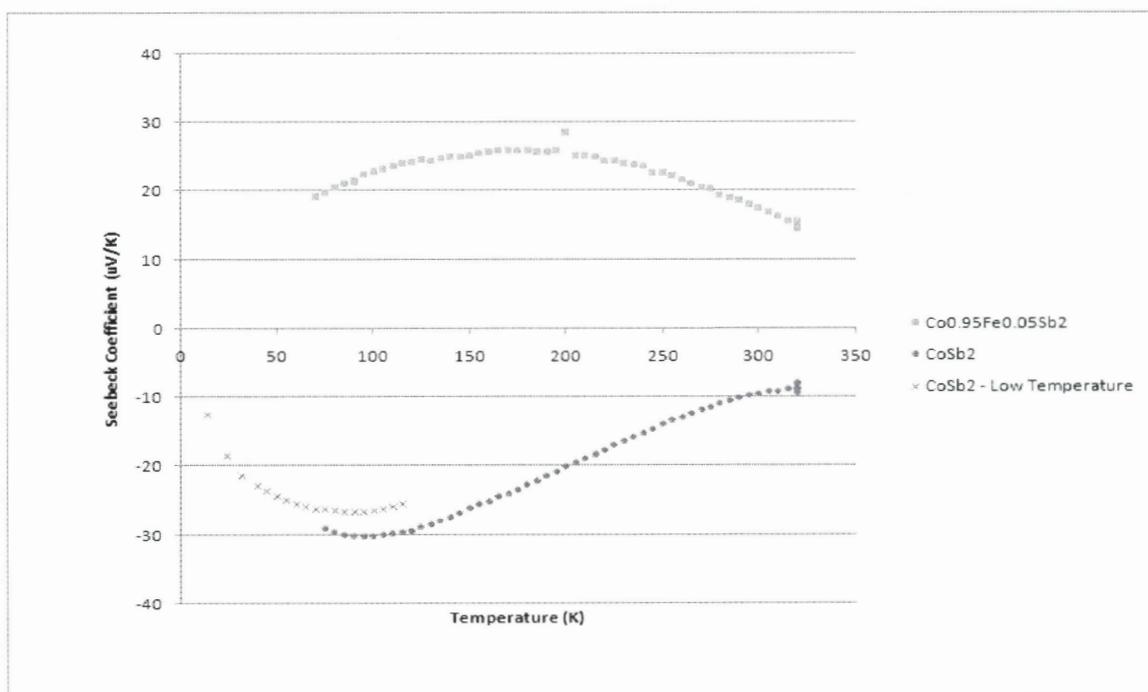
The resistivity in $MnTe_2$ was much too high to be useful in thermoelectric device applications. As antimony was doped onto the tellurium sites however, the resistivity decreased drastically. This factor coupled with a high Seebeck coefficient made this material an ideal candidate for thermoelectric device applications.

CoSb₂ Structure Type

A study of $CoSb_2$ and a doped counterpart was conducted in order to determine whether or not the compounds exhibited favorable thermoelectric characteristics. $CoSb_2$ had a relatively small Seebeck coefficient, approximately $15\mu V/K$ at room temperature. The Seebeck coefficient did increase as the temperature decreased, however the increase was only on the order of $10\mu V/K$. A 5% Iron dope on the cobalt sites in $CoSb_2$ was conducted to create $Co_{0.95}Fe_{0.05}Sb_2$. This created a p-doped version of $CoSb_2$. The 5% iron dope was enough to push the compound over to a p-type compound, with p-type carriers, and a Seebeck coefficient of approximately $25\mu V/K$ at 175 Kelvin. The doping also increased the magnitude of the Seebeck coefficient of the compound. This is likely due to the increased number of carriers present within the doped material relative to the un-doped

material. Since the compound was easily pushed from an n-type carrier to a p-type carrier with only moderate amounts of doping onto the cobalt site, the compound was likely semi-metallic and doped into a semiconductor type compound.

Figure 18: CoSb_2 System Seebeck coefficients

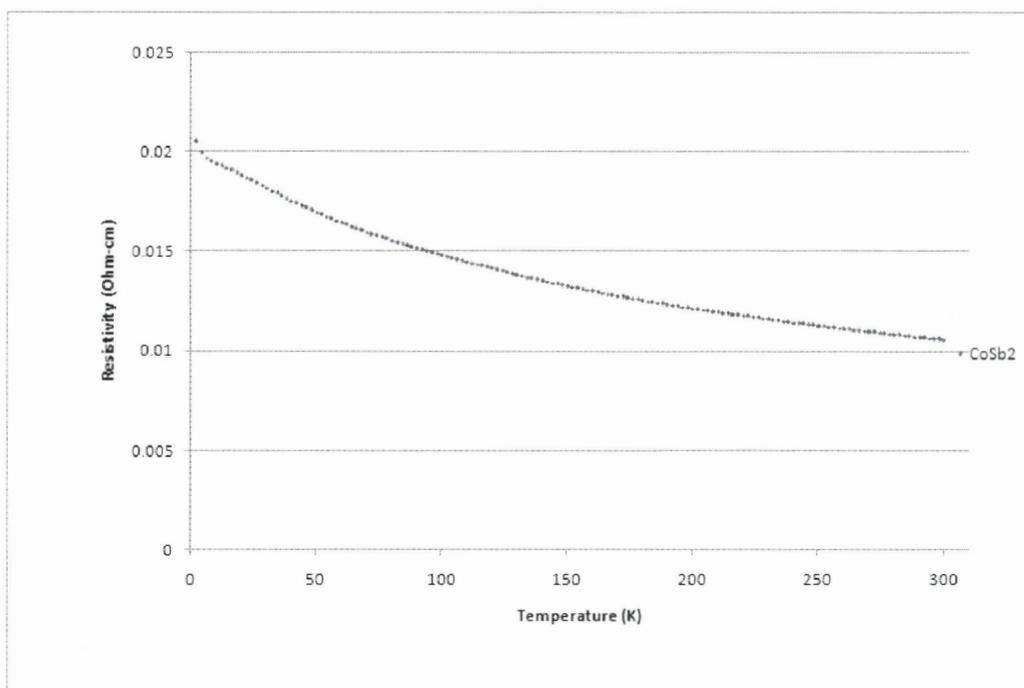


CoSb_2 was an n-type material with a Seebeck coefficient of approximately $-30 \mu\text{V/K}$ at 100 Kelvin. A 5% iron dope on the cobalt site changed the compound to a p-type material with a Seebeck coefficient of approximately $27 \mu\text{V/K}$ at 200 Kelvin.

The resistivity of the un-doped compound CoSb_2 decreased as temperature increased, exhibiting semiconductor like behavior. The compound was determined to be a semimetal. This low resistivity made the compound CoSb_2 interesting and a thermopower calculation was performed for the compound. The increased Seebeck coefficients in the

doped samples were not large enough to make this compound a good thermoelectric material for device applications.

Figure 19: CoSb_2 Resistivity



The resistivity as a function of temperature was determined for CoSb_2 . The resistivity decreased as temperature was increased. The resistivity of this compound was not as low as others and the Seebeck coefficient was only $-30 \mu\text{V/K}$ so no further research was done on this compound.

CONCLUSIONS

Summary

The Seebeck coefficient of Co_9S_8 was p-type and reached a maximum of approximately $22\mu\text{VK}^{-1}$ around 300K (Figure 7). Co_9S_8 behaved as a metal with its resistivity increasing with temperature. The thermopower of Co_9S_8 was calculated to be approximately $2.0 \times 10^8 \mu\text{V}^2 / \Omega \cdot \text{cm} \cdot \text{K}^2$ at 50 Kelvin.

The Co_9Se_8 -CoSe solid solution exhibited a large first-order magnetic ordering around 8 Kelvin and had a low electrical resistivity. The compound was not determined to be a superconductor or a useful thermoelectric material.

The CoTe_2 compound was n-type and the Seebeck coefficient was approximately $-6.5\mu\text{VK}^{-1}$ at 95K. There were no additional experiments performed on this compound due to its low Seebeck coefficient.

The CoSbSe compound exhibited p-type behavior with a maximum Seebeck coefficient less than $13\mu\text{VK}^{-1}$. The room temperature resistance measured for a small, approximately 4mm x 1.5mm x 2mm, piece of a sintered powder pellet was less than one Ohm. The Seebeck coefficient of this material was not high enough to merit an electrical resistivity measurement or a power factor calculation.

The CoSbSe compound exhibited characteristics typical of a p-type semiconductor with a low Seebeck coefficient. The CoSbS compound exhibited behavior characteristic of an n-type insulator. The CoSbS compound itself was too resistive for the Seebeck Effect Measuring System from MMR Technologies Inc. to measure the value. The room temperature resistance of a small piece of sintered CoSbS powder with approximate dimensions of 4mm x 1.5mm x 2mm was just over 1.5k Ω . The concentration of selenium and antimony were changed according to CoSbSe_xS_{1-x} (x=0, 0.25, 0.50, 0.75, 1.0). A simple digital multi-meter showed that the resistance across the CoSbSe pellet was approximately 1 Ω while the resistance across the CoSbS pellet was close to 1500 Ω . With just a 25% substitution of selenium on the sulfur site, the resistance of the CoSbSe_{0.25}S_{0.75} sample was only 200 Ω , approximately seven times less than that of the CoSbS compound. As the compounds transitioned from CoSbSe towards CoSbS with increasing amounts of sulfur on the selenium site the compound transitioned from the FeS₂ (CoSbSe) to the NiAs₂ (CoSbS) structure type. Often time's transitions from a metallic compound to an insulator often result in an intermediate superconducting phase. This is currently being studied for this system. This system exhibited very interesting behavior going from a p-type metal to an n-type insulator; however there is no thermoelectric device application for these materials as they either have a low Seebeck coefficient and low electrical resistivity or a high Seebeck coefficient with high electrical resistivity.

The CoSbTe compound exhibited n-type behavior with a maximum Seebeck coefficient of approximately -17 μ VK⁻¹ at a temperature of 320K. No additional experiments were

performed on this compound. The small Seebeck coefficient made it an unlikely candidate for an efficient thermoelectric device application.

The $\text{Au}_{0.95}\text{Pt}_{0.05}\text{Te}_2$ compound exhibited peculiar Seebeck coefficient behavior over the 200K-320K temperature range. This was most likely due to an impurity within the sample. Solid platinum shot was used and may not have been entirely homogenized throughout the sample. This non-homogeneity within the sample was not enough to interfere with the X-ray diffraction pattern, but may have been enough to offset the Seebeck measurement. Gold-telluride exhibited a Seebeck coefficient of approximately $-44\mu\text{V/K}$ at 320K. The doped samples took on intermediate values which can be seen in Figure 14. Additional doping studies should be carried out on this compound including mercury and cadmium doping.

The MnTe_2 system had some of the most promising material properties found in these experiments. The compound MnTe_2 exhibited a very large Seebeck coefficient and a high resistivity. The antimony doped versions of this compound had high Seebeck coefficient's on the order of $200\mu\text{V/K}$ at room temperature, but the resistivity dropped drastically in comparison to the case of undoped MnTe_2 . The decreases in resistivity between doped and undoped samples was likely due to the increased carrier concentration within doped compounds. All of these compounds seemed to undergo some sort of magnetic ordering around 70 Kelvin. The magnetic ordering in the MnTe_2 compound was most distinct and resulted in a $200\mu\text{V/K}$ drop in the Seebeck coefficient as the temperature decreased from 100K down to around 70K. The standard, approximately

4mm x 1.5mm x 2mm piece of material used for the resistivity measurement had a room temperature resistance as measured by a digital multi-meter that was on the order of 1.5k Ω for MnTe₂. The 5% antimony doped sample showed a room temperature resistance of approximately 150 Ω and the 10% antimony doped sample had a room temperature resistance of less than 10 Ω . Additional doping studies should be performed on this compound including an arsenic dope on the tellurium site and an iron dope on the manganese site.

CoSb₂ had a relatively maximum Seebeck coefficient of approximately -30 μ V/K at 175 Kelvin. A 5% Iron dope on the cobalt sites in CoSb₂ was conducted to create Co_{0.95}Fe_{0.05}Sb₂. This created a p-doped version of CoSb₂. The 5% iron dope was enough to push the compound over to a p-type compound, with p-type carriers, and a Seebeck coefficient of approximately 25 μ V/K at 175 Kelvin. Since the compound was easily pushed from an n-type carrier to a p-type carrier with only moderate amounts of doping onto the cobalt site, the compound was likely semi-metallic and doped into a semiconductor type compound. The resistivity of the un-doped compound CoSb₂ decreased as temperature increased, exhibiting semiconductor like behavior. The compound was determined to be a semimetal.

Suggestions for Future Research

An in depth continuation of the doping study on the MnTe₂ and AuTe₂ systems would be the most promising leads discovered in this set of experiments. Doped compounds of each structure type were found to exhibit very peculiar and interesting characteristics.

BIBLIOGRAPHY

- 1.) CRC Handbook of Thermoelectrics. Rowe, D.M.1995. ISBN: 0-8493-0146-7
- 2.) Seebeck, T.J., 1822, Magnetische Polarisation der Metalle und Erzedurch Temperatur-Differenz. Abhand Deut. Akad. Wiss. Berlin, 265-373. (English Translation)
- 3.) Peltier, J.C., 1834, Nouvelles experiences sur la caloriecete des courans electriques. Ann. Chem., LVI, 371-387. (English Translation)
- 4.) See Ioffe, A.F., 1957, Semiconductor Thermoelements and Thermoelectric Cooling, Infosearch, London.
- 5.) Altenkirch, E., 1909, Physikalische Zeitschrift, 10, 560-580. (English Translation)
- 6.) Altenkirch, E., 1911, Physikalische Zeitschrift, 12, 920-924. (English Translation)
- 7.) http://www.uq.edu.au/School_Science_Lessons/32.1.1.3.GIF
- 8.) Complex Thermoelectric Materials, G.Jeffrey Snyder & Eric S. Toberer. Materials Science, California Institute of Technology, 1200 East California Boulevard, Pasadena, California 91125, USA
- 9.) <http://hyperphysics.phy-astr.gsu.edu/hbase/electric/conins.html#c1>
- 10.) <http://www.mmr.com/seebeck.html> - Seebeck Device
- 11.) <http://www.qdusa.com/products/ppms.html> - PPMS Device

APPENDICES

Appendix A

Measurement Equipment

Seebeck Measurement Systems

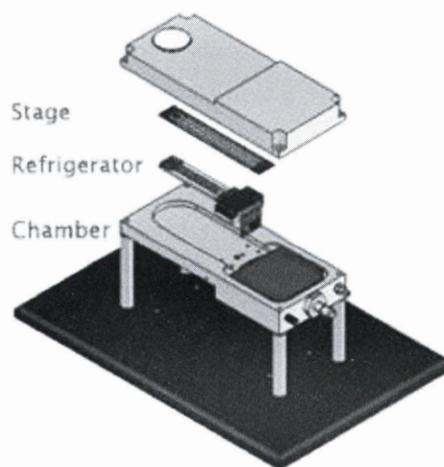


MMR's SB-100 Seebeck Measurement System allows users to make automatic measurements of the temperature-dependent Seebeck potential of metals, semiconductors and other electrically conductive samples over a temperature range from 70 K to 400 K, and from 200K to 730K. Sample mounting is simple permitting rapid interchange of samples. The Seebeck system is compatible with a variety of computers through an IEEE-488 (GPIA) or RS-232 interface. The MMR Programmable Seebeck Measurement System

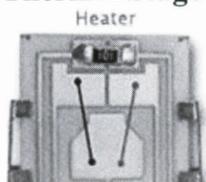
includes the SB-100 Programmable Seebeck controller, the K-20 Programmable Temperature Controller, the Seebeck Thermal Stage and accessories, a computer (PC), and MMR supplied software.

The Seebeck Thermal Stage includes two pairs of thermocouples. One pair is formed of junctions of copper and a reference material of known Seebeck emf. The other pair is formed of junctions of copper and the material whose Seebeck emf is to be determined. The system uses a sophisticated parametric double reference measurement technique developed at MMR Technologies, that yields precise, highly reproducible results, even with difficult samples.

s



Detail of Seebeck Thermal Stage



MMR Seebeck stages cover a wide operating range



All alumina stage allows measurements at temperatures above

400K.



BLACK: Studied

Material Polyimide stage allows measurements

RED: Reference at temperatures below 400K.

Material

Features

- Operating Temperature: 70K to 730K
- Two 16 bit A/D Converters
- Resolution: 50 nV
- Mismatch of Gains of reference and test channels: <0.1%
- Minimum Heater Step Size: 0.1 mW
- Number of Readings Automatically Averaged: Up to 128
- Full software provided for all measurements
- Sample Length: >2 mm and <10 mm
- Power Input: 110 V, 60 Hz and 220 V, 50 Hz

The Quantum Design Physical Properties Measurement System

The Quantum Design PPMS® represents a unique concept in laboratory equipment: an open architecture, variable temperature-field system, designed to perform a variety of automated measurements. Use the PPMS with options designed for it or easily adapt it to your own experiments. Sample environment controls include fields up to ± 16 Tesla and temperature range of 1.9 - 400 K. Its advanced expandable design combines many features in one instrument to make the PPMS the most versatile system of its kind.

PPMS Features:

- Sealed sample chamber with 2.6 cm diameter sample access
- Novel sample mounts couple easily to the 12 electrical leads built into the cryostat insert
- The Model 6000 is a self contained microprocessor-controlled device, eliminating the need to use or purchase external bridges, current or voltage sources or lock-in amplifiers.
- Continuous Low-Temperature Control - maintains temperature below 4.2 K for indefinite periods of time and offers smooth temperature transitions when warming and cooling through the 4.2 K.
- Temperature Sweep Mode
- User Experiments - External instruments may be controlled automatically using Visual C++, Delphi



Optional PPMS® EverCool™ Dewar

or Visual Basic in our Windows-based MultiVu control software. **[Click here for more details.](#)** In addition, our Grapher utility displays data as it is being collected.

PPMS Magnet Options:

- Select from 7, 9, 14 & 16 Tesla magnets.
- Or order a system with no magnet, and add a magnet when needed.
- A split-coil 7 Tesla transverse magnet is also available.

