EFFECT OF CoSb3 NANOPARTICLES ON THE THERMOELECTRIC PROPERTIES OF FILLED AND UNFILLED CoSb3 SKUTTERUDITES

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EFFECT OF CoSb$_3$ NANOPARTICLES ON THE THERMOELECTRIC PROPERTIES OF FILLED AND UNFILLED CoSb$_3$ SKUTTERUDITES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Physics

by
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August 2009

Accepted by:
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Dr. Catalina Marinescu
This study explores the possibility of somewhat decoupling the electrical and thermal conduction, thereby being able to limit the thermal conduction while minimizing the effect on the electrical conduction. The approach is using a nanoparticle layer with a slight compositional mismatch as compared to the bulk skutterudite. A hydrothermal nanoparticle-plating technique has been employed to grow a layer of CoSb$_3$ nanoparticles on the surface of skutterudite bulk matrix grains. Skutterudites of various forms were fabricated and studied in order to assess the effect of this nano-plated layer as a viable method in the improvement of thermoelectric properties of CoSb$_3$ nanocomposites. The skutterudite materials studied include Ni doped, rare earth (La, Ce, or Yb) filled, and Yb and Ce double filled skutterudites. The nanoparticles have a typical size of 30-40 nm while the nano-layer can be up to several hundred nm thick. The nanoparticle layer, which is at the grain boundary after hot pressing, provides an extra scattering channel for phonons, in addition to the “rattler” atoms, grain boundary scattering and mass fluctuation mechanisms found within the bulk matrix grain.

The electrical resistivity, Seebeck coefficient, thermal conductivity, and Hall coefficient have been investigated as a function of temperature and the weight percentage (%) of nanoparticles and will be reported with respect to their potential as thermoelectric materials. Improvement in the ZT can be seen in the filled skutterudite series, though the mechanisms providing this improvement are not identical. This nano-plating process shows itself to be a viable method that can be used in conjunction with other techniques, such as doping and void filling, to improve the thermoelectric properties of skutterudites.
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CHAPTER ONE
INTRODUCTION TO THERMOELECTRICS

1.1 - Thermoelectrics

Motivated by the impending energy crisis, thermoelectric (TE) materials became a renewed field of study. Now more than ever, with the decreasing fossil fuel supplies and increasing energy demand worldwide, people are looking into different avenues for new, sustainable sources of usable energy.[1] TE materials fall into this category and therefore there is pressure to improve current materials or discover new ones with improved properties.

With the discovery of semiconductors and the developed theory of semiconductor transport, TE materials were a popular field of study because these materials possess many of the properties that define thermoelectrics: large electrical conductivity, high Seebeck coefficient and low thermal conductivity. TE materials are already in use today but only in certain limited applications because of their conversion efficiencies are low compared to other appliances in current use. TE materials are used in two ways, refrigeration and power generation. This divergence means these materials must, therefore, work under very different temperature regimes. Currently different state-of-the-art materials are used in each different temperature regime. For refrigeration applications, alloys of (Bi$_{1-x}$Sb$_x$)$_2$(Te$_{1-y}$Se$_y$)$_3$ are used for room temperature and the Bi$_{1-x}$Sb$_x$ system is used for low temperatures. In the power generation mode high temperature thermoelectric materials, such as the PbTe system or the Si$_{1-x}$Ge$_x$ system for even higher temperatures are employed.
TE devices are advantageous for many reasons. TE materials are long lasting because the lack of mechanical, moving parts produces no wear. TE materials are environmentally green due to their long term chemical stability, producing no waste by-products or toxins. In addition, they contribute no noise pollution to the surrounding environment. Because of the compactness of the TE module, these devices are ideal for spot cooling and for use in spaces inaccessible to larger devices. Because of their varied particular uses, aspects that must be considered when testing and designing new TE materials include: Long term stability; stability over large temperature ranges and gradients; reproducibility over temperature cycling; ease and speed of manufacture; and cost. Thermoelectric materials are just now beginning to branch out of their niche applications into a wider market but must at least double their thermal-to-electrical energy conversion efficiencies to become competitive with other commercial energy conversion technologies.

TE materials are used in modules set-up like a Carnot engine, between a heat source and heat sink, where the media are the electrons. Both p-type materials, materials with holes as carriers, and n-type materials, materials with electrons as the primary carriers, are necessary for a TE module to function. A TE module has an array of alternating n-type and p-type thermoelectric materials arranged electrically in series but thermally in parallel as shown in Fig. 1.1. This array of n and p couples is connected electrically by electrical contact pads and thermally with a ceramic substrate. Using this set-up, the two modes, refrigeration and power generation, can be utilized. In the refrigeration method a current is passed through the module as depicted in Fig. 1.2. As
the current passes up the p-type materials the holes travel to the top, and as it then flows down through the coupled n-type materials the electrons flow opposite the current and also flow to the top, therefore the carriers flow in the same direction. This action gives a temperature gradient across the samples with one side heating up and the other side cooling down. To switch the temperature of the surface, the current is simply reversed. In order to utilize the power generation mode, the process is merely inverted as Fig. 1.3 shows. A temperature gradient is applied across the module, with one side being the hot side and the other being the cold side. This temperature gradient then causes the carriers to flow in the same electrical direction which causes a current to flow which can then be used to generate power.

TE materials are best described through three effects: the Seebeck effect, the Peltier effect, and the Thompson effect. Discovered in 1821 by T. J. Seebeck, the Seebeck effect occurs when two dissimilar materials are joined forming a closed loop with two junctions where the materials meet.[2] If these two junctions are held at dissimilar temperatures forcing a temperature gradient between them, as shown in Fig. 1.4, a voltage is produced. The relationship between the temperature difference, \( \Delta T \), and the difference in voltage, \( \Delta V \), produced is the Seebeck coefficient, defined as

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

(1.1)

where \( \alpha \) is the Seebeck coefficient. This voltage between the two ends then causes current to flow if the circuit is closed. If the temperature gradient is reversed then the current is also reversed.
The most common and basic application currently in use for this effect is the thermocouple. Using materials with known Seebeck values, the thermocouple is calibrated and utilized for temperature measurements by measuring voltage differences. In applications, this effect is used to produce the power generation mode. Examples are shown in Fig. 1.5. Currently this application is in use powering space vehicles such as the Cassini mission, in which decaying Pu and the coldness of space produce the temperature gradient. Because of this temperature difference, a current is produced and used in powering the shuttle. This area of application has progressed into using TE materials for waste heat recovery. This method can be used to recover waste heat from factory exhaust and could also be a possible method to increase the gas mileage in automobiles. In cars only about 30% of the energy in gasoline is used by the car, much of the rest is lost in heat. More mainstream power generation, such as body heat powered watches and camping lamps, are becoming more visible. The Seebeck coefficient is one of the terms defining a material’s ZT and will be discussed in more detail in Chapter 2.

The complementary effect to the Seebeck effect is the Peltier effect, which was discovered in 1834.[3] When two different materials are placed in contact with each other and a current is passed through them, heat will be either expelled or absorbed at their junction as depicted in Fig. 1.6. Whether heat is expelled or absorbed at the junction depends on the individual Fermi energies, $\varepsilon_F$, of the two materials. If the current goes from a material with a higher Fermi energy to a material with a lower one then heat is given off, and the converse is also true. The Peltier effect is defined as

$$\mathcal{Q} = \Pi_{AB} I$$

(1.2)
with the time derivative of $Q$ as the heat absorbed per unit time, $\Pi$ as the Peltier coefficient, and $I$ the current. This effect generates the refrigeration application of a thermoelectric material. As a current is passed through a thermoelectric material, a cool side and a hot side are produced. When the current is reversed, so are the temperatures across the material. Either function can be utilized depending on whether cooling or heating is desired.

This effect is in use spot cooling in computer chips and refrigeration of biological material in space. More common applications are now utilizing the cooling and heating effect like thermoelectric coolers/warmers and car seat coolers/warmers. Examples are seen in Fig. 1.6.

The Thompson effect was discovered by W. Thompson (Lord Kelvin) in 1851.[4] The Thomson relation gives us the relationship between the Seebeck and Peltier effect,

$$\Pi = \alpha T$$

(1.3)

where $\Pi$ is the Peltier coefficient, $\alpha$ is the Seebeck coefficient, and $T$ is the temperature. The Thompson effect is the cooling or heating of a homogeneous conductor resulting from the flow of an electrical current in the presence of a temperature gradient.

1.1.1 - Figure of Merit

TE materials are assessed by their figure of merit value. A TE material’s dimensionless figure of merit, or $ZT$, is defined by

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{\alpha^2 T}{\rho(\kappa_L + \kappa_E)}$$

(1.4)
where \( \alpha \) is the Seebeck Coefficient in \( \text{VK}^{-1} \), \( \rho \) is the electrical resistivity in \( \text{\Omega} \text{m} \), \( \kappa \) is the thermal conductivity in \( \text{Wm}^{-1}\text{K}^{-1} \), and \( T \) is the temperature in K. The electrical properties alone are coined the Power Factor and defined as

\[
PF = \alpha^2 \sigma T = \frac{\alpha^2 T}{\rho}.
\]  

The thermal conductivity is composed of two parts, the lattice and the electronic contributions, \( \kappa_L \) and \( \kappa_E \) respectively.

The efficiency of a thermoelectric is related to its ZT.[5] We can define the Carnot efficiency, \( \eta_C \), as

\[
\eta_c = \frac{T_H - T_C}{T_H}.
\]  

To find the max efficiency for our thermoelectric module

\[
\eta_{\text{max}} = \frac{I[(\alpha_p - \alpha_n)\Delta T - IR]}{K\Delta T + (\alpha_p - \alpha_n)IT_H - \frac{1}{2}I^2R}
\]  

where the first term in the denominator comes from the Fourier heat, the second from Peltier heat and the third from Joule heating. Note that this efficiency is achieved at a specific ratio of the thermal and electric currents.[6] Putting this in terms of ZT and \( \eta_C \), \( \eta_{\text{max}} \) becomes

\[
\eta_{\text{max}} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}.
\]  

To achieve \( \eta_{\text{max}} \) for a thermoelectric module, ZT must be large and \( \Delta T \) should be maximized. It is unlikely that any one material will maintain a high ZT during a large
temperature range. Maximizing $\Delta T$ is done via two methods, segmented or cascaded modules as seen in Fig. 1.8 [7].

In a segmented module thermoelectric materials, with high efficiencies at different temperature ranges, are pieced together in a leg of a thermoelectric module. In this manner each material works in its own temperature range. Because the current density stays fairly constant throughout the module, materials with high ZT’s must also have similar ratios of electric current density to heat current density when operating. To do this, the materials must have compatibility factors that are as nearly equal as possible. The compatibility factor, $s$, of a material takes into account the materials ZT and temperature as shown

$$s = \frac{\sqrt{1 + ZT} - 1}{\alpha T}. \tag{1.9}$$

For a segmented thermoelectric to reach $\eta_{\text{max}}$, materials need to have similar $s$. To bypass this compatibility issue, cascading set-up can be used. In this method, modules with optimized ZT’s at different temperatures can be stacked in different stages, and the ratio of the two currents can be varied to give high efficiency in each material.

Until recent years, the ZT for current state of the art TE materials was approximately one, as seen in Fig. 1.9 Skutterudites with ZT’s higher than one are seen at temperatures above 700 K. This value was the attained upper limit for almost 50 years.[1] New results show promise in finding new and enhanced thermoelectric materials. New directions have surfaced in finding these materials, with nanostructures like quantum dots and superlattices showing much promise. As can be seen, any effort to
improve the $ZT$ value of a TE material means enhancing the $PF$ while reducing the $\kappa$. Unfortunately, these properties are intricately coupled to each other and as a general rule, a change in one property affects the others. A possible way to attack this challenge and enhance $ZT$ is in finding methods that somewhat decouple these properties and allows them to be tuned individually. This topic will be discussed in more detail under project direction, but first it is important to start with an already promising TE material.

1.1.2 - Phonon Glass Electron Crystal Concept

In 1995 Glen Slack proposed a model of characteristics that comprise a good thermoelectric material in order to systematize a way of discovering new potential materials. He termed this model the Phonon Glass Electron Crystal (PGEC) concept.[8] This concept describes the behavior required in the electrical and thermal properties. It states that the desired characteristics in a thermoelectric material are thermal properties like a glass, meaning low thermal conductivity, and good electrical properties like a crystal, meaning high electrical conductivity. Reaching a balance in these conditions is essential for maximum results.

Using reasonable estimates for $\alpha$, $\rho$, and $\kappa$, a practical value of $ZT$ approximately equal to four was established for values between 77 and 300 K as a theoretically achievable value for a bulk material.[9] A material must hold certain properties for consideration as a good TE material. Low $\kappa$ is a significant requirement as stated earlier. Minimum $\kappa_L$ can be reached in a material when all the phonons have a mean free path close to their lattice parameter. Kittel tells us that glasses possess this quality; their
phonon mean free paths are of atomic dimensions. Glasses or amorphous materials are known for their inherently low $\kappa$. One method of finding a material with a low $\kappa$ that produces a $ZT$ greater than one may be to use binary or ternary compounds formed from heavy elements.

Slack proposed some criteria for these materials. The main criteria proposed go as follows:

1. $\kappa_L \approx \kappa_{\text{min}} \sim 1$ to 5 mWcm$^{-1}$K$^{-1}$
2. $\mu_N = \mu_p = 1800 \left(300 / T \right)^{2.30}$ cm$^2$V$^{-1}$s$^{-1}$ where $\mu$ is the mobility of the carriers
3. $m^* \sim m_0$
4. $E_g \geq 0.25$ eV
5. $\mu$, $\kappa_L$, and $m^*$ are independent of carrier concentration and $\kappa_L$ and $m^*$ are also independent of temperature

In these PGEC materials, the phonon mean free paths should be as short as possible while the electron mean free paths should be as long as possible. $\kappa_L$ should be as close to $k_{\text{min}}$ as possible, necessitating the phonon mean free paths to be on the order of the lattice parameter. The carrier mobility should have a value at least double the value for p-type PbTe, 1800 cm$^2$V$^{-1}$s$^{-1}$, and have a similar temperature dependence, $\mu = AT^{-b}$ with $b$ equal to 2.30. The density of states (DOS) effective mass ($m^*$) of the charge carriers needs to have a value equal to that of the free electron mass ($m_0$). These materials should also have a single valance band and single conduction band, both with $m^*$ equal to $m_0$.

The optimum energy band gap needs to be greater than or equal to $10kT$. This gives one predominant carrier so that the Seebeck coefficient remains high. If the band
gap is much larger the mobilities are low or the thermal conductivity is high. If the band
gap is much smaller the Seebeck coefficient decreases due to minority contributions and
bipolar thermal conductivity goes up. Multiple carrier types reduce the Seebeck
coefficient as seen in the two carrier Seebeck coefficient

\[ \alpha_{SB} = \frac{\alpha_n \sigma_n + \alpha_p \sigma_p}{\sigma_n + \sigma_p} \] (1.10)

where \( n \) and \( p \) denote the hole or electron contribution to the particular variable.
The values for \( \alpha_n \) and \( \alpha_p \) are opposite in sign. The carrier concentration in a
semiconductor is generally controlled by the substitution of a p-type or n-type dopant in
the structure. These dopants scatter the mobile charge carriers by the long range coulomb
interaction.

An idea of the magnitude of values needed for a good \( ZT \) can be found through
simple estimates. Setting \( \kappa_L \) equal to zero, for a hypothetical material, the \( \kappa \) will be
described by the electronic portion described by the Wiedemann-Franz relationship,

\[ \kappa_E = \sigma L_0 T \] (1.11)

where \( \sigma \) is the electrical conductivity, and \( L_0 \) is the Lorentz number. \( ZT \) then reduces to

\[ ZT = \frac{\alpha^2 \sigma T}{\sigma L_0 T} = \frac{\alpha^2}{L_0} \] (1.12)

To reach a \( ZT \) greater than one requires \( \alpha \) to be greater than 100 \( \mu \)V/K. Therefore
semiconductors, rather than metals which have lower \( \alpha \)'s, must be investigated. \( \kappa_L \) must
be the focus of \( \kappa \) reduction due to the close relationship between the \( \kappa_E \) and \( \sigma \), as seen in
Equation 1.11. A change in the \( \sigma \) leads to a change in \( \kappa_E \) which makes these qualities
hard to optimize simultaneously. The mean free path of the phonons needs to be reduced with as little effect on charge carriers as possible. The dependence of the $\kappa_L$ on the mean free path is seen in the approximate relation

$$\kappa_L = \frac{1}{3} C_v v_s l_{ph}$$

(1.13)

with $C_v$ is the heat capacity, $v_s$ is the velocity of sound, and $l_{ph}$ is the mean free path of the heat carrying phonons. Inserting rattlers into systems with voids is one way of reducing $l_{ph}$ without affecting the charge carriers. Filled skutterudites were hailed as an example of this PGEC concept.

1.2 - Skutterudites

Skutterudites are minerals that are named after the town in which they were discovered. These minerals were mined extensively in a small town in Norway named Skutterud. The chemical formula of the mineral was CoAs$_3$. This material was identified and studied by Oftedal in 1928.[11] In the 1950’s there was early interest in the Soviet Union for these materials. In the 1970’s the first filled skutterudite was created by Jeitschko and his colleagues after they realized that the skutterudite’s open structure might accept atoms or ions. They synthesized filled skutterudites using ions from the lanthanide group.

Skutterudites are an example of a PGEC. They are binary compounds that can be doped and have a large, complex unit cell as seen in Fig. 1.10 Their electrical properties are excellent for thermoelectrics. Their setback was an extremely high $\kappa$. By inserting
rattlers into the cages in order to scatter the low energy phonons, their $\kappa$ was decreased from 100 Wm$^{-1}$K$^{-1}$ to less than 5 Wm$^{-1}$K$^{-1}$ at room temperature as seen in Figure 1.11.

When in the 1990’s there was a resurgence in the field of thermoelectrics, at the suggestion of Glen Slack, the Jet Propulsion Lab began reinvestigating skutterudites for their TE potential. In 1994 Slack proposed his PGEC concept naming filled skutterudites as a prime example. Since that time skutterudites have been extensively researched. These studies will be summarized. [12,13,14]

Much of the research that has been done over the years in skutterudites, both unfilled and filled, will be discussed. Focus will rest primarily on CoSb$_3$ since that is the material studied during this course of study. Our focus will stand at lowering the $\kappa_L$ without degrading the electrical properties. This will be done by adopting several techniques: doping, filling, double filling, and nano-engineering. The focus will be on CoSb$_3$ since this is the parent compound that forms the basis of all our skutterudite compounds. A review of the parent compound followed by the doping, filling, double filling and nano-engineering techniques will be presented.

1.2.1 - Binary Skutterudites

Cobalt triantimonide is a composition sensitive semiconductor.[15-21] Any deviation from the 1:3 ratio, even in minute amounts, can give dramatically different properties as seen in Figure 1.12. These are CoSb$_3$ skutterudites grown by the same method but in what resulted in faintly different compositions, one sample being slightly Sb heavy and the other being slightly Sb deficient. A sample grown in Sb rich conditions
has an absence of Co atoms, therefore forming holes and giving rise to p-type conduction. On the other hand, a sample grown in Sb poor conditions has excess electrons in the conduction band, giving rise to n-type behavior.\cite{22} CoSb$_3$ is most generally p-type and from the behavior of the resistivity it can be concluded that CoSb$_3$ is a semiconductor. Its band gap is approximately 0.5 eV. Theoretical calculations agree with this gap size concluding that CoSb$_3$ has a nonparabolic valence band structure and is a zero to narrow gap semiconductors, or pseudo-band-gap.\cite{23,24} Experimental results agree with these numbers. These skutterudites are diamagnetic and have large $\alpha$’s and high mobilities. The Seebeck coefficients reveal a phonon drag effect. The Seebeck coefficient scales inversely with hole concentration. The electronic structure is due to the strong covalent bonding. This has been shown theoretically and backed up experimentally with XPS where there are small core level shifts showing a small charge transfer from the metal to the pnicogen atoms which leads to a hybrid between the metal d states and the pnicogen p states. The Co-Sb interaction is attributed to the octahedral CoSb$_6$.\cite{18,19}

The predominant contribution to $\kappa$ for these materials comes from the lattice due to the largely covalent nature of the bond. Pure CoSb$_3$ shows a steep rise in $\kappa$ with decreasing $T$ which is characteristic of the predominance of Umklapp phonon-phonon scattering and an intrinsic lattice contribution down to 10 K\cite{24}. In other words, as $T$ decreases, phonon-phonon scattering decreases, and $\kappa_L$ increases.

Several types of doping on the metal site have been done, among them is iron.\cite{25,26} Fe doped CoSb$_3$ has been shown to have a reduced $\kappa_L$ as compared to pure
CoSb₃. Tunneling studies reveal that Fe doping produces structural disorder states leading to more carrier scattering.

Nickel doping on the cobalt site has also produced good a good effect on the TE properties.[26,27] It produces n-type behavior and dramatically lowers the κ of CoSb₃. Ni doping produces an electron-phonon scattering mechanism that works especially well at low temperatures, which is an important role in the heat conduction of n-type materials. There is also additional point defect scattering. These results are seen with nickel substitution at less than 1% of the cobalt. There is a strong suppression of κₐ with nickel substitution but it saturates at higher concentrations. The low temperature electron mean free path is much shorter than the phonon wavelength. The σ at low temperature is dominated by hopping of electrons among the impurity states. Electron-phonon interaction occurs between the dopant electrons and the phonons.

Doping on the pnicogen site has also been used for charge compensation in the filled skutterudites, but the reduction in κ that is seen when doping on the metal site is absent here. [28,29] Few studies on pnicogen doping have been done on the unfilled skutterudites.

Another study done on the binary or unfilled skutterudite is the effect of grain boundaries or particle size.[29,30] Most recently studies were focused on nanostructuring. This was done using nickel doped CoSb₃. The nanostructuring was then hot pressed for three different lengths of time. Grain size and porosity were related to the details of the hot pressing. As hot pressing time increased, the porosity decreased
but more growth in grain size was seen. $\kappa$ was improved but there was no $ZT$ improvement because the electrical properties were adversely affected.

1.2.2 - Filled Skutterudites

Filled skutterudites were first synthesized in the 1970’s. Since then much extensive and exhaustive research has been done with many different fillers in hopes of finding the right element to fully minimize $\kappa_L$.\textsuperscript{[22,31-35]} Doping studies are also included, because doping is necessary to charge compensate for the different charges fillers, though rare earth fillers with a $3^+$ charge are the most common. As compared to their unfilled counterparts, filled skutterudites exhibit larger $m^*$ and smaller $\mu$. Large atomic displacement parameters offer proof that the filler ions rattle within the cages in the skutterudite structure as shown in Figure 1.13\textsuperscript{[16,17]} X-ray measurements have shown that the ions with smaller size but larger mass reside in the corners of their cages as opposed to the larger ions with lower mass which reside in the center of their cage. But the smaller ions tend to rattle more effectively. This rattling effect produces a drastic reduction, by orders of magnitude, in $\kappa_L$. Although $\kappa$ is effectively reduced, the temperature dependence of a crystalline solid remains. The Seebeck coefficient at room temperature is dominated by extrinsic carriers. The mean free path of these carriers is approximately equal to the separation of the nearest neighbor filler and is on the order of 8Å. Filled skutterudites tend to have high carrier concentrations due to the rare earth sites. Partial filling has shown to be helpful for increasing $\mu$ in these materials. Some studies have shown that perhaps the best method of thinking about these materials is as a
solid solution between a completely filled skutterudite (i.e. Ce$_3$Fe$_4$Sb$_{12}$) and its corresponding unfilled skutterudite (Fe$_4$Sb$_{12}$).[32,36] This method of analyzing the skutterudites shows that the predominant mass fluctuation is not on the doping site but between the filled and the empty voids. It has also been shown that these rattlers behave like Einstein oscillators, individually oscillating in their own cages without interaction with the other filler ions[37,38]. Each element used for a filler ion has its own filling fraction limit with respect to that skutterudite composition.[34] Any percent of filler ions introduced beyond that limit forms impurity phases, generally with antimony. To increase this limit doping for charge compensation can be done. This filling fraction limit is sensitive to the filler ion’s electronegativity.

One of the first studies of great significance in this field was conducted by Nolas et. al. on the IrSb$_3$ parent compound.[13] IrSb$_3$ and its filled versions show p-type behavior and high carrier mobility. The rare earth filling atoms chosen were lanthanum, neodymium, and samarium and all had a 3$^+$ charge. These samples were fully filled and charge compensated on the pnicogen site with germanium for the trivalent rare earth ions. The $\kappa$ of the unfilled sample was 40 times higher than that of the expected $\kappa_{\text{min}}$, calculated by setting the phonon mean free path on the order of $a_0$. Fig. 1.11 shows that while the void filling the $\kappa_L$ was drastically reduced, it did not reach the $\kappa_{\text{min}}$ value. The void filling allowed a broader spectrum of phonons to be scattered therefore reducing the mean free path. Large thermal x-ray parameters showed that the ions were rattling inside their voids. Ions rattle more inside larger voids; IrSb$_3$ has the largest void of an unfilled skutterudite. The reduction in the Nd and Sm was lower than the La filled, possibly due
to the low lying 4f energy levels producing additional phonon scattering. The Ge doped, unfulfilled skutterudite showed a $\kappa_L$ which was 56% of the value of the undoped IrSb$_3$ due to mass fluctuation scattering. The filled skutterudites showed $\kappa_L$ values 9%, 7% and 7% of the undoped, unfilled skutterudite for La, Nd, and Sm respectively. The lanthanide contraction impacts how the rattlers will behave. As the mass of the elements in the lanthanide series increases, the radius decreases. Because the radius for Nd and Sm are smaller than La, the atoms are freer to rattle around inside their cage which interacts with lower frequency phonons producing a lower $\kappa_L$. Although the effect on the thermal transport is greatly improved by the addition of these rare earth fillers, the electronic properties were negatively affected. So from this study it can be seen that both adding fillers and doping can improve the thermal properties but much more research has to be conducted in order to keep the electrical properties from being destroyed.

The next study of major note was also by Nolas et. al. and it discerned the effect of partially filling instead of fully filling the voids in a skutterudite.[39] La was chosen because it does not bring any 4f electrons that would help with the lowering of the $\kappa_L$. Thus the effect of the rattling from the La ion could be isolated. Some of the samples were charge compensated by doping on the pnicogen site with Sn. This was done to increase the filling fraction so there would be a range of samples from unfilled to filled. This study revealed, shown in Fig. 1.14, that partial filling the void sites of a skutterudite material was more effective than fully filling. Partial filling may introduce additional phonon scattering especially if the skutterudite is considered in terms of two solid solutions. Then half filling provides the most mass fluctuation between the filler and the
voids. Also, partial filling gives a random distribution of La across the sample giving point defect type scattering. This rattling together may scatter a broader spectrum of phonons. The temperature dependence of $\kappa_L$ is still crystalline. From this study it is seen that partial filling is more effective than fully filling. Many fillers have been used in an effort to follow these previous studies and lower the $\kappa_L$. A review of many of these fillers will be given.

Besides being a focus in these two papers, La has also been investigated in other studies.[13,31,40,41,17,33,42] Doping on both the metal and pnicogen sites have been used for charge compensation in La filled skutterudites. No compensation and Sn compensation on the pnicogen site show larger carrier mobilities than Fe compensation on the metal site. Using heat capacity and inelastic scattering it has been shown that low energy optical vibration modes are associated with filler ions. LDA theoretical calculations of vibrational density of states show that La is responsible for the low energy vibrational modes in LaFeSb. Theoretical work has also shown that anharmonic scattering can be caused by harmonic La or rare earth motions and causes a La-Sb hybridization.

Cerium is another filler that has been expansively studied. [43-46,22,31,36,32,] N-type doping for Ce is expected to produce a good TE material. Ce filled skutterudites can be either p or n--type depending on the filler and dopant concentrations. In simplified terms, lower amount of filling is generally used to produce n-type behavior and higher amounts of filling usually produce p-type behavior, though this is not a strict rule. A skutterudite that can produce both p and n type of nearly identical compounds is
attractive for use in the TE modules. Ce is trivalent with one 4f electron which is active in the bonding via hybridization with Fe 3d electrons which is important for the formation of band gaps around the $\varepsilon_f$. For $\text{Ce}_y\text{Co}_x\text{Fe}_{4-x}\text{Sb}_{12}$ more Fe means less mobility because there is more carrier scattering on the Fe site. For $\text{CoSb}_3$ with no charge compensation, the filling limit for cerium is 10%. As Ce concentration is increased in skutterudites, the low temperature $\kappa$ peak is suppressed. Ce filling provides phonon scattering without significantly demolishing the electron mobility.

Ytterbium is another filler that has shown good results.[47,48,35,49] Although Yb also seems like it would be in a trivalent state, studies have shown that it is generally in an intermediate valent state between 2 and 3. Yb has a smaller radius than La or Ce so it tends towards being divalent in an effort to better fill the void. As Yb is placed inside $\text{CoSb}_3$ the behavior becomes metallic, but semiconducting behavior can be returned by charge compensation on the Sb site by Sn. The Yb filled $\text{CoSb}_3$ has a higher $ZT$ than the Yb filled $\text{FeSb}_3$ but the doping by Sn negates this improvement. The Sn gives a p-type increase in the $\alpha$ which is negative in this compound, therefore lowering it. The $\kappa$ is unaffected by the Sn as is the $\varepsilon_f$ although there is an enhanced $m^*$. Germanium substitution instead of Sn does not increase the $ZT$. The Seebeck coefficient turns over at higher temperatures. Yb was found to work best in low filling amounts, less than or equal to 0.2.

Europium is one of the small radii, heavy ions that reside in the corner of its cage as opposed to the center, and this is seen in atomic vibrational modes.[50,51] Ge compensation for Sb has been used. These samples showed relatively high $\mu$, $PF$, and a
low $\kappa$. The minimum $\kappa_L$ is almost reached. The resistivity transition temperature decreases with increasing Co concentration. The Eu ion also does not have a stable valence state but changes from approximately 2.2 to 2.6 depending on the filling amount.

After rare earth filling, other materials were tried to see if there were different affects on the properties of the skutterudite. Synthesizing these new fillers usually called for more rigorous synthesis techniques as the ions were not readily accepted as fillers by the structure. Thallium filled skutterudites were synthesized.[52,37] These materials must be handled extremely carefully as they are toxic. These materials have been made with both Fe doping on the metal site and Sn doping on the pnicogen site. They show large atomic displacement parameters, meaning they rattle readily within their voids. Localized vibrational modes that are associated with the rattling mode in skutterudites are not found in the binary form, therefore giving more proof that Tl acts as an Einstein oscillator. They also have higher $\mu_e$, similar $\kappa$ dependence, and no evidence of mass fluctuation scattering. These materials show exciting results because at nearly full void filling they show their lowest value for $\kappa$ which is the closest seen to $\kappa_{\text{min}}$.

Other more arbitrary elements have been investigated as possible filler ions but did not show results more promising than what has already been discussed.[53-57,49] For example, strontium was used as a filler.[58] This skutterudite was able to accommodate 40% void filling and lattice parameters were seen to increase with the increase in Sr content. This showed an n-type behavior and the $\kappa$ was lowered. Hafnium was also used as a filler but the compound was metastable.[59] It had a very low $\kappa$, p-type behavior, and high $\rho$. Indium filled skutterudites have also been recently studied.
[63,64]. They have been shown to have excellent TE properties but their $\kappa$ still remains too high. These are now being studied in double filling to lower $\kappa$.

Elements that were used for charge compensation have also been inserted into the voids. Tin filled samples were grown under high pressure and temperature.[60,61] These samples showed large atomic displacement parameters which show that the Sn is not bonded to the framework. They Sn atoms rattle and interact strongly with the lattice vibrations to shift and broaden the Sb modes. They had very low $\kappa$ with typical crystalline dependence and a decent $\alpha$ for an unoptimized skutterudite. Germanium was also used as a filler under high pressure synthesis[61,62]. They show a weak interaction with the lattice but show no signs of rattling inside the cage, and actually seem to be found in the cages but also doped the pnicogen sites where it is normally used. The $\kappa$ is lowered from that of the binary but higher than most other filled skutterudites. It shows n-type behavior.

Overall the most promising skutterudites after years of study are still the Ce and Yb filled skutterudites. Because of this, new methods, including filling with both of the elements, have been explored. Since new skutterudites have not shown more promising results, new methods or new ways of optimization have been tried.

1.2.3 - Double Filling

Because results in single filled systems have reached a plateau, the researched has progressed into the area of multiple filling with various different filling elements. The first double filled skutterudites were two rare earth elements at different ends of the
lanthanide series probably to promote their different masses therefore add to the mass fluctuation scattering.[65,66] These double filling can be looked at as a solid solution between the two different filled skutterudites, in this case Ce$_2$Fe$_4$Sb$_{12}$ and Yb$_2$Fe$_4$Sb$_{12}$. Ce remains trivalent in every case while Yb changes from 2.16 to 2.71 as Ce content is added. This double filling enhanced the $\alpha$ by 20% and enhances the $PF$. The $\kappa$ is lowered beyond the previously seen decrease by single filled skutterudites, but reaches the same minimum no matter the amount of double filling. Double filling causes a greater suppression of $\kappa_L$ but does not increase with amounts of fillers but instead all the different compositions achieve relatively the same value. Fe doping for charge compensation on the Co side is more effective for the properties of these skutterudites than Ni doping.

La and Ce double filled skutterudites were also synthesized although these two elements have more similar properties.[67] Again the $\alpha$ is higher for the double filled than for the skutterudites that are single filled. There is a decrease in the carrier concentration and increase in $m^*$. The $\sigma$ is decreased but there is also a decrease of $\kappa$ to a low value.

1.2.4 - Nano-engineering

Another topic that has had drastic effects on the field of thermoelectrics is this idea of moving from three dimensional transport to one dimensional. Thinking from this new point of view could give us the advantage of a new method that may provide us a way to “decouple” the electrical and thermal transport properties. Decoupling these
properties would provide us with more ease in tuning each property. Looking at these materials from a classical stance, the transport is controlled by the limitation of the mean free path of both the phonons and electrons from scattering mechanisms. As the dimensionality decreases, quantum size effects develop due to confinement induced change in the electronic band structure and vibration properties. The length scale for quantum size effects to occur is the size of a quantum dot, the diameter of a nanowire, or the period in layered systems like a superlattice. An approach to using this reduced size is picking a grain size smaller than the mean free path of the phonons, which reduces $\kappa$, yet larger than the electron mean free path, preserving the electrical properties.

In 1993 Hicks and Dresselhaus predicted that lowering the dimensionality could result in improved electrical properties, using

$$\alpha \propto \frac{dDOS}{dE} \bigg|_{E_f}$$

and

$$\sigma \propto DOS \ . \ [68]$$

From these relations, it is seen that the $\sigma$ is proportional to the magnitude of density of states while $\alpha$ is related to the slope of the curve. Fig. 1.15 shows the DOS versus the dimensionality. As we move down in dimensionality the magnitude of the DOS remains the same, while as the shape of the curve becomes changes, becoming more and more delta function like. This means if a 3D material is made into a lower dimension material, the magnitude of the $\sigma$ could remain unchanged as dimensionality is decreased while the $\alpha$, reflected in the slope of the curve, has the possibility of greatly increasing.
From another point of view moving to one dimension could also have promising results for the $\kappa$. Moving down in dimensionality causes greater numbers of grain boundaries or other scattering centers.[69] These scatters or boundaries would in turn scatter a greater number of phonons reducing the mean free path. If the relationship between the $\kappa_L$ and the phonon mean free path $l$

$$\kappa_L = \frac{1}{3}Cvl$$

is considered, this reduction of mean free path could drastically reduce $\kappa_L$. Materials exhibiting some of these qualities have already shown good numbers. Layered structures like superlattices have managed to retain their electrical properties while lowering $\kappa_L$. Other studies on embedded nanoparticles have shown large decreases in $\kappa_L$, doubling their ZT.

Nano-engineering both the bulk and nano properties would merge benefits from each. Using favorable bulk thermoelectric materials and including some kind of nanostructure helps somewhat decouple the interrelated transport properties. The nanostructures improve the the properties of the bulk in two ways: increasing the PF through improved $\alpha$ and reducing $\kappa$ by increasing the interfaces.

**1.3 - Project Direction**

Over years of study, filled skutterudites have remained promising compounds for use in thermoelectrics. In order to continue improving their properties, new ways of optimizing these skutterudites must be found. Good results have been seen with doping, filling and now double filling of the skutterudite structure. This present study takes past
approaches that have shown good results and tries to further improve upon them by using these past techniques and nano-engineering them into skutterudite nanocomposites.

Promising skutterudite compositions were grown and nano-plated with nanoparticles in order to gain the best results from the traditional skutterudite optimization methods and the new nano-engineering technique.

The focus is on how to reduce $\kappa$ without degrading the electrical properties. Doping, filling, double filling and nanocompositing are being implemented to find a combination that shows improvement. Our final result will comprise a combination of these tools. The proposal is designing a barrier that complements the electrical transport properties of our skutterudites while scattering the phonons and lowering $\kappa_L$. 
Figure 1.1 – A picture[70] and drawing of a thermoelectric module using the current to show that they are thermally in parallel while electrically in series.
Figure 1.2 – Schematic of the refrigeration mode of thermoelectric module.
Power Generation

Figure 1.3 – Schematic of the power generation mode of thermoelectric module.
Figure 1.4 – Diagram of a thermocouple showing how the Seebeck Effect works.

\[ \alpha = \frac{V_{AB}}{\Delta T} \]
Figure 1.5 – Different examples of TE materials used for power generation or waste heat recovery. From top clockwise: Cassini mission[71], Seiko TE watch[72], waste heat in cars[73].
Figure 1.6 – Diagram showing how heat is expelled or absorbed during the Peltier Effect.

Heat:
- absorbed
- expelled

depending on $\varepsilon_F$ of the materials
Figure 1.7 – Different refrigeration applications of TE materials. A TE warmer/cooler (left)[74] and a TE module for cooling computer chips (right)[75].
Figure 1.8 – Diagram of a segmented thermoelectric (top) and a cascading thermoelectric (bottom) module.
Figure 1.9 – ZT Plot of current state of the art thermoelectrics.[76]
Figure 1.10 – Cubic representation of a skutterudite structure.
Figure 1.11 – Plot showing the reduction of the lattice thermal conductivity by filling the voids of a skutterudite.[13]
Figure 1.12– Plots showing the drastic changes in properties that can occur with slight compositional differences. Both samples have the nominal composition CoSb$_3$. 
Figure 1.13 – Plot showing the much larger atomic displacement parameters showing the rattling motion for the filler ion in filled skutterudites.[16]
Figure 1.14 – Plot showing the effect of partial filling in a skutterudite on the lattice thermal conductivity. [39]
Figure 1.15 – The effect of reducing dimensionality on the density of state (DOS) of a material.[68]
CHAPTER TWO
BACKGROUND AND MEASUREMENT OF ELECTRICAL TRANSPORT PROPERTIES

2.1 - Electrical Resistivity

Resistivity is a material’s resistance to the flow of electrical current. A better understanding can be formulated through exploring a model of electrical conduction such as the Drude model.[77,78] Electrical conduction occurs from the net movement of the charge carriers in a material that has been placed under the influence of an applied electric field in the direction of the field. This movement of the carriers gives rise to an electric current density, $J$, which is defined as the net amount of charge that flows across a unit area per unit time,

$$J = \frac{\Delta q}{\Delta t}.$$  \hspace{1cm} (2.1)

If electrons are the carriers in material and become mobile from the presence of an electric field, they will move opposite the field and conventional current. These electrons undergo a Coulombic force, $eE_x$, due to their negative charge. The electrons in a material move about randomly, but when an external electric field is present, it causes them to acquire a net velocity in the direction of the field called a drift velocity. This drift velocity is calculated by averaging the velocities $v$ of the electrons in the x-direction at a time $t$ as follows

$$v_{dx} = \frac{1}{N} \left[ v_{x1} + v_{x2} + \Lambda \right].$$ \hspace{1cm} (2.2)
If \( n \), the concentration of conduction electrons, is defined as the number of electrons per unit volume \((N/V)\), and at a \( \Delta t \) the displacement of the electrons is given as \( \Delta x = v_{dc} \Delta t \), then the amount of charge passing through an area \( A \) can be written as

\[
\frac{\Delta q}{A} = e(nA\Delta x) = enA v_{dc} \Delta t \tag{2.3}
\]

which is the number of electrons crossing this area for a certain amount of time \( \Delta t \). The electron current density is then rewritten

\[
J_x = \frac{\Delta q}{A \Delta t} = \frac{enA v_{dc} \Delta t}{A \Delta t} = en v_{dc}. \tag{2.4}
\]

The drift velocity can be rewritten to be

\[
v_{dc} = \frac{e\tau}{m_e} E_x = \mu_d E_x \tag{2.5}
\]

where \( e \) and \( m_e \) is the charge and mass of the electron respectively, and \( \tau \) is the mean free time or time between collisions. The formulation of these variables as shown is given as the drift mobility, \( \mu_d \). The drift mobility is a measure of how fast the electrons will drift when driven by an electric field if the electrons are not highly scattered. So if the time between collisions, \( \tau \), is large \( \mu_d \) is also large. The mean frequency of the collisions is defined as \( \tau^{-1} \). Using the drift mobility, the current density can again be rewritten as

\[
J_x = en \mu_d E_x. \tag{2.6}
\]

The first part of this equation

\[
en \mu_d = \sigma \tag{2.7}
\]

is called the electrical conductivity, \( \sigma \). The electrical resistivity is the inverse of \( \sigma \):
The energy corresponding to the highest filled state at 0 K is called the Fermi energy, $\varepsilon_f$. The conduction band is the lowest lying electron energy band that is empty of electrons at $\varepsilon_f$. The valence band is the energy band that contains the valence electrons. Metals have conduction bands and valence bands that overlap. Therefore, metals have loosely bound electrons that are able to move freely. Very little energy is required to move the valence electrons into the low lying empty states in the conduction band. Because of the freedom of these electrons, electrical conductivity is high in metals.

In semiconductors there is a gap between the conduction band and valence band. Valence electrons must be promoted across an energy gap, $E_g$, into the conduction band. The larger the band gap, the more energy that is needed to promote the electrons into the conduction band, and the lower the electrical conductivity. A large band gap makes the material an insulator. In all materials, an increase in temperature increases the thermal excitation promoting some electrons from the valence band(s), and leaving hole in the valence band and therefore gives rise to a higher electrical conductivity, so the electrical conductivity is temperature dependent. In metals this gives rise to a linear dependence.

The electrical properties of semiconductors are very sensitive to even the smallest amount of impurities. Intrinsic semiconductors have electrical properties that are based on the electronic structure inherent to the pure material. An extrinsic semiconductor’s electrical behavior is determined by the impurities which introduce excess carriers. Introduction of excess carriers can be done by doping, which can changes the properties
of the semiconductor. When the number of electrons far exceeds the number of holes in the valence band, the semiconductor is said to be n-type (donor impurities). When holes are in higher concentration, the semiconductor is p-type (acceptor impurities). Generally there are both holes and electrons present in any material. The one with the higher concentration is considered the majority carriers and the other is the minority carrier. The type of carrier in control of the properties can change over the temperature range.

If the electrons in a metal are only being scattered by the thermal vibrations in the lattice, the resistivity can be written as

$$\rho_T = \frac{m_e T}{e^2 nc}$$

(2.9)
giving it a linear temperature dependence. Impurities in a material hinder the electrons movements causing the electrical resistivity to be larger. These impurities distort the crystal structure. As the electron is traveling through the lattice, it feels a force due to the change in the potential energy as it reaches the impurity. The electron has one scattering time from the thermal vibrations, $\tau_T$, and one due to the scattering from the impurities, $\tau_I$. Matthiessen’s rule states that these can be thought of as independent of each other. To find the electron’s probability of being scattering, the terms can be added as

$$\frac{1}{\tau} = \frac{1}{\tau_T} + \frac{1}{\tau_I}$$

(2.10)
where the final scattering time, $\tau$, is smaller than either contribution. Because of their relationships with $\tau$,

$$\mu_d = \frac{e \tau}{m_e}$$

(2.11)
\[ \rho = \frac{1}{en\mu_d} \]  

(2.12)

the mobility and electrical resistivity can both be rewritten using Matthiessen’s rule as follows

\[ \frac{1}{\mu_d} = \frac{1}{\mu_t} + \frac{1}{\mu_i} \]  

(2.13)

and

\[ \rho = \rho_t + \rho_r \]  

(2.14)

where the contribution due to thermal vibrations has a linear temperature dependence and the residual contribution which includes impurities, dislocations, defects, grain boundaries, and vacancies, is constant.

2.2 - Seebeck Coefficient

The Seebeck Effect is one of the effects that defines thermoelectric materials. [77,78] If a temperature gradient is applied across a conducting material, a potential difference develops along the conductor. The electrons in the hot region become more energetic than the ones in the cold region and therefore have a higher velocity. The electrons form a net diffusion from the hot region to the cold region of the material. This migration leaves behind positive metal ions in the hot region and an accumulation of electrons in the cold region. This build up continues until the electric field that develops between the positive ions and negative electrons becomes strong enough to prevent further electron diffusion, thus causing a voltage to develop across the material. The
voltage difference, $\Delta V$, formed due to the applied temperature difference, $\Delta T$, is the Seebeck effect and is defined by

$$\alpha = -\frac{dV}{dT}. \quad (2.15)$$

The Seebeck Effect is an effect that can only be measured between two materials. When two materials with different Fermi energies, $\varepsilon_f$, are joined together, the electrons from the material with the higher $\varepsilon_f$ move to the empty states of the material with the lower $\varepsilon_f$. A contact voltage develops until the Fermi energies reach equilibrium. The Fermi energy of a material represents the free energy per electron (or the electrochemical potential). $\varepsilon_f$ is a measure of the potentials of a material’s electrons to do electrical work through chemical or physical processes. For two materials, if they are the same, no net voltage appears because the voltage across the second opposes the first. With two different materials, the thermoelectric voltage is different across the second so there is a net voltage across the two materials. To find $\alpha$ of a new material, it is usually measured with respect to a material with a known value. So for 2 materials

$$V_{AB} = \int_{T_0}^{T} (\alpha_A - \alpha_B) dT = \int_{T_0}^{T} \alpha_{AB} dT \quad (2.16)$$

By convention, the sign of the Seebeck coefficient is taken to be the potential of the cold side with respect to the hot side. If electrons move from the hot to cold, the cold side become negative and the Seebeck is negative. This does not always hold true. Other factors such as how electrons at the Fermi level contribute to conduction and scattering by impurities, defects, and lattice vibrations influence the length of the mean free path and therefore, impact the Seebeck coefficient. The Mott-Jones equation was developed
to take these factors into consideration and correctly calculates the Seebeck coefficient of many metals,

$$S \approx -\frac{\pi^2 k^2 T}{3eE_{f0}} x$$

(2.17)

where $x$ is a numerical constant that contains the transport parameters for the material.

Both types of carriers could also be involved in creating the Seebeck effect. The primary carriers are the majority contribution and the less significant carriers are the minority contribution. When the minority carriers start making a significant contribution, the value of the Seebeck coefficient decreases because the carriers have opposite charge.

The material should have predominantly one carrier. This is not typically the case. Many materials have a much more complicated structure with multiple bands where minority carriers come into the transport. Multiple carrier types reduces the Seebeck coefficient as seen in the two band Seebeck coefficient

$$\alpha_{2B} = \frac{\alpha_n \sigma_n + \alpha_p \sigma_p}{\sigma_n + \sigma_p}$$

(2.18)

where $n$ and $p$ denote the electron or hole contribution to the particular variable. $\alpha_n$ and $\alpha_p$ have opposite sign therefore canceling each other out and lowering the $\alpha$. This bipolar effect shows up in the high temperature $\alpha$ and $\kappa$. The minority carriers come into the conduction and there is a turn over in the behavior of both $\alpha$ and $\kappa$ at the same temperature.

2.2.1 - Low Temperature Resistivity and Seebeck Coefficient Measurement
Before mounting, samples were prepared by sanding of the surface and thorough cleaning using acetone or alcohol to remove surface contaminations such dirt particles or thin oxide layers in an effort to ensure good electrical contact. Typical sample size is 8 mm by 2 mm by 2 mm. Samples were mounted individually on a custom designed 24-pin chip using InSn Ostalloy solder (#244 In (52%) Sn(48%)) as shown in Fig. 2.1. [79] Figure # part & shows the main copper block which was used to establish a consistent, stable temperature match with the rest of the measurement system. One end of the sample was mounted to this cold end of the sample mount. On the other end, a small copper block was soldered onto the sample. This second end was established as the hot end because this small block carried a 39 $\Omega$ resistor, attached with Devcon 5 minute (S-209) epoxy, which was used as a heater to provide the temperature difference during measurement. Slits were cut into in both the main block and the heater block in which the two junctions of a 3-mil AuFe (0.07% Fe) - Chromel differential thermocouple, constructed in the lab used for temperature measurement, were embedded. Imbedding the thermocouples in the copper block ensured good thermal matching and more accurate temperature reporting, while cigarette paper was used to electrically isolate the thermocouple from the mount. Three #34 AWG copper wires, used for the ground, current input, $I^+$, and TE voltage measurement, $V_{TEP}^+$, were soldered onto the back of the main copper block. Two #34 AWG copper wires were soldered in between the sample and small hot copper block in order to produce the current output, $I$, and TE voltage output, $V_{TEP}^-$, as shown in Fig. 2.1. To measure the sample voltage, $V_R^\pm$, used in the resistivity measurement, two #34 AWG copper wires were onto the top surface of the
Sample dimensions were measured using a digital Vernier caliper with an uncertainty of ±0.005mm except for the distance between the $V_R$ leads which was made under the microscope using a calibrated graticule.

Resistivity and the Seebeck coefficient were measured simultaneously on a custom designed closed-cycle refrigerator system from approximately 10 K to 300 K. The individual sample mounts could be plugged in two at a time as shown in Figure. Because samples could be mounted while other samples were running there was minimal down time between runs. The system incorporated a radiation cap placed over the samples to reflect radiation back onto the sample to ensure homogeneous heating. Two more radiation shields enclosed the measurement system. The entire measurement process is governed by a Labview® program. The system took over 800 points from 10 K to 320 K and measured $\rho$ and $\alpha$ while cooling and again while warming taking roughly 15 hours.

Sample dimensions and current are entered into the program. The program cooled the system down at 0.75 K/min and the temperature difference from the hot end to the cold end of the sample was set for 5 K. At each point the current was pulsed for approximately 1 s and the voltage across the sample was measured by the $V_R$ leads on the top of the sample by a Keithley 2000 multivoltmeter. The current was supplied by a Keithley 2400 sourcemeter and was first run through a standard resistor with resistance comparable to the sample in order to measure the true current. The voltage produced was

$$V_{tot} = IR + V_{TEP}$$

(0.1)
where $I$ is the current applied and $R$ is the resistance through the sample plus a thermoelectric voltage. The current was then set to zero. At this point the temperature gradient across the sample was established and measured using the AuFe-Chromel thermocouple, and the TE voltage was measure through the $V_{TEP}$ leads on the ends of the sample. The current was then applied in the reverse direction so that the $V_{TEP}$ could be subtracted out. Therefore we get the resistance of the sample from

$$R = \frac{(V_{att}^- - V_{att}^+)}{I^+ - I^-} = \frac{(V_R^+ - V_R^- + V_{TEP} - V_{TEP})}{I^+ - I^-} = \frac{2V_R}{2I}$$

(2.19)

Then using

$$\rho = \frac{Rl}{A}$$

(2.20)

where $l$ is the length of the sample in m, $A$ is the cross sectional area in m$^2$, and $R$ is the resistance in $\Omega$, the resistivity $\rho$ of the sample was calculated in $\Omega\cdot$m by the program.

The $\alpha$ was measured when the current was set to zero using the measured thermoelectric voltage and temperature gradient. Then using

$$\alpha = \frac{\Delta V}{\Delta T}$$

(2.21)

$\alpha$ was determined by the system in $\mu$V/K. Both were measured at temperatures between 10 K and 320 K. Keithley 2000 multivoltmeter, 2010 multimeter, 2400 sourcemeter and scanner cards were used for the data taking.

Because there are multiple systems, the samples were always remounted onto different sample mounts between runs and run on different systems. Different samples from the same pellet were also used. This was to ensure that the data was consistent and
as a marker for any problems such as a bad sample mount or a short in the system. The system utilized, mount used, voltage between the leads, and any other pertinent information was recorded.

2.2.2. – High Temperature Resistivity and Seebeck Coefficient Measurement

High temperature resistivity and Seebeck coefficient is measured on an Ulvac ZEM-2 high temperature system from 300 K to 700 K using a 4-probe configuration.[80] The samples were nickel plated on both ends to produce even, electrical contact with the system. The sample was pressure mounted between two ceramic, spring loaded posts that allowed for sample expansion during heating. A thermocouple was mounted onto the sample also using pressure contacts.

The system was pumped down for 10 min, flushed with Ar and pumped down again. A small amount of gas was released back into the system to allow the system to reach temperature stability more easily. The sample was then tested for ohmic behavior. For the skutterudites, the current was set at 50 mA. The samples dimensions were inputted into the system and run from room temperature up to 625°C.

2.3 – Hall Effect

The Hall effect occurs when charge carriers are exposed to a magnetic field in a direction orthogonal to the carrier motion, thus causing a Lorentz force on the carriers, which deflects them enabling the calculation of the type of carrier, carrier concentration, and carrier mobility.[77,78] More concretely, take charge carriers that are moving
through a material with a certain velocity in the x direction, \( v_x \), due to a current when a magnetic field, \( B_z \), is applied perpendicular to the motion of these charged particles in the z direction, a force in the y direction is exerted on the carriers perpendicular to both the direction of the motion of the particles and the magnetic field. This force on the charge carriers will cause them to deflect in that perpendicular direction. The positively charged carriers (holes) will deflect in one (right) direction and the negatively charged carriers (electrons) will deflect in the opposite direction as following the right hand rule using:

\[
F = qv \times B. \tag{2.22}
\]

The separation of the charges carriers to different sides of the samples establishes a Hall voltage across the sample in the y direction given as

\[
V_H = \frac{R_H I_x B_z}{d} \tag{2.23}
\]

Where \( V_H \) depends on the current, \( I_x \), due to the movement of the carriers in the x direction, the thickness of the sample, \( d \), and the Hall coefficient, \( R_H \), which is a constant for a given material. For metals

\[
R_H = \frac{1}{ne} \tag{2.24}
\]

where \( n \) is the carrier concentration and \( e \) is the charge of the electron. The sign of the charge is negative when the conduction is by electrons and positive when the conduction is by holes, therefore the carrier type can be identified. The Hall voltage can be measured and the current, magnetic field, and thickness can be known, therefore the carrier concentration can be found using
\[ V_H = \frac{I_s B_s}{dne} \]  

(2.25)

and solving for \( n \)

\[ n = \frac{I_s B_s}{d e V_H} \]  

(2.26)

Then using the sample’s electrical resistivity, the mobility, \( \mu \), can be calculated as shown

\[ \mu_e = \frac{\sigma}{ne} = R_H \sigma \]  

(2.27)

Therefore the Hall effect is a useful tool in determining majority charge carrier type, concentration, and mobility which cannot be found from a normal electrical conductivity measurement. For semiconductors or metals with more than one band of carriers or complicated Fermi surface topology these computations are more complicated.

2.3.1 - Hall Effect Measurement

The samples were mounted onto a removable Physical Properties Measurement System (PPMS®) puck.[81] Up to two samples were run simultaneously on a puck. Apiezon N-grease was used to thermally contact the sample with the puck, and silver wires were soldered to the sample in order to have better electrical contact between the puck and sample. The five wire Hall Voltage setup in Figure 2.2 was used as it is more reliable than the four wire technique because it requires exact positioning of the voltage leads across from each other. Instead, with the five wire method three voltage leads were soldered onto the top of the sample forming a triangle, two on one side and one across but situated between the other two. These wires are then balanced in the system to eliminate
any voltage component that may be dependent on the magnitude of the electric bias field and the sample resistance. Adding the fifth voltage lead, parallel to one of the other voltage leads, allows zeroing of the offset due to the sample’s resistance in the system by a potentiometer between the leads. The puck, pictured in Figure 2.2, was then installed in the PPMS and the Hall measurement was conducted.

### 2.3.2 Hall Analysis

The PPMS® took measurements from 2 to 300 K, and at each temperature the Hall voltage was measured from ±1 Tesla. From this, the carrier concentration and mobility were calculated, assuming a single band. The Hall coefficient can be found by plotting the resistivity versus the magnetic field at a constant temperature. The data should have a linear fit or a least a large portion of it should be linear as seen in Figure 33. The slope of the linear data line is the Hall coefficient. The Hall coefficient gives clearer information for single crystals but can be used to get an idea of the number of charge carriers in a polycrystalline sample. Rearranging Equation 2.24 into

\[
\frac{1}{n} = \frac{1}{e \cdot R_H} \quad (2.28)
\]

\( n \) was calculated.

Our mobility was found using Equation 2.27. Our conductivity was measured using our low temperatures resistivity and Seebeck coefficient measurement system. Our mobility can be written using Mattheissen’s rule

\[
\frac{1}{\mu} = \frac{1}{\mu_{ph}} + \frac{1}{\mu_i} + \frac{1}{\mu_{ss}} 
\quad (2.29)
\]
where the total mobility has contributions from what we expect to be the main contributions, phonon-phonon or lattice, impurities, and grain boundaries. Phonon-phonon scattering has a $T^{-3/2}$ dependence most evident as temperature increases to room temperature. Impurity scattering is seen at lower temperatures and has a $T^{3/2}$ dependence. These curves are plotted on the mobility data curves as they apply. We also expect to have contributions due to grain scattering. The behavior of the mobility due to grain boundaries can be written as

$$\mu = \frac{el}{\sqrt{8k_B\pi Tm^*}} e^{-\frac{E_B}{k_B T}}$$

(2.30)

where $e$ is the electron charge, $l$ is the grain size, $k_B$ is the Boltzmann constant, $m^*$ is the effective mass, $E_B$ is the energetic barrier, and $T$ is the temperature[82]. Equation 2.30 holds at low temperature where grain boundary scattering dominates. It must also be assumed that $l$, $E_B$, and $m^*$ are temperature independent. Equation 2.30 can then be rewritten as

$$\mu T^{1/2} \left[ \frac{\left(8k_B\pi m^*\right)^{1/2}}{el} \right] = e^{-\frac{E_B}{k_B T}}$$

(2.31)

and then take the natural log of both sides and rearrange it, it becomes

$$\ln(\mu \sqrt{T}) = -\frac{E_B}{k_B T} - \ln \left[ \left(\frac{8k_B\pi m^*}{el}\right)^{1/2} \right].$$

(2.32)

Then, $\ln(\mu \sqrt{T})$ vs. $1/T$ is plotted. A linear fit implies that there is grain boundary scattering at low temperatures. The slope of the line, $\frac{E_B}{k_B}$, will give the energetic barrier
at the boundaries, while the $y$-intercept, the last term will give an estimate of the grain size. To calculate the grain size the effective mass, $m^*$, must be found. This can be done using Fermi statistics with the assumption of acoustic phonon scattering in a single parabolic-band model. $\alpha$ and $n$ can be written as

$$\alpha = \pm \frac{k_B}{e} \left( \frac{2F_i(\eta)}{F_0(\eta)} - \eta \right)$$  \hspace{1cm} (2.33)$$

$$n = \frac{4}{\sqrt{\pi}} \left( \frac{2\pi m^* k_B T}{h^2} \right)^{\frac{3}{2}} F_i(\eta)$$  \hspace{1cm} (2.34)$$

$$F_i(\eta) = \int_0^\infty \frac{x^i \, dx}{1 + e^{(x-\eta)}}$$ \hspace{1cm} (2.35)$$

where $F_i$ are Fermi integrals, $E_F$ is the Fermi level measured from the conduction band, $h$ is Planck’s constant and $\eta = \frac{E_F}{k_B T}$. Using our measured values for $\alpha$ and $n$, $m^*$ was calculated using this model[83]. The grain size was then calculated using Equation 2.32.
Figure 2.1 – Picture and diagram of the low temperature resistivity and Seebeck coefficient system and mount.
Figure 2.2 – Schematic of the hall effect and a PPMS Hall effect mount.
CHAPTER THREE

BACKGROUND AND MEASUREMENT OF THERMAL TRANSPORT PROPERTIES

3.1 - Heat Capacity

Solids absorb energy through heat which causes its temperature to rise and the dimensions to increase in most cases.[78] A measure of a material’s ability to absorb heat is called heat capacity. This is the amount of energy it takes for a unit temperature increase. Heat capacity, $C_v$, is defined mathematically as

$$c_v = \left( \frac{\partial Q}{\partial T} \right)_v$$

(3.1)

Where $\partial Q$ is the change in energy required for the temperature change, $\partial T$. Heat capacity is given in units of $\text{Jmol}^{-1}\text{K}^{-1}$ whereas specific heat is given per unit mass. Heat capacity can be measured by keeping a constant sample volume, $C_v$, or constant external pressure, $C_p$. $C_p$ is greater than $C_v$ and their relationship is given by

$$\frac{C_p}{C_v} = \gamma.$$  

(3.2)

As thermal energy is added to a solid, the vibrational energy of the atoms in the material increases. Atoms in solids are constantly vibrating with high frequencies and small amplitudes and are coupled to each other through atomic bonding. Traveling lattice waves propagate through the crystal with low frequencies and long wavelengths at the velocity of sound. Only certain frequencies of these elastic series of waves are allowed. The quanta in energy are called phonons. The total number of phonon modes allowed in
a solid is \( 3N \), with \( N \) being the number of atoms and each atom having 3 degrees of freedom. In crystalline solids this becomes \( dpn \) where \( d \) is the dimensionality, \( p \) is the number of atoms per unit cell, and \( n \) is the number of unit cells. These waves are a method of thermal conduction, or in quantum terms, the phonons can carry energy.

At low temperatures, it can be shown that the number of phonons increase with the cube of the temperature, and thus \( C_v \) can be represented by

\[
C_v = AT^3
\]

where \( A \) is a constant. Vibrations of wavelength less than the lattice spacing are not possible, and hence there is a highest energy phonon. The temperature at which the thermal energy per degree of freedom, \( kT \), is equal to the energy of the shortest possible wavelength is called the Debye temperature, and all possible vibrations of the crystal can absorb energy. At the Debye temperature, \( \theta_D \), the heat capacity approaches its limit and becomes temperature independent. This Dulong-Petit limiting value of \( C_p \) is approximately \( 3R \), where \( R \) is the gas constant. The higher the Debye temperature of a material, the more rigid the lattice is. The main contribution to heat capacity comes from this vibrational energy.

3.1.1 - Low Temperature Heat Capacity Measurement

\( C_p \) was measured on the PPMS® using a heat capacity puck represented in Fig. 3.1.[84] Sample size for this measurement was 10 to 20 mg. To obtain the piece needed, part of the sample was mechanically cut off from the original sample. The small sample was then mounted onto the puck using N-grease ensuring good physical and thermal
contact between the sample platform and the sample. The sample platform was suspended from the rest of the puck by radial wires that provide a thermal link as seen in Fig. 3.1. The puck was then capped and inserted into the PPMS®. The $C_p$ was measured from approximately 2 to 300 K. A higher density of points was taken at the lower temperatures because this low temperature range is used to calculate the $\theta_D$. The PPMS® uses a comparison method to find the heat capacity. First the puck is run with the N grease but without the sample. The heat capacity for this system is taken and used as a baseline. The sample is then mounted onto the puck and the system is run again. The $C_p$ is measured using a relaxation technique. The Cernox heater on the sample platform increases the temperature and the thermometer measures the temperature of the sample as it cools. The PPMS® subtracts the baseline from the new $C_p$ and the $C_p$ for our sample is left.

3.1.2 - High Temperature Heat Capacity

For high temperature $C_p$ measurements a Netzsch Pegasus 404c Differential Scanning Calorimeter was used.[85] The temperature range for this system is from room temperature, approximately 25°C, to 1500°C. A small, several mg, piece of a sample, preferably with a flat side which makes good thermal contact with the sample holder is used. The sample was mounted into the platinum-alumina sample holder, the system was evacuated to $10^{-4}$ mbar and flushed with Ar twice, then set to an Ar flow rate of 50 mL/min. This flow with an inert gas was to help eliminate any reactions between the
samples, crucibles, or atmosphere at the higher temperatures. The sample temperature was measured using a Pt10%Rh-Pt (type S) thermocouple.

A typical programmed run would have a small, slow temperature rise at 5 K/min up to 40°C and an isothermal wait at this temperature for 10 min. This slow ramp and hold was done in order to have a better temperature equilibration between the sample and system. The sample is then allowed to increase in temperature at 10 K/min until the desired temperature was reached. The temperature was generally well under 1500°C as the skutterudite samples suffered decomposition before reaching such high temperatures. This ramping rate and procedure was chosen after several trials at different rates to have the best agreement with low temperature measurements and best reproducibility. Before each run the system was baked out at 1300°C to remove past residue, then a baseline was run using an empty crucible. Another run was made using a standard, in our case sapphire, and finally a run was made with the sample itself. These runs were made as close together as possible, preferably done all in one day, in an effort to minimize changes to ambient conditions which could affect the results. Then using a ratio method, the sapphire run is compared to the sample run, the heat capacity is calculated. It is expected that above $\theta_D$, the $C_p$ will plateau just under the Dulong-Petit limit.

Before running a sample for $C_p$, a piece of sample would be run on the DSC for stability measurement and for decomposition temperature.
3.2 - Thermal Conductivity

Thermal conductivity is the heat flow rate across a unit cross section perpendicular to the heat flow rate and absolute temperature.[CB,CC] Thermal energy can flow through a material by means of electrical carriers (electrons or holes), lattice waves (phonons), electromagnetic waves, spin waves, or other excitations. Most of the thermal transport in metals is done by electrons or holes while insulators use phonons as the dominant heat carrier. The total \( \kappa \) is a sum of all these components. \( \kappa \) can vary greatly from material to material and is dependent on single crystal versus polycrystalline, lattice defects or imperfections, dislocations, anharmonicity of the lattice forces, carrier concentrations, interaction between the carriers and the lattice waves, interactions between the magnetic ions and lattice waves, and so forth. Thus, being able to isolate the thermal transport in a material and then trying to tailor it to specific properties is very complicated and difficult. The total \( \kappa \) can usually be represented in our samples simply by the sum of the electronic and lattice contributions.

\[
\kappa_T = \kappa_L + \kappa_E
\]  

(3.4)

Useful \( \kappa \) relationships can be found using simple kinetic theory and focusing solely on the contributions from the electrons and phonons. Thermal conductivity, \( \kappa \), is the diffusion of thermal energy from one end of a material to the other end due to a temperature difference. For conduction in gases by kinetic theory, \( c \) is the heat capacity of each particle, and \( n \) is the concentration of particles. If there exists a temperature gradient of \( \Delta T \), for a particle to travel with velocity \( v \), its \( E \) must change at the rate of
\[ \frac{dE}{dt} = cv\Delta T. \quad (3.5) \]

By calculating the average distance this particle would travel, \( v\tau \) (\( \tau \) is relaxation time).

Summing over all the particles, the average total heat flow rate per unit area is

\[ Q = \frac{1}{3} nc v^2 \Delta T. \quad (3.6) \]

Combining these equations we have

\[ k = \frac{1}{3} nc v^2 = \frac{1}{3} Cv \]

where \( C = nc \) the total heat capacity and \( l = v\tau \) is the particle mean free path. If heat conduction were not limited by scattering mechanisms and were allowed to flow unobstructed, the \( l \) could be infinite and therefore \( \kappa \) would be infinite. This solution can be used in good approximation for various excitations and can be generalized by summing over all the different excitations.

All the portions of the lattice and electrical contributions of the thermal conductivity can follow Matthiessen’s rule of electrical resistance. This works only when there is one dominant scattering mechanism in the equation, otherwise the cross terms will complicate the data analysis. Therefore it works as a first order approximation. The thermal resistances are inversely related to the thermal conductivities.

\[ W = \kappa^{-1} \quad (3.8) \]

For the different thermal resistances, it can be written

\[ W_L = W_{\text{lat-lat}} + W_B + W_{\text{imp}} + W_{\text{dis}} + W_{\text{lat-el}} \quad (3.9) \]
where the contributions come from lattice-lattice interactions, boundaries, impurities, dislocations, and lattice-electron interaction respectively. This can also be found for the thermal resistances for the electrical portion as

$$W_E = W_{el-el} + W_{imp} + W_{el-lat}$$  \hspace{1cm} (3.10)

where the contributions come from electron-electron, electron-impurities, and electron-phonon interactions respectively.

In looking at the different scattering mechanisms, it is assumed that the scattering processes are not influenced by each other. This is not strictly true, but this treatment can give a good first order approximation of the behavior. The predominant scattering mechanisms for phonons reviewed will be phonon-phonon interactions, boundary scattering, point defect scattering, and scattering by dislocations.

$\kappa_L$ is dominant in nonmetals and can be a significant portion of the thermal conductance for semiconductors and alloys as well. The atoms of the material in a solid vibrate around their equilibrium position in the crystal lattice. They are coupled to their neighbors and thereby the crystal lattice vibrations can be characterized by the normal modes produced. The quanta of the crystal vibrations are called phonons. When a temperature gradient is present, the thermal energy propagates by wave packets consisting of various normal modes, or phonons. The phonons can be found to have either acoustic or optical modes if there is more than one atom per unit cell. The acoustic phonons are low frequency and correspond to the atoms in the unit cell moving in the same phase. The optical phonons are high frequency and occur when the atoms in the unit cell move in opposite phases. The acoustic phonons are the main heat carriers.
because the optical phonons have low group velocities, and therefore are not effective heat carriers. However, they may interact with the acoustic phonons and therefore retard the heat conduction. At low temperature, boundary scattering dominates, then at intermediate temperature point-defect, and at high temperature “Umklapp” scattering is dominant.

Interactions between phonons are one of the most significant contributions to the lattice thermal conductivity. If thermal vibrations were harmonic, the mean free path of the phonons could be infinite in a pure crystal. As temperature rises, the lattice vibrations grow more anharmonic which causes the mean free path to vary inversely with temperature at high temperatures. The scattering events caused are of two kinds, normal (N) processes and umklapp (U) processes. N-processes conserve momentum and energy and do not directly lead to any thermal resistance, but redistribute the momentum within the phonon system. By changing the momentum of the phonons, N-processes can significantly change the scattering effects of other process and therefore make a notable impact on the thermal conductivity. U-processes in which momentum is not conserved are responsible for the observed finite thermal conductivity. For a U-process to occur the frequency of at least one of the phonons has to be greater than half the maximum frequency of the lattice as predicted by Debye,

\[ h\nu_{\text{max}} = k_B\theta_D. \]  \hspace{1cm} (3.11)

Therefore one incident phonon must have at least half of \( \nu_{\text{max}} \) as shown

\[ \frac{1}{2}\nu_{\text{max}} = \frac{k_B\theta_D}{2h}. \]  \hspace{1cm} (3.12)
At low temperature \((T \leq \theta_D)\) U-processes are improbable and vary as

\[
\kappa_L \approx \exp\left(\frac{\theta_D}{T}\right)
\]

but as temperature increases \((T \geq \theta_D)\) there is an increasing probability of U-processes because the wave numbers are large and \(\kappa_L\) varies as

\[
\kappa_L \approx \frac{1}{T}.
\]

Phonons can also be scattered by point defect scattering which includes impurities, vacant lattice sites, interstitial atoms, and other crystal defects. These defects disrupt the periodicity of the lattice. At low temperature, the average distance between the impurities is smaller than the mean free path of the long wavelength phonons. When defects are dominant at higher temperatures the lattice thermal conductivity is given by

\[
\kappa_L \approx T^{-\frac{3}{2}}.
\]

Boundary scattering can also play a significant role in \(\kappa_L\). As temperature decreases the phonon mean free path increases therefore reducing scattering by point mechanisms because the wavelengths are much larger than the defects. At this point the mean free path is constrained only by crystal size or sample dimensions. At a certain point, even as the temperature decreases further, there is no longer an increase in mean free path due to size constraints. The temperature dependence of \(\kappa\) is due solely to the temperature dependence of \(C\) and varies as

\[
\kappa_L \approx T^3.
\]
The free electron theory of electron conduction in solids in the first instance considers each electron moving in a periodic potential produced by the ions and other electrons without disturbance, and then regards the deviation from the periodicity due to the vibrations of the lattice as a perturbation. If we take the general statement for the thermal conductivity

\[ \kappa = \frac{1}{3} Cv' l \]  

(3.17)

and impose the condition that the mean free path of the electrons and of the phonons are similar, the equation can be modified via some classical equations. The mean free path between collisions, \( l \), can be replaced by

\[ l = v \tau_{ph} \]  

(3.18)

where \( v \) is the velocity and \( \tau_{ph} \) is the phonon relaxation time. The heat capacity can be replaced by

\[ C_{el} = \frac{\pi^2 n k_B^2 T}{mv^2} \]  

(3.19)

Because the mean free path of the electrons and phonons are similar, \( \tau_e = \tau_{ph} \). If the heat capacity and mean free path are substituted into the original equations, it becomes

\[ \kappa_E = \frac{\pi^2 n k_B^2 T \tau}{3m} = \left[ \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 \left( \frac{ne^2 \tau}{m} \right) \right] T \]  

(3.20)

Knowing that the electrical conductivity is

\[ \sigma = \frac{ne^\tau}{m} \]  

(3.21)

the electrical contribution of the thermal conductivity becomes
\[ \kappa_E = L_0 \sigma T \]  

(3.22)

where \( L_0 \) is the Lorentz number and is given by

\[ L_0 = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2. \]  

(3.23)

This gives us the Wiedemann-Franz relationship which illustrates that the \( \kappa_E \) is related to the electrical conductivity of the material. This relationship holds as long as the mean free path of the phonons and electrons are almost the same. This relation is well obeyed at higher temperatures \( (T \geq \theta_D) \) but not in the intermediate temperature regimes where it does not account for the inelastic scattering of the charge carriers.

In summary the thermal conductivity is made up of a lattice and electrical contribution. The scattering processes are summed and can be assumed not to be influenced by each other for a good approximation. At lower temperature boundary scattering dominates and at higher temperature scattering by U-process dominate. In reality analyzing the thermal conductivity is not that simple. Beyond the scattering mechanisms that have been discussed, skutterudites also have atoms that can rattle within the structure and also influence the thermal conductivity which was discussed earlier and will be seen in the data.

3.2.1 - Low Temperature Thermal Conductivity Measurement

Samples were prepared by sanding of the surfaces and thorough cleaning with acetone or alcohol to remove any surface oxidation or grime. The sample width and thickness dimensions were taken using a digital Vernier caliper. The sample puck was
capable of holding 2 samples at a time as shown in Fig. 3.3. The pucks were modified from Quantum Design Physical Properties Measurement System (PPMS)® pucks and redesigned for the κ systems. The sample was soldered into the copper base plate and screwed onto the puck using a thin layer of Apiezon N grease between the base plate and mount to increase the thermal contact between them. The sample temperature was regulated to the system temperature at this contact point. Two insulated #38 copper wires were placed parallel to each other across each sample with Stycast® epoxy, electrically isolating them from the sample but maintaining a good thermal contact. Using an exacto knife, the top surface of stycast and insulation was carefully scraped off the wires. The junctions of a 1-mil differential chromega-constantan thermocouple, made in-house and used to measure the temperature gradient across the sample, were soldered onto these wires using InSn Ostalloy solder. The small size of the thermocouples was chosen to reduce heat loss by conduction. A 120 Ω Omega Strain Gage was attached on the top end of the sample with Devcon 5 minute (S-209) epoxy to heat one end of the sample and create a temperature gradient. In order to reduce heat loss from the strain gage, the majority of the copper wires coming off the strain gage were cut and replaced with phosphor bronze wires because of their much lower thermal conductivity. All wires were checked for shorts and the measurement of the distance between the copper wires was measured using the microscope graticule.

Thermal conductivity (TC) was measured on a custom designed cryocooler system from 10 K to 300 K using a steady-state technique.[88] The system is pumped down using a Leybold Turbotronik NT 151/361 turbo pump until a vacuum less than $10^{-5}$
torr is reached, measured with a Varian SenTorr BA2 vacuum gauge, reducing convection losses. The system was cooled down using a closed cycle helium cryocooler, APD Displex Close Cycle System model CSW-202N cryostat with a model HC2 helium compressor. The system was controlled by a Labview® program (IEEE 488.2 GPIB interface) which took measurements during the warming of the system at approximately 25 different temperature points and generally required 24 – 36 hours to run, depending on number of samples and how quickly those samples stabilized at a given temperature. Measurements were taken during warming because of the difficulty stabilizing the system while cooling. At each temperature point the system stabilized to within approximately 50 to 100 mK of the desired temperature for 180 s before taking a measurement.

The TC puck containing the two samples was plugged into the head of the cryocooler as seen in Fig. 3.3. A radiation cap, containing a thin gold coating to reflect radiation back onto the samples, and additional radiation shields were placed on top to minimize radiation losses. A Lakeshore 340 temperature controller stabilized the system temperature using measurements from silicon diode thermometers embedded at the base of the system. At the specified temperatures, after equilibrium was reached, current was inserted into the heater using a Kepco model ABC 125-1DM power supply. The minimal sample heater current began at 0.5 mA and increased for each new point by a factor of $2^{1/2}$. The $\Delta T$ on the thermocouples was measured using a Keithley 2001 Digital multimeter. With the known amount of input power from

$$P = I^2 R \quad (3.24)$$

where $R$ is the resistance of the strain gage and then the conductance $K$ was found using
\[ K = \frac{P}{\Delta T} \]  

(3.25)

with \( P \) as the power and \( \Delta T \) as the change in temperature in Kelvin. This process was performed for several currents to plot a power sweep versus \( \Delta T \) which gave a line whose slope was the total thermal conductance, \( K \), which was then converted into thermal conductivity by the system using sample dimensions as follows

\[ \kappa_T = K \frac{l}{A} \]  

(3.26)

where \( l \) is the length between the thermocouple junctions and \( A \) the cross-sectional area of the sample. In the simplest case, the total \( \kappa \) is composed of two separate components, lattice and electronic.

\[ \kappa_T = \kappa_L + \kappa_E \]  

(3.27)

In the analysis section \( \kappa_T \) will be divided into these two components and discussed. Radiation from the sample also had to be accounted for and will be discussed. Radiation can be minimized by using a sample with less surface area, a shorter, fatter sample. Since all the measurements are run on the same sample this perfect size for thermal conductivity, short and fat, is compromised with the perfect size for resistivity and Seebeck coefficient measurements, which is long and thin. Typical sample size is on average 8 mm by 2 mm by 2 mm, therefore there will be some radiation effects. The samples are measured for temperatures between 10 K and 300 K. CAML lab has three TC systems. The samples were always remounted onto different pucks between runs and run on different systems. This was to ensure that the data was consistent and to catch any
problems such as a bad sample puck or a short. The system utilized, mount used, voltage between the leads, and any other pertinent information was recorded.

Radiation effects show up on some of the data and are corrected for. This error occurs because of sample size. For the sake of consistency the same samples are used for both the R/S and TC measurements. In doing this, we sacrifice perfect dimensions for either measurement. A long, thin sample is more suited for R/S and a short, fat sample is more appropriate for TC. In compromising to be able to measure both on the same sample, are samples are approximately 8 by 2 by 2 mm$^3$. This compromise leads to radiation affecting the TC data. Any rise after 200 K reveals what might be radiation effects. The power radiated from the sample is expressed by

$$P_{RAD} = A\sigma_s\varepsilon(T^4 - T_s^4)$$  \hspace{1cm} (3.28)

$$T_s = T + \Delta T$$  \hspace{1cm} (3.29)

where $P$ is the power radiated, $A$ is the surface area, $\sigma_s$ is the Stefan-Boltzmann constant, $\varepsilon$ is the emissivity, $T_s$ is the sample temperature, and $T$ is the base temperature.

Expanding Equation \textbf{Error! Reference source not found.} (3.4) into a Taylor’s series, $P_{RAD}$ is found to be proportional to $T^3\Delta T$. The radiation loss is proportional to $T^3$ as a function of the sample temperature. Radiation losses produce a linear fit when $\Delta\kappa$ versus $T^3$ is plotted which illustrates that $P_{RAD}$ is proportional to $T^3$. If there is a linear fit, it can be safely assumed that it is due to radiation. An example of this is shown in Fig. . We are comfortable correcting the data for radiation losses less than approximately 20%. For larger losses a different geometry of sample should be measured. Measurements are
made on different samples with slightly different size geometries as a way of cross checking data. This analysis was done for the low temperature system.

3.2.2 - High Temperature Thermal Conductivity Measurement

High temperature thermal conductivity is measured using thermal diffusivity in the Nezstch 457 Microflash system as seen in Fig. 3.4.[89] Measurements can be made in this system from room temperature (25°C) up to 1100°C, but in the case of skutterudites it is not needed to go to these temperatures because they either start to decompose or the thermal conductivity reaches a point where it starts to increase again.

Samples of size approximately 7 mm by 7 mm and 1-3 mm thick were prepared for the laser flash method by thorough cleaning and then spraying a light coating of graphite using on top surfaces. Because graphite has a high thermal conductivity, this layer of graphite insures that the entire surface is heated evenly and simultaneously when flashed and then is evenly measured on the other side. The samples were placed in SiC sample holders and then placed in the system, which could measure up to three samples at a time. The system was pumped down, flushed with Ar, and this process was repeated, and then left to have a 75 mL/min flow rate of Ar. The inert atmosphere helped the samples not react to air molecules or anything else trapped in the chamber at higher temperatures.

The system would ramp up to temperature at 10 K/min and then would stabilize at the desired temperature. The system temperature was measured using a type S thermocouple. Once the temperature and baseline was stabilized the Nd-glass-laser was
flashed onto the bottom of the sample which heated up the bottom side of the sample. The Nd-glass-laser has a maximum pulse energy of 15 J and pulse length of 0.33 ms. The heat induced propagates through the sample and causes the temperature to increase on the top surface of the sample, measured using a liquid nitrogen cooled indium antimonide (InSb) infrared detector. The rise in temperature is measured and plotted versus time and then from the half time, the thermal diffusivity is calculated using the Cowan + pulse correction model. At each temperature the thermal diffusivity is measured 3 times and averaged.

Once the thermal diffusivity is measured, it is converted to thermal conductivity using the formula

\[ \kappa(T) = \rho(T)D(T)C_p(T) \]  

where \( \rho \) is the density as a function of temperature, \( D \) is the thermal diffusivity, and \( C_p \) is the specific heat. The density was calculated using the sample’s mass and dimensions and confirmed using a gas pycnometer and assumed to be constant throughout the temperature range. The specific heat was measured using the Nezstch Pegasus Differential Scanning Calorimeter 404C.

### 3.2.3 - Data Analysis

The system measured thermal conductance which was converted to thermal conductivity using previously assessed sample dimensions. The total thermal conductivity is then divided into its electronic and lattice components as shown in

\[ \kappa_T = \kappa_L + \kappa_E. \]  

(3.31)
Since the TC system takes its measurements while warming, the warming curve of the resistivity is also used. The resistivity is converted to conductivity defined by

$$\sigma = \rho^{-1}.$$  \hspace{1cm} (3.32)

The conductivity versus the warming temperature is plotted and curve fit, and extrapolated into the TC temperatures. Assuming the Wiedemann-Franz relation holds, the electronic contribution to the $\kappa$ is found by using

$$\kappa_E = L_0 \sigma T$$ \hspace{1cm} (3.33)

where $L_0$ is the Lorentz number, $\sigma$ is the electrical conductivity, and $T$ is the temperature.

A note regarding the thermal conductivity and the separation of lattice and electron components: $L_0$ was defined as $2.45 \times 10^{-8} \text{ W} \cdot \Omega^{-1} \text{ K}^{-2}$, when the mean free path of the phonons and electrons are almost the same. But what we are trying to do, in some sense, is to violate that relation. Namely, we want to keep the electrical conductivity high and reduce the thermal conductivity. The lattice contribution is then found by using

Error! Reference source not found.(3.1) and rewriting it

$$\kappa_L = \kappa_T - \kappa_E$$ \hspace{1cm} (3.34)

This $\kappa_L$ is what we’re trying to effectively minimize.
Figure 3.1 – Picture of a Quantum Design Heat Capacity puck for low temperatures.
Figure 3.2 – Picture of a Netzsch Pegasus DSC 404c system for high temperature heat capacity.
Figure 3.3 – Picture and schematic of the low temperature thermal conductivity sample mount and system.
Figure 3.4 – Netzsch 457 Microflash system used for high temperature thermal conductivity measurement.
4.1 - Structure

An unfilled binary skutterudite has the form MPn₃, where M is a transition metal and Pn is a pnictogen element. Skutterudites are materials that have the structure of that initial CoAs₃ mineral. They are body centered cubic and have spacegroup IM3. They have a simple cubic framework made of 27 metal atoms, usually Co, Rh, or Ir. This framework forms 8 cages. Inside of six of these cages square planar pnictogen rings, usually P, As, or Sb, can be found with the rings oriented along either the (100), (010), or (001) crystallographic direction as seen in Fig. 1.10 and Fig. 4.1. This leaves two of the voids empty in a skutterudite. This conventional unit cell is composed of a total of 32 (34) atoms and 144 valence electrons. An excess of this electron count produces n-type behavior. Another way, and some think better way, to look at this structure is a framework formed by MPn₆ octahedra with the other metal atom inside shown in Fig. 4.1. Voids would be surrounded by eight of these octahedra. In filled skutterudites, some of these voids are filled with ions that rattle inside the cages.

These materials can be grown using several different methods. These methods include electrochemical, solid state, gradient freeze, and solvothermal.
4.2 – Synthesis Techniques

4.2.1 - Binary Skutterudites

Bulk polycrystalline samples of Co$_{0.99}$Ni$_{0.01}$Sb$_3$ were prepared using the following solid state reaction. Stoichiometric amounts of cobalt (99.998% Alfa Aesar Puratronic powder), nickel (99.999% Alfa Aesar Puratronic powder) and antimony powder (99.999% Aldrich) were mixed together via ball milling with a molar Co:Sb ratio of 1:3, under ambient conditions. The mixture was sealed in an evacuated quartz tube, heated at 800 °C for 48h. The skutterudite was allowed to cool to room temperature, ball milled for another 20 min, then annealed for 48hrs at 700°C, and allowed to cool.

4.2.2 - Filled Skutterudites

The skutterudite samples were grown using Fe (Alfa Aesar 99.998%, 22 mesh), Co pieces (Alfa Aesar 99.94%), Sb shots (Alfa Aesar 99.999%), and a La rod (Alfa Aesar 99.9%). The stoichiometric amounts were placed in a carbonized tube under argon and then sealed under vacuum. The admixture was heated to 1050 °C in a Lindberg/BlueM BF51732C-1 Box Furnace for approximately 20 hrs, water quenched, and then subsequently annealed in the same quartz tube at 700°C for at least 30 hrs and allowed to cool.

4.2.3 - Hydrothermal Growth

In a typical solvothermal nano-plating process, precursors of CoCl$_2$ and SbCl$_3$ (Alfa Aesar) with a Co:Sb molar ratio of 1:3 were weighed and mixed with 10 ml
absolute ethanol, as shown in Fig. 4.3. This solution was then mixed with an appropriate amount of CoSb$_3$ bulk matrix material and stirred for 10 min. The mixture was transferred into a 45 ml Teflon-lined autoclave. It was then mixed with 30 ml ethylenediamine and an appropriate amount of NaBH$_4$ reductant. The autoclave was sealed and maintained at 240°C for 80 hr before it was allowed to cool to room temperature. Finally, the precipitates were filtered, washed with distilled water, ethanol and acetone, and dried via pumping under ambient conditions. The estimated yield of nanoparticles (in wt %) is based on more than 30 related growths under similar conditions.[91]

4.2.4 - Nanocompositing

After ball milling the powder was separated into equal portions for 2, 5, and 10 wt % hydrothermal CoSb$_3$ nanoparticle growth, while one portion was maintained without any hydrothermal treatment, as seen in Fig. 4.4. The nanoparticles were grown directly onto the surface of the bulk matrix grain in order to increase homogeneity. The resulting powders were then subjected to a hot-pressing process at 600°C under 0.2 GPa of pressure for 30 min in a Thermal Technology Hot Press.

4.3 - Sample Preparations

After hot pressing, a disk with a roughly 13 mm diameter by 2 mm thickness was produced. Thin graphite sheets on the surface, remaining from the hot press, are sanded off. Density measurements are then made on the disks. The samples densities were
measured by the Archimedes method and confirmed in a gas pycnometer. The results showed a 91-94% of theoretical density with a correlation between a slight decrease in density with the increasing nanoparticle concentration. Fig. 4.5 shows the disks are then cut into pieces using a South Bay Technologies Model 650 Diamond Wheel Saw. The samples were cut into approximately one 7 mm by 7 mm square, two 8 mm by 2 mm bars, and there were extra pieces as shown in Fig. 4.5. The wax was removed by soaking in acetone and thorough cleaning. The large square was for laser flash measurements while the bars were used for Hall, resistivity and Seebeck coefficient, and thermal conductivity measurements. The additional pieces were used for heat capacity and SEM.

Since our skutterudites samples are polycrystalline, direction of measurement was not important. Therefore although LFA and TC measurements were made in different directions the results are valid and comparable. The micro-morphology and phase purity of the powders was inspected by Hitachi S4800 field emission scanning electron microscope and X-ray powder diffraction on a Rigaku MiniFlex II benchtop system.

With the ability test both the high and low temperature regimes separately and with different methods, we are able to validate our measurements.
Figure 4.1 –Octohedral representation of a skutterudite structure.[92]
Figure 4.2 – Phase diagram of Co and Sb. [11]
Co (Bi, lead)-salts
Sb salts / Te powder
or Te-salts

+ reductant (NaBH₄)
and/or alkali

Teflon-lined Autoclave

Organic solvents
or water

Figure 4.3 – Diagram of the hydrothermal method for CoSb₃ growth and SEM pictures of the resultant nanoparticles.
Figure 4.4 –Diagram of nano-plating for CoSb$_3$ growth.
Figure 4.5 – Thermal Technology Hot Press and sample preparations for the resultant pellet.
CHAPTER FIVE
DATA ANALYSIS FOR THE THERMEOLECTRIC PROPERTIES OF SKUTTERUDITES

5.1 - Introduction to Data and Analysis

Our goal for this project was to study the effect of nanoparticles on the electrical and thermal properties of skutterudite materials. To reach this end in a clear fashion, skutterudites with a progression of techniques were studied successive in an attempt to isolate the effect of the nanoparticles at each step. At each step there were two objectives to accomplish with the nanoparticle incorporation: impede the thermal conduction and allow the electrical conduction. The target is to develop an interface that reaches these objectives.

A selection of different series of CoSb₃ skutterudite materials was made. The complete list can be found in Table 4.1. Each series progresses in complexity. This progression followed in order to clarify the understanding of how each process affects the material. Each series begins with a parent compound and then increasing amounts of nanoparticles are incorporated by weight %. Each series has 0, 2, 5, and 10 wt % of incorporated nanoparticles with exception to the first which also has 15 wt % as part of its series. The 15 wt % sample was not continued because hydrothermal growth above 10 wt % on the matrix powders became increasingly difficult and samples showed larger improvements at lower nanoparticle concentrations. As the series progressed, the nano-plating focused on the 5 wt % nano-plating as the most promising percentage was
repeatedly the 2% or 5%. The higher percentages were more detrimental to the properties, and so were not continued. All nanoparticles were of the composition CoSb₃.

The selections began with binary skutterudites. The progression can be seen in Fig. 4.1. The first series was CoSb₃ with nanoparticles mechanically mixed into the system. After this first series, mechanically mixing was discontinued in favor of nano-plating, where the nanoparticles are hydrothermally grown directly on the bulk powder. The second series was CoSb₃ with nano-plating. These two series provide comparisons between the two processes, mechanical mixing and nano-plating. The next binary series was nickel doped CoSb₃: Co₀.₉₉Ni₀.₀₁Sb₃. The doped series was made in order to minimize the composition difference between bulk and nanoparticles, thus preserving the electronic properties while impeding the thermal conduction. Doping is used to optimize the properties of skutterudites.

After doping, filled skutterudites were studied. Void filling of skutterudites is used to lower the thermal conductivity. When void filling, doping is also done to charge compensate for the filler ion. Several series of differently filled skutterudites were made in order to study the differences in the properties between the nano-plated unfilled and filled. Also, since filled skutterudites already exhibit lower thermal conductivities, this result could be enhanced by the nanoparticles. There were two series synthesized with Ce as the filler: Ce₀.₈Fe₃CoSb₁₂ and Ce₀.₂₅Fe₀.₇₅Co₃.₂₅Sb₁₂. The same filler was used so as to minimize changes between two series in order to understand the affects of the nanoparticles. Other filled skutterudites were also grown to see if the affects were different with varying fillers. The other filled skutterudites were La₀.₈Fe₃CoSb₁₂ and
Yb$_{0.2}$Fe$_{0.6}$Co$_{3.4}$Sb$_{12}$. The Fe doping on the Co site is the charge compensate for the charges introduced by the filler atoms.

The next progression is into double filled skutterudites, which has shown a further reduction as compared to single filling. Yb and Ce were chosen to as the two fillers. In the past 0.2 has proved to be the optimal filling fraction for Yb. Ce amounts were varied (0.1, 0.2, and 0.3) while the Yb fraction was kept fixed. These materials then had 5 wt % of the CoSb$_3$ nanoparticles incorporated into them.

Not all series had the electrical properties measured into high temperatures or had Hall data taken. These measurements were done as deemed necessary. Our lab is particular in that we have the ability test both the high and low temperature regimes separately in order to validate the measurements.
Table 5.1.1 – List of skutterudites studied.

<table>
<thead>
<tr>
<th></th>
<th>List of Series of Samples</th>
<th>Nanoparticle Incorporation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Binary Series</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CoSb$_3$ - Mechanically mixed</td>
<td>0, 2, 5, 10, 15 %</td>
</tr>
<tr>
<td></td>
<td>CoSb$_3$</td>
<td>0, 2, 5, 10 %</td>
</tr>
<tr>
<td></td>
<td>Co$<em>{99.9}$Ni$</em>{0.01}$Sb$_{12}$</td>
<td>0, 2, 5, 10 %</td>
</tr>
<tr>
<td><strong>Filled Series</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>La$_{0.8}$Fe$<em>3$CoSb$</em>{12}$</td>
<td>0, 2, 5, 10 %</td>
</tr>
<tr>
<td></td>
<td>Ce$<em>{0.25}$Fe$</em>{0.75}$Co$<em>{3.25}$Sb$</em>{12}$</td>
<td>0, 2, 5, 10 %</td>
</tr>
<tr>
<td></td>
<td>Ce$_{0.8}$Fe$<em>3$CoSb$</em>{12}$</td>
<td>0, 2, 5, 10 %</td>
</tr>
<tr>
<td></td>
<td>Yb$<em>{0.2}$Fe$</em>{0.6}$Co$<em>{3.4}$Sb$</em>{12}$</td>
<td>5%</td>
</tr>
<tr>
<td><strong>Double filled</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Yb$<em>{0.2}$Ce$</em>{0.1}$Fe$<em>{0.9}$Co$</em>{3.1}$Sb$_{12}$</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>Yb$<em>{0.2}$Ce$</em>{0.2}$Fe$<em>{1.2}$Co$</em>{2.8}$Sb$_{12}$</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>Yb$<em>{0.2}$Ce$</em>{0.3}$Fe$<em>{1.5}$Co$</em>{2.5}$Sb$_{12}$</td>
<td>5%</td>
</tr>
</tbody>
</table>
Table 5.1.2 – List of sample densities.

<table>
<thead>
<tr>
<th>List of Series of Samples</th>
<th>Nanoparticle Incorporation</th>
<th>Theoretical Densities</th>
<th>% of TD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Binary Series</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoSb$_3$</td>
<td>0, 2, 5, 10, 15 %</td>
<td>7.502 g/cm$^3$</td>
<td>97, 95, 94, 94, 91</td>
</tr>
<tr>
<td>CoSb$_3$</td>
<td>0, 2, 5, 10 %</td>
<td>7.502 g/cm$^3$</td>
<td>94, 94, 93, 96</td>
</tr>
<tr>
<td>Co$<em>{0.99}$Ni$</em>{0.01}$Sb$_3$</td>
<td>0, 2, 5, 10 %</td>
<td>7.502 g/cm$^3$</td>
<td>95, 93, 94, 92</td>
</tr>
<tr>
<td><strong>Filled Series</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$_{0.8}$Fe$<em>3$CoSb$</em>{1.2}$</td>
<td>0, 2, 5, 10 %</td>
<td>7.95 g/cm$^3$</td>
<td>95, 94, 92, 84</td>
</tr>
<tr>
<td>Ce$<em>{0.25}$Fe$</em>{0.75}$Co$<em>{3.25}$Sb$</em>{1.2}$</td>
<td>0, 2, 5, 10 %</td>
<td>7.65 g/cm$^3$</td>
<td>95, 94, 96, 94</td>
</tr>
<tr>
<td>Ce$_{0.8}$Fe$<em>3$CoSb$</em>{1.2}$</td>
<td>0, 2, 5, 10 %</td>
<td>7.96 g/cm$^3$</td>
<td>94, 92, 91, 80</td>
</tr>
<tr>
<td>Yb$<em>{1.2}$Fe$</em>{0.6}$Co$<em>{3.4}$Sb$</em>{1.2}$</td>
<td>0, 5%</td>
<td>7.65 g/cm$^3$</td>
<td>91, 93</td>
</tr>
<tr>
<td><strong>Double filled</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb$<em>{1.2}$Ce$</em>{0.1}$Fe$<em>{0.9}$Co$</em>{3.1}$Sb$_{1.2}$</td>
<td>0, 5%</td>
<td>7.65 g/cm$^3$</td>
<td>95, 96</td>
</tr>
<tr>
<td>Yb$<em>{0.2}$Ce$</em>{0.2}$Fe$<em>{1.8}$Co$</em>{2.8}$Sb$_{1.2}$</td>
<td>0, 5%</td>
<td>7.65 g/cm$^3$</td>
<td>98, 96</td>
</tr>
<tr>
<td>Yb$<em>{0.2}$Ce$</em>{0.3}$Fe$<em>{1.5}$Co$</em>{3.5}$Sb$_{1.2}$</td>
<td>0, 5%</td>
<td>7.65 g/cm$^3$</td>
<td>96, 94</td>
</tr>
</tbody>
</table>
Figure 5.1 – Flow chart for the progression of skutterudites studied

1. **CoSb$_3$**
2. **Doping (Ni)**
3. **Filled (La, Ce, Yb)**
4. **Double filled (Ce, Yb)**

- **Nano-particles – Mechanically mixed**
- **Nano-plating – 2%, 5%, 10%**
5.2 – CoSb$_3$ mech mixing

This first series of samples was composed of binary CoSb$_3$[93]. It was grown using high purity powders. After the powder was grown it was divided into five samples to be mixed in with 0%, 2%, 5%, 10% and 15% of nanoparticles respectively. The nanoparticles were hydrothermally grown separate from the bulk and mixed into the bulk matrix powder using a Mixer for approximately 15 min. The samples were then hot pressed and prepared as stated in Chapter 4.

X-ray diffraction shows these samples to be primarily single-phase (CoSb$_3$, PDF #03-065-3144). SEM pictures, Fig. 5.2.1, show aggregation of the nanoparticles into clusters at the grain boundaries. Nanoparticles should not be visible when mixed into the sample but the clumping was so severe that the groups could be seen with the naked eye on the samples. By themselves nanoparticles have a tendency to cluster, and the mixing was not enough to break them apart for even dispersion throughout the bulk material.

Looking first at their electrical properties, promising results are seen. The $\alpha$ shows improvement. Because of the inhomogeneity due to the nanoparticle clustering, the increase is not systematic while the shape of the curve stays fairly consistent with the original. Although there was inhomogeneity, the sample data was very reproducible using different samples. The $\rho$ is not as favorable, though definitely remains fairly stable. The $\rho$ of the samples increased though not in a systematic way possibly due to the inhomogeneities of the samples. The variation of the $\rho$ values is also not as consistent as the $\alpha$, though not enough to change the order of the samples, and the curves remained identical. Unfortunately, because the increase in the $\rho$ was much greater than their
increase in $\alpha$ for most of the samples, the $PF$ showed an overall decrease for the samples as shown in Fig. 5.2.2. The $PF$ decreased mostly systematically with the worst clearly being the 15% nanoparticle sample, with exception to the 5% nanoparticle sample. This sample showed a 15% improvement from 137 to 157 $\mu$VK$^{-1}$ at room temperature over the control sample. The $\rho$’s were almost identical but the 5% sample still showed a 10% increase over the control from 2.45 to 2.7 m$\Omega$-cm. This led to a 25% improvement in the $PF$ from 0.22 to 0.275 Wm$^{-1}$K$^{-1}$.

The $\kappa$ showed a very systematic decrease of the $\kappa_L$ with increase of nanoparticle concentration as seen in Fig. 5.2.3. Overall the $ZT$ for all the samples were the same, with exception to the 5% nanoparticle sample. The improvement of the $PF$, plus the reduction in the $\kappa_L$, gave this sample a 57% improvement in the $ZT$ at room temperature, seen in Fig. 5.2.3.

This improvement shows proof of concept. The nanoparticle inclusions scatter the phonons as expected, systematically with increase in nanoparticle concentration, yet can also possibly leave the electrical properties intact. These inclusions also unfortunately scattered most of our carriers for this series, but due to the inhomogeneity the results were not systematic although there was an overall trend to higher $\rho$ with the increase of nanoparticle inclusions.
Figure 5.2.1 - SEM pictures show the aggregation of the mechanically mixed nanoparticles at grain boundaries. a) CoSb$_3$ b) 2\% NP c) 5\% NP d) 10\% NP e) 15\% NP.
Figure 5.2.2 – Electrical properties of CoSb$_3$ with mechanically mixed nanoparticles.
Figure 5.2.3 – Thermal conductivity and ZT of CoSb$_3$ with mechanically mixed nanoparticles.
5.3 - CoSb$_3$ hydrothermal

This second series is another binary CoSb$_3$ sample, in which nano-plating is introduced. It was grown using high purity cobalt powder and antimony shots that were ball milled into a powder. Unlike the first series, the nanoparticles were hydrothermally grown directly on the bulk powder in order to increase homogeneity. This series was grown for comparison to the first series and future comparison to the other nano-plated series.

The x-ray diffraction pattern for this series shows a single phase CoSb$_3$ (CoSb$_3$, PDF #03-065-3144) seen in Fig. 5.3.1. The SEM pictures for this series, Fig. 5.3.2, present valuable information. First, our bulk powders are not of consistent size but have a wide range in size. Also our nanoparticles can be found on the grain boundaries encircling the individual particles. Although there is some aggregation the dispersion is more homogeneous than in the previous series. Finally the pictures show a difference in structure between the 0, 2, and 5% and the 10% nanoparticle sample. The nanoparticles have a lower melting point than the bulk and it seems that immersing 10% into the matrix has lowered the melting point of our sample enough to produce at least partial melting. This melting shows aberrant behavior in the data for this sample, which is shown but not discussed.

The $\alpha$ for this series is negative suggesting that electrons are the majority carriers. The series $|\alpha|$ is largely reduced in an unsystematic way from $-500$ $\mu$V/K as low as $-100$ $\mu$V/K at room temperature. The samples that underwent the hydrothermal treatment all show a lower $\alpha$ and have a similar temperature dependence which is different from the
0% sample, as seen in Fig. 5.3.3. The $\rho$ of the control sample with 0% of nanoparticles exhibits very different temperature behavior than those with hydrothermal treatment, decreases with an increase in temperature. Any addition of nanoparticles has a positive effect by greatly reducing the $\rho$ of the sample and giving rise to a nearly temperature independent resistivity. The $\rho$ shows no correlation to the density. The behavior of the 10% sample differs noticeably from the other nanoparticle compositions, but this seems to be due to the melting observed by the SEM pictures. Unfortunately for even the best samples the resistivity of 30 m$\Omega$-cm is too high to be used for thermoelectrics. Overall the $PF$ of our samples was not improved and in most cases detrimentally decreased, shown in Fig. 5.3.3. Only the 5% nanoparticle composition was on par with the control sample.

The low temperature and high temperature $\kappa$ data show consistent and systematic results. It should be noted that $\kappa_L$ makes up nearly 100% of the total $\kappa$, so the measured $\kappa_L \approx \kappa$. Fig 5.3.4 shows that as the nanoparticle concentration increases, the $\kappa_L$ is systematically reduced with the exception of the 10% sample. The unique behavior of the 10% sample can most easily be explained by the structural difference observed in the SEM pictures. The peak at low temperatures is suppressed with the addition of the nanoparticles. At elevated temperatures, the $\kappa_L$ curves reach a similar value of 7 Wm$^{-1}$K$^{-1}$. This is unfortunate, because with no improvement in the $\kappa$ at higher temperatures, then there is no improvement in $ZT$ in the temperature range in which these materials are utilized. Fig. 5.3.4 shows that at room temperature there was a slight increase in $ZT$ for the 5% sample, but a large reduction for all other samples as compared to the control.
Figure 5.3.1 – X-ray diffraction pattern of nano-plated CoSb$_3$ series.
Figure 5.3.2– SEM pictures of the structure differences with increase of nanoparticle concentration for nano-plated $\text{Ce}_{0.8}\text{Fe}_3\text{CoSb}_{12}$ a) shows the parent sample b) 2%, c) 5%, and d) 10%.
Figure 5.3.3 — Electrical properties of nano-plated CoSb$_3$. 
Figure 5.3.4 – Thermal conductivity and $ZT$ of nano-plated CoSb$_3$. 
5.4 – Ni doped

Nicked doping of the parent compound was studied because favorable results have been shown in both the electrical properties and in thermal conduction with small amounts of doping.[26,27] The single-phased nature (CoSb$_3$, PDF #03-065-3144) for all samples was confirmed, seen in Fig. 5.4.1. Some slight broadening of the X-ray peaks was observed after the nano-plating process and hence attributed to the size effect in view of the Scherer equation. The SEM pictures in Fig. 5.4.2 for this series show similar information to the previous series. First, our bulk matrix powders have wide size distribution that ranges from micrometer to nanometer in size. Second, the nanoparticles are found on the grain boundaries encircling the individual bulk matrix grain showing a fairly uniform distribution of the nanoparticles throughout the samples. Finally, there is some sign of melting in the samples with 10% nanoparticles and explains why the 10% sample shows behavior that is quite distinct from the other samples.

Fig. 5.4.3 shows the temperature dependence of the effective carrier concentration and carrier mobility. The effective carrier concentration shows fairly strong temperature dependence for all samples: first decreasing with decreasing temperature and then forming a broad minimum between 50 K and 150 K before making a fast upturn until 2 K. The effective carrier concentration is on the order of $10^{19}$ cm$^{-3}$ for all 4 samples and systematically decreases with increasing nanoparticle concentration. As shown in Fig. 5.4.3, the carrier mobility for the 2% sample shows a limited increase while the 5% and the control samples’ mobility curves are on top of each other. The temperature dependence of the carrier mobility for our samples is similar to that reported by Dycke et.
al. for the 1% Ni-doped sample [26,27]. The mobility curves show a turn over at approximately 175 K, below which the shape shows impurity scattering, $T^{3/2}$, most likely due to the Ni doping and the positive slope also suggests a grain boundary scattering mechanism. The turn over decreases with increasing nanoparticle concentration. Near room temperature the samples show a $T^{-3/2}$ dependence, which is indicative of acoustic phonon scattering. Table 5.4.1 shows the values for $m^*$ found from using the single parabolic-band model and the calculated grain size. For this series $m^*$ is roughly 2.5 $m_e$.

Fig. 5.4.4 shows an Arrhenius plot, where $\ln(\mu T^{1/2})$ is plotted versus $T^{-1}$. The 2% sample was not fitted because data at the lowest temperatures were disregarded. All other samples show a linear fit consistent with grain boundary scattering at low temperatures. The slopes of the linear fits can give information about the energetic barrier at the boundaries. For this series of samples, all the values remain fairly consistent for all concentrations of nanoparticles implying that the energetic barrier for these samples doesn’t change with an increase of nanoparticles. On the other hand, the grain size, seen in Table 5.4.1, that is dominating the scattering decreases as the nanoparticle concentration increases. This behavior makes sense because we are increasing the amount of smallest particles in the samples.

The incorporation of nanoparticles had profound effects on the electrical properties. As shown in Fig. 5.4.5, $\alpha$ exhibits n-type behavior suggesting electrons as the dominant charge carriers in this series. $\alpha$ continues to increase up to its maximum of -390 $\mu$VK$^{-1}$ at 450 K for the 0% nanoparticles sample where it begins to decrease. The $\alpha$ value decreases systematically as the percent of nanoparticles increases. There is an over
10% drop in the value of $\alpha$ from the maximum of -380 $\mu$VK$^{-1}$ in the control to the 5% sample at 450 K. As shown in Fig. 5.4.5, the $\rho$ was not a strong function of the nanoparticle concentration. Although the $\rho$ initially has high values, they quickly drop to below 10 m$\Omega$-cm and continue decreasing during the full temperature range. Because of the decrease in Seebeck coefficient the $PF$ shows a decrease of 20% from the control sample to the 5% sample at its peak value. Although there is an exact match on the slope, there is a small offset in the magnitude of the $\rho$ and $\alpha$ due to size constraints on the samples and the high temperature system which was corrected for. The $PF$ peaks at around 550 K to a value of 1.25 Wm$^{-1}$K$^{-1}$ as shown in Fig. 5.4.5.

The $\kappa_L$ from 10 to 650 K is shown in Fig. 5.4.6. It should be noted that $\kappa_L$ makes up nearly 100% of the total $\kappa$, so the measured $\kappa \approx \kappa_L$. The $\kappa$ showed the favorable change that we expected, however, this was only observed in the low temperature range. Unfortunately, the reduction is limited to the temperature regime below room temperature, while the $\kappa$’s of all samples converge to the same value at higher temperatures. The aberrant behavior of the 10% nanoparticle sample could be due to the structural difference caused by the partial melting during hot pressing. The low temperature $\kappa_L$ is more sensitive to the grain boundary scattering of phonons, as is expected, the thermal conductivity decreasing systematically with increasing nanoparticle concentration. Since the $\kappa_L$ was not lowered at these higher temperatures, it could not compensate for the deterioration of the power factor. As can be seen in Fig. 5.4.6, at the higher temperatures in which skutterudites are used the $ZT$ is not improved.
Figure 5.4.1 – X-ray diffraction pattern of nano-plated Co$_{0.99}$Ni$_{0.01}$Sb$_3$ series.
Figure 5.4.2 – SEM pictures of the structure differences with increase of nanoparticle concentration for nano-plated $\text{Co}_{0.99}\text{Ni}_{0.01}\text{Sb}_3$ a) and b) show the control sample c) 2%, d) 5%, and e) 10%.
Figure 5.4.3 – Carrier concentration and mobility of nano-plated \( \text{Co}_{0.99}\text{Ni}_{0.01}\text{Sb}_3 \) series.
Table 5.4.1 – Modeling values for the Co$_{0.99}$Ni$_{0.01}$Sb$_3$ series.

<table>
<thead>
<tr>
<th>sample</th>
<th>$n$ (m$^{-3}$)</th>
<th>$\alpha$ (VK$^{-1}$)</th>
<th>$m^*$</th>
<th>$l$- grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$<em>{0.99}$Ni$</em>{0.01}$Sb$_{1.2}$</td>
<td>1.96E+25</td>
<td>-3.23E-04</td>
<td>2.67</td>
<td>13.1</td>
</tr>
<tr>
<td>2% nanoparticles</td>
<td>1.81E+25</td>
<td>-3.42E-04</td>
<td>2.95</td>
<td></td>
</tr>
<tr>
<td>5% nanoparticles</td>
<td>1.79E+25</td>
<td>-3.06E-04</td>
<td>2.27</td>
<td>12.0</td>
</tr>
<tr>
<td>10% nanoparticles</td>
<td>1.70E+25</td>
<td>-3.03E-04</td>
<td>2.07</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Figure 5.4.4 – Arrhenius plot for nano-plated Co$_{0.99}$Ni$_{0.01}$Sb$_3$ series.
Figure 5.4.5 — Electrical properties of nano-plated Co$_{0.99}$Ni$_{0.01}$Sb$_3$ series.
Figure 5.4.6 – Thermal conductivity and ZT of nano-plated $\text{Co}_{0.99}\text{Ni}_{0.01}\text{Sb}_3$ series.
5.5 – La filled

This nanoplating technique was also applied to a variety of filled skutterudites. The first series discussed is \( \text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12} \), chosen because La contains no 4f electrons thus isolating the role of the rattler.[13,94]

In Fig. 5.5.1, the XRD pattern confirmed the samples were a single phase skutterudite (\( \text{CoSb}_3 \), PDF #03-065-3144) with exception to the 10% sample which showed small amounts of additional phases from Sb and \( \text{LaSb}_2 \). The presence of La in the structure of the skutterudite was confirmed by EDX. The density showed a systematic decrease with increase of wt % of the nanoparticles. The SEM pictures in Fig. 5.5.2 show that ball milling produced samples that exhibit a wide and varied ranged of particle size ranging from grains in the several hundred microns to nm. The microstructure shows that the samples consist of larger \( \text{La}_{0.9}\text{CoFe}_3\text{Sb}_{12} \) skutterudite bulk grains encapsulated by the small grains of the same bulk matrix and the \( \text{CoSb}_3 \) nanoparticles. The SEM pictures also reveal the influence of hydrothermal treatment on the microstructure. Figure a shows the \( \text{CoSb}_3 \) nanoparticles while b,c show different magnifications of the bulk sample that underwent no hydrothermal treatment. Fig. 5.5.2 d, e, and f show the 2, 5, and 10 wt % samples respectively. The nanoparticles have been found to be approximately 30 nm in size while the nanoparticle layer can be several hundred nm thick. Although there is a wide variety of particle size in the control sample, they all exhibit the same very sharp and fractured shaped grains but the samples that underwent hydrothermal treatment have smoother and more rounded appearance to their grains. The 10% sample appears to have undergone even further processing, as it is
evident in this sample that the hot pressing induced some amount of melting of the nanoparticles or nanocomposite as a whole. This difference in microstructure for the 10% sample causes transport properties that do not fall in line with the other samples of the series as revealed in the data. The data for this sample is shown but not discussed.

The carrier concentration and mobility are shown in Fig. 5.5.3. The temperature dependence of the carrier concentration is quite similar for all the samples: increasing with increasing temperature except for a local minimum at approximately 15 K. The carrier concentration values are on the order of $10^{20}$ cm$^{-3}$. The value of the control and 2% sample are almost identical at $1.9 \times 10^{20}$ cm$^{-3}$ at room temperature while the 5% sample is about 25% greater. The mobility decreases with increasing temperature, the slope of which is less pronounced as the percentage of nanoparticles increases. The overall value is also decreased with the increase of nanoparticles by about 80% at the lowest temperature and 50% at 300 K from the value of the control to the 5% nanocoated sample. The nanoparticle samples show a $T^{-3/2}$ dependence that dominates their mobility, which is indicative of acoustic phonon scattering. The turn over to positive slope at lowest temperatures also suggests a grain boundary scattering mechanism. Table 5.5.1 shows the values for $m^*$ found from using the single parabolic-band model and the calculated grain size. For this series $m^*$ is roughly 1.3 $m_e$. Fig. 5.5.4 shows an Arrhenius plot, where $\ln(\mu T^{1/2})$ is plotted versus $T^{-1}$. All samples show a linear fit consistent with grain boundary scattering at low temperatures. The slopes of the linear fits can give information about the energetic barrier at the boundaries. For this series of samples, the value for the slope increases with increase in concentration of nanoparticles,
implying that the energetic barrier for these samples increases with an increase of nanoparticles. This trend makes sense considering that as we add nanoparticles we add more compositional mismatch to the boundaries. The grain size, seen in Table 5.5.1, that is dominating the scattering decreases as the nanoparticle concentration also increases for this series. This behavior makes sense because we are increasing the amount of smallest particles in the samples.

The $\alpha$ shows a small, but definite, systematic increase with the increase of the weight % of nanoparticles, as seen in Fig. 5.5.5. The positive $\alpha$ implies that holes are the primary charge carriers, which is also consistent with the sign of the Hall coefficient (not shown). The temperature dependence of $\alpha$ is consistent in all samples, increasing until the maximum at approximately 700 K where it begins to turn over presumably due to the contribution from the minority carriers. Final $\alpha$ values show an over 20% increase from 140 $\mu$VK$^{-1}$ for the control to 170 $\mu$VK$^{-1}$ for the 5% sample. The $\rho$ also systematically increases with the increase of the wt % of nanoparticles and increases with increasing temperature up to 650 K as shown in Fig. 5.5.5. This could be due to the systematic decrease in density and/or the systematic mobility decrease with increasing percent of nanoparticles. The $\rho$ values of the 0, 2, and 5% samples at highest temperatures have been measured to be between 1.2 and 1.5 mΩ–cm but show no sign of saturation. As a result, the $PF$ increases with increasing temperature but the overall effect of the addition of the nanoparticles is decrease in value. Although the $PF$ decreases systematically with the increase of nanoparticles, it is by a margin of less than 10%. The $PF$ reached its maximum between 700 and 750 K because of the maximum of $\alpha$ at that temperature.
Recall that the main focus of this investigation is to study the effect of introducing a nanoparticle layer in order to lower the lattice $\kappa_L$. The $\kappa$ was measured for these samples from 10 to 825 K using the two different methods as described earlier and the data are shown in Fig. 5.5.6. The $\kappa_L$ was calculated from the total $\kappa$ using the Wiedemann-Franz Relationship, $\kappa_e = L_o \rho / T$, and accounts for greater than 75% of the total thermal conductivity for all the samples studied. $\kappa_L$ shows a systematic decrease with an increase in the wt % of nanoparticles through the entire temperature range. This result is encouraging given that in previous binary skutterudites studied, the decrease occurred only at the lower temperature range. [ ] The low temperature peak has flattened out and broadened and is shifting to higher temperatures with increasing nanoparticles. $\kappa_L$ is reduced by approximately one-third from the control sample to the 5% sample throughout most of the temperature range. Using the measured Debye temperature from low temperature heat capacity and this lattice thermal conductivity data, the mean free path was estimated via $l = \frac{3\kappa_L \hbar}{2C_p k_B a_0 \theta_D}$. The mean free path was calculated to be 11Å, 10Å, and 9Å for the control, 2%, and 5% samples respectively.

Finally, the $ZT$ values are discussed and shown in Fig. 5.5.6. At 725 K the $ZT$ exhibits its maximum, and the 5 wt % nanocomposite shows the highest $ZT$ with an improvement of almost 15% over that of the control sample that contains no nanoparticles. Our best sample reached a $ZT$ of 0.47 at 725 K. These results are exciting because in this case it shows that nanoparticles can be used in conjunction with already optimized skutterudite systems in order to further reduce the thermal conductivity and
therefore improve $ZT$ in the temperature range that we investigated. The results for the thermoelectric properties for this La$_{0.9}$CoFe$_3$Sb$_{12}$ series with incorporated nanoparticles were quite promising.
Figure 5.5.1 – X-ray diffraction pattern of nano-plated \( \text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12} \) series.
Figure 5.5.2 –SEM pictures of the structure differences with increase of nanoparticle concentration for nano-plated La$_{0.9}$Fe$_3$CoSb$_{12}$ series. a) shows CoSb3 nanoparticles. b), c) show different magnifications of the control sample. d), e), f) show the 2, 5, and 10% samples respectively.
Figure 5.5.3 – Carrier concentration and mobility of nano-plated $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ series.
Table 5.5.1 – Modeling values for the La$_{0.9}$Fe$_3$CoSb$_{12}$ series.

<table>
<thead>
<tr>
<th>sample</th>
<th>$n$ ($m^{-3}$)</th>
<th>$\alpha$ (VK$^{-1}$)</th>
<th>$m^*$</th>
<th>$l$ - grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{0.9}$Fe$<em>3$CoSb$</em>{12}$</td>
<td>1.87E+26</td>
<td>8.50E-05</td>
<td>1.38</td>
<td>32.2</td>
</tr>
<tr>
<td>2% nanoparticles</td>
<td>1.84E+26</td>
<td>9.40E-05</td>
<td>1.53</td>
<td>13.0</td>
</tr>
<tr>
<td>5% nanoparticles</td>
<td>2.35E+26</td>
<td>9.70E-05</td>
<td>1.21</td>
<td>8.5</td>
</tr>
<tr>
<td>10% nanoparticles</td>
<td>1.34E+26</td>
<td>1.12E-04</td>
<td>1.52</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Figure 5.5.4 – Arrhenius plot for nano-plated La$_{0.9}$Fe$_3$CoSb$_{12}$ series.
Figure 5.5.5 — Electrical properties of nano-plated La$_{0.9}$Fe$_3$CoSb$_{12}$ series.
Figure 5.5.6 – Thermal conductivity and ZT of nano-plated La$_{0.9}$Fe$_3$CoSb$_{12}$ series.
5.6 – Ce Filled small amount

The second filled skutterudite series has a small amount of Ce filling. Ce was chosen as a filler because Ce filled skutterudites are one of the currently used thermoelectric materials[44]. Also Ce skutterudites can be grown to be p or n type. The intention was to have one series with holes as carriers and one with electrons. The nominal composition for this series is Ce$_{0.25}$Fe$_{0.75}$Co$_{3.25}$Sb$_{12}$ and should be n-type. During the first part of the growth the heater in the box furnace died about an hour right before the quenching. The growth materials were at 650-700 °C instead of 1050°C when they were quenched. Once again the powder was divided up for hydrothermal growth of 0, 2, 5, and 10 wt % of nanoparticles.

The XRD pattern confirmed the samples were a single phase skutterudite (CoSb$_3$, PDF #03-065-3144) which was surprising considering the complications during the growth. The skutterudite is single phase with no secondary phases visible as seen in Fig. 5.6.1. The presence of Ce in the structure of the skutterudite was confirmed by EDX. The densities of the samples are pretty consistent but with the 10% showing the lowest density and the 5% sample showing the highest.

The carrier concentrations and mobilities are shown in Fig. 5.6.2. The carrier concentrations for the 0% and 2% sample increase from $6 \times 10^{19}$ cm$^{-3}$ at low temperature to $1.4 \times 10^{20}$ cm$^{-3}$ at room temperature. The value for the 5% and 10% sample are slightly lower increasing from $4 \times 10^{19}$ cm$^{-3}$ to $6 \times 10^{19}$ cm$^{-3}$. The carrier mobility shows a nice systematic increase in mobility of 25% at the lowest temperature and 100% at room temperature with increase in nanoparticle concentration from 0% to 5%. The
mobility is temperature dependent and decreases as temperature increases to a room temperature value of roughly $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Near room temperature the nanoparticle samples show a $T^{-3/2}$ dependence, which is indicative of acoustic phonon scattering. Table 5.6.1 shows the values for $m^*$ found from using the single parabolic-band model and the calculated grain size. For this series $m^*$ is roughly $0.8\ m_e$. Fig. 5.6.3 shows an Arrhenius plot, where $\ln(\mu T^{1/2})$ is plotted versus $T^{-1}$. All samples show a linear fit consistent with grain boundary scattering at low temperatures. The slopes of the linear fits can give information about the energetic barrier at the boundaries. For this series of samples, the value for the slope increases with increase in concentration of nanoparticles, implying that the energetic barrier for these samples increases with an increase of nanoparticles. This trend makes sense considering that as we add nanoparticles we add more compositional mismatch to the boundaries. Contrary to previous results, the grain size, seen in Table 5.6.1, that is dominating the scattering increases as the nanoparticle concentration also increases for this series. This behavior is not as we expected but perhaps makes sense with the other behaviors we see for this series, and increase in electrical and thermal conduction.

The $\alpha$ of our samples shows p-type behavior suggesting holes as carriers. The values are slightly lower for the samples with the incorporated nanoparticles but remain roughly the same with a room temperature value of $65\ \mu\text{VK}^{-1}$. The $\rho$ for our samples improved for all but the 10% sample. Their $\rho$'s all show a similar temperature dependence, weakly increasing with increase in temperature. Their room temperature values decreased from $1.7\ \text{m}\Omega\cdot\text{cm}$ for the 0% sample to $1.2\ \text{m}\Omega\cdot\text{cm}$ for the 5% sample.
As seen in Fig. 5.6.4, this almost 30% improvement in the resistivity generated a 15% improvement in the PF for the 2% and 5% incorporated nanoparticle samples at 300 K.

The $\kappa$ shows behavior unlike the previous skutterudite series. The $\kappa_L$ is greater than 85% of $\kappa$ for these samples. The $\kappa_L$ systematically increases with an increase in nanoparticle concentration at low temperature with the exception of the 10%. At the low temperature peak, 5% sample shows a 10% increase over the control sample. At elevated temperatures, the samples once again meet at similar value, about 3 Wm$^{-1}$K$^{-1}$ for all samples. Again this is unfortunate because with no improvement in $\kappa$ at these elevated temperatures, then there is no improvement in $ZT$ in the temperature range in which these materials are utilized. The $ZT$, in Fig. 5.6.5, shows relatively no change in the $ZT$ with addition of the nanoparticles. The increase in $\kappa_L$ was matched by the decrease in $\rho$. In this series, the addition of the nanoparticles did not improve our properties, and affected the thermal conduction opposite of what was expected.
Figure 5.6.1 – X-ray diffraction pattern of nano-plated $\text{Ce}_{0.25}\text{Fe}_{0.75}\text{Co}_{3.25}\text{Sb}_{12}$ series.
Figure 5.6.2 – Carrier concentration and mobility of nano-plated $\text{Ce}_{0.25}\text{Fe}_{0.75}\text{Co}_{3.25}\text{Sb}_{12}$ series.
Table 5.6.1 – Modeling values for the Ce$_{0.25}$Fe$_{0.75}$Co$_{3.25}$Sb$_{12}$ series.

<table>
<thead>
<tr>
<th>sample</th>
<th>$n$ (m$^{-3}$)</th>
<th>$\alpha$ (VK$^{-1}$)</th>
<th>$m^*$</th>
<th>$l$ - grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.25}$Fe$</em>{0.75}$Co$<em>{3.25}$Sb$</em>{12}$</td>
<td>1.34E+26</td>
<td>7.00E-05</td>
<td>0.90</td>
<td>10.3</td>
</tr>
<tr>
<td>2% nanoparticles</td>
<td>1.40E+26</td>
<td>6.30E-05</td>
<td>0.83</td>
<td>12.7</td>
</tr>
<tr>
<td>5% nanoparticles</td>
<td>8.02E+25</td>
<td>6.30E-05</td>
<td>0.57</td>
<td>17.3</td>
</tr>
<tr>
<td>10% nanoparticles</td>
<td>6.93E+25</td>
<td>6.15E-05</td>
<td>0.51</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Figure 5.6.3 – Arrhenius plot for nano-plated Ce$_{0.25}$Fe$_{0.75}$Co$_{3.25}$Sb$_{12}$ series.
Figure 5.6.4 — Electrical properties of nano-plated $\text{Ce}_{0.25}\text{Fe}_{0.75}\text{Co}_{3.25}\text{Sb}_{12}$ series.
Figure 5.6.5 – Thermal conductivity and ZT of nano-plated \( \text{Ce}_{0.25}\text{Fe}_{0.75}\text{Co}_{3.25}\text{Sb}_{12} \) series.
5.7 – Ce filled larger amount

This was the second Ce filled series, and it had a larger amount of Ce. The nominal composition for this series of samples for the bulk matrix is Ce$_{0.8}$Fe$_3$CoSb$_{12}$. Using two different series with the same filler was a way to see if the nanoparticles always had the same effect. During this growth, problems with the furnace arose. The furnace temperature never stabilized but oscillated 40 °C in the positive and negative direction. The resultant powder was then split into different samples for 0, 2, 5, and 10 wt% hydrothermal nanoparticle growth on them before being hot pressed.

The XRD pattern showed a skutterudite but with a significant amount of secondary phases as seen in Fig. 5.7.1. This could have been caused by the unstable temperature during growth. The presence of Ce in the structure of the skutterudite was confirmed by EDX. The SEM pictures reveal a considerable structural change for the 10% nanoparticle sample with respect to the other samples. Fig. 5.7.2 shows melting throughout the sample, more predominant than seen in other samples. This structural difference made for unusual behavior of the data and made it difficult to match high temperature measurement with their low temperature counterparts for $\kappa$. The density of the samples decreases slightly as the % of nanoparticles increases.

Like the previous series, the $\alpha$ is positive suggesting that holes are the majority carriers for this system. The $\alpha$ is relatively low and there is not much change in value with the introduction of nanoparticles. At 300 K the values range from 60-70 $\mu$VK$^{-1}$ with the introduction of the nanoparticles causing a small reduction. The introduction of the nanoparticles slightly lowers the value of the $\alpha$ and changes the slope of the Seebeck
coefficient with temperature. All hydrothermally treated samples have a similar slope which is different from the parent sample that underwent no hydrothermal treatment. The $\rho$ of the parent composition is already low, with a value of 1.4 m$\Omega$-cm at room temperature. The addition of nanoparticles decreases the resistivity by about 65% for both the 2% and 5% sample. Because of this huge reduction in $\rho$, the $PF$ shows an 80% improvement at room temperature, although the value remains quite low at 0.225 Wm$^{-1}$K$^{-1}$ as shown in Fig. 5.7.3. This much improvement of the electrical properties shows promise for finding a barrier that would be friendly to $\rho$ and $\alpha$.

The low and high temperature $\kappa$ data show a similar trend as the previous series as seen in Fig. 5.7.4. With an increase in the wt % of added nanoparticles, the $\kappa_L$ increases systematically with the exception of the 10%. The low temperature peak shows the largest increase with the amount of nanoparticles, and the increase in $\kappa$ from the 0% to the 5% becomes less pronounced as the temperature is increased. The $\kappa_L$ is also not correlated to the density. One would expect that a decrease in density, as seen in these samples, would also precipitate a decrease in $\kappa$. With the large improvement in $PF$, an increase is seen in the $ZT$ of the samples with nanoparticles, even though there was an increase in $\kappa_L$. The 2% sample shows a 50% increase in $ZT$ at room temperature as compared to the parent sample.
Figure 5.7.1 – X-ray diffraction pattern of nano-plated Ce$_{0.8}$Fe$_3$CoSb$_{12}$ series.
Figure 5.7.2– SEM pictures of the structure differences with increase of nanoparticle concentration for nano-plated Ce$_{0.8}$Fe$_3$CoSb$_{12}$ a) shows the parent sample b) 2%, c) 5%, and d) 10%.
Figure 5.7.3 — Electrical properties of nano-plated \( Ce_{0.8}Fe_{3}CoSb_{12} \) series.
Figure 5.7.4 – Thermal conductivity and ZT of nano-plated Ce$_{0.8}$Fe$_3$CoSb$_{12}$ series.
5.8 – Yb filled

A third filled skutterudite was tested. The Yb filled skutterudite was chosen because of previous good results as a skutterudite material.[35] This series has a nominal composition of Yb$_{0.2}$Fe$_{0.6}$Co$_{3.4}$Sb$_{12}$.

The XRD pattern confirmed the samples were a single phase skutterudite (CoSb$_3$, PDF #03-065-3144) with no secondary phases visible. The presence of Yb in the structure of the skutterudite was confirmed by EDX. This series was one in which only a 5% nano-plated sample was tested.

Looking at the Fig 5.8.1, the $\alpha$ was increased by more than 25% at room temperature up to 80 $\mu$VK$^{-1}$ with the 5% nanoparticle sample. At the same time the $\rho$ was also increased. The $\rho$ showed a linear temperature dependence to a value of 5.5 mW-cm, about a 20% increase from the parent sample with no nanoparticles. Overall the 5% of nanoparticles improved the PF by about 30% at room temperature.

Fig. 5.8.2 shows the $\kappa_L$ for both samples. At elevated temperatures there is a decrease in $\kappa_L$ with the 5% nanoparticle sample.
Figure 5.8.1 — Electrical properties of nano-plated Yb$_{0.2}$Fe$_{0.6}$Co$_{3.4}$Sb$_{12}$ series.
Figure 5.8.2 – Thermal conductivity of nano-plated Yb$_{0.2}$Fe$_{0.6}$Co$_{3.4}$Sb$_{12}$ series.
Double filling has been recently studied by several groups. For our study we chose ytterbium in a low filling amount that was previously shown in our lab to be the optimal filling amount. For the second filler we chose another element in the rare earth series with a much different mass, cerium. We considered that using two elements with such different masses would create a larger mass fluctuation. Yb was chosen to remain steady at 0.2 filling concentration and the Ce was varied from 0.1, 0.2, and 0.3. We also have single filled from previous series we can use to compare. The single-phased nature (CoSb$_3$, PDF #03-065-3144) for all 4 samples was confirmed for each sample and is shown in Fig. 5.9.1. The double filled skutterudites have been plotted with the single filled Yb and Ce for comparison.

The $\alpha$ for the parent Yb skutterudite is negative signifying electrons as the carriers, but as Ce was introduced the $\alpha$ became positive as was seen previously in the two Ce series as seen in Fig. 5.9.2. For the single Yb sample, the $\alpha$ has a low value of $-60 \, \mu$VK$^{-1}$, while the Ce doping creates a positive $\alpha$ that is improved above single filled Ce sample to $100 \, \mu$VK$^{-1}$ for the highest Ce concentration sample. All samples have a linear temperature dependence for $\alpha$. The $\rho$ is also improved with increasing amounts of Ce filling atom moving from the value of the Yb single filled to the Ce single filled. The sample with highest Ce concentration shows a very shallow, almost constant, temperature dependence, while the other samples show a much steeper slope, showing an increasing $\rho$ with increasing temperature. At 300 K there is nearly a 40% improvement in $\rho$ from the
Yb single filled to the sample with highest Ce concentration, with a value of 3 mΩ-cm. The PF is then greatly improved by the addition of Ce. At room temperature, PF is increased from 0.02 Wm⁻¹K⁻¹ to 0.15 Wm⁻¹K⁻¹ with increasing Ce concentration as seen in Fig. 5.9.2.

κ is where the greatest improvement is expected. Throughout the entire temperature range, the Ce filling decreases the κ_L as compared to both of the single filled samples as seen in Fig. 5.9.3. The κ_L is reduced by half as compared to the La single filled and reduced by a quarter as compared to the Ce single filled. The amount of Ce filling does not appear to change the value of the κ_L. Any amount Ce double filling causes κ_L to reach the same level of reduction. Because of the improvement of both the electrical and thermal properties, the ZT is improved.
Figure 5.9.1 – X-ray diffraction pattern of the Yb$_{0.2}$Ce$_y$Fe$_x$Co$_{4-x}$Sb$_{12}$ series.
Figure 5.9.2 — Electrical properties of the Yb$_{0.2}$Ce$_x$Fe$_x$Co$_{4-x}$Sb$_{12}$ series.
Figure 5.9.3 — Thermal Conductivity of the Yb$_{0.2}$Ce$_x$Fe$_{x}$Co$_{4-x}$Sb$_{12}$ series.
5.10 – Yb$_{0.2}$Ce$_{y}$Fe$_{x}$Co$_{4-x}$Sb$_{12}$ with Nano-plating

The double filled series were then processed through the nano-plating technique incorporating 5 weight % of CoSb$_3$ nanoparticles. The nanoparticle inclusions slightly increased the value of $\alpha$, though the temperature dependence remained identical. The behavior for the $\rho$ was not so clear. For the single filled Yb and the sample with the $y=0.3$ Ce filling the electrical resistivity increased. For the $y=0.2$ Ce sample the electrical resistivity remained the same, while for the $y=0.1$ Ce sample and the single Ce filled sample $\rho$ decreased. Overall the PF was slightly decreased, though the Power Factor still increased systematically with an increase in the amount of Ce.

The $\kappa$ of these samples were measured in the high temperature regime, where skutterudites are used. This series showed similar results to the previous series, in that any increase in the concentration of Ce saw the same reduction in $\kappa$. They also saw a small reduction due to the incorporation of nanoparticles.
Figure 5.10.1 — Electrical properties of the nano-plated $\text{Yb}_{0.2}\text{Ce}_4\text{Fe}_x\text{Co}_4$.
Figure 5.10.2 — Thermal Conductivity of the nano-plated $\text{Yb}_{0.2}\text{Ce}_{y}\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ series.
6.1 - Conclusions

This present study used past approaches that have shown good results and attempted to further improve upon them by mixing of the various techniques. Skutterudites are enhanced by doping on the Co site, filling with rare earth elements, and by nano-plating CoSb$_3$ into the bulk. Promising skutterudite compositions were grown and combined with nanoparticles in hopes of gaining the best results from all methods. Forming nanocomposites could improve the properties of these materials while not bringing on the disadvantages of going to the nanoscale. The complexity is in creating a barrier that agrees with the electrical properties while scattering the phonons. The results were not as clean as we had hoped for and can be seen in Table.

6.1.1 - Electrical

There were several possible expectations for the electrical properties as discussed in Chapter 1. One of the possible effects from the addition of the nanoparticles is that it could cause the scattering for the carriers, causing an increase in the electrical resistivity. The addition of the nanoparticles could also possibly causing doping, changing the carrier type and therefore could change both the electrical resistivity and Seebeck coefficient in an unpredictable manner.

The theory behind reducing dimensionality says that as the dimensionality is decreased, the electrical resistivity should remain intact and the Seebeck coefficient
should increase. Because the nanoparticles that have been incorporated into our materials are so close in composition to our bulk, the electrons would not be scattered and therefore leave the electrical resistivity intact. From this same method, if the carriers in the nanoparticles and bulk are comparable, then the Seebeck coefficient could possibly increase.

In these samples series, the results are not quite so clear. There were no consistent trends in how the electrical properties responded to the nanoparticles. For the mechanically mixed CoSb3 and the Ni doped the electrical resistivity remain unchanged. While for the nano-plated CoSb3 and the Ce filled series the electrical resistivity decreased. The Yb and La filled skutterudites both show and increase in the electrical resistivity with increase in nanoparticle concentration. The same variation was seen in the Seebeck coefficient. The Seebeck coefficient increased for the mechanically mixed CoSb3 and the La and Yb filled skutterudites while remaining the same or slightly decreased with the incorporation of the CoSb3 nanoparticles.

Because of this inconsistency in the electrical properties, few statements can be made about the effect of the nanoparticle incorporation into the samples. Overall the effect of the nanoparticles on the electrical properties is small and unclear. The electrical resistivity could also be affected by the sample density, oxidation between the grains, or grain size as well as the nanoparticles. The Seebeck seems to be relatively unchanged by the nanoparticles. The Power Factor only increases for the Yb and both Ce filled skutterudites and decreases for all other series with increase in nanoparticles.
6.1.2 - Thermal Properties

We expect the nanoparticles to add grain boundaries in our samples and because of the small composition mismatch, to also act point defect scattering. As discussed in Chapter 3, grain boundary scattering is seen mostly in the low temperature range, and point defect scattering is seen in the mid temperature range. We hope that the nanoparticles will produce a reduction in lattice thermal conductivity throughout the whole temperature range.

A lowering of the lattice thermal conductivity is definitely seen in many of the sample series. All of the filled and unfilled sample series, with the exception of the two Ce filled skutterudite series, show a decrease in the lattice thermal conductivity with increase in nanoparticle concentration. For the binary CoSb3 and Co0.99Ni0.01Sb3, the lattice thermal conductivity was only affected at the low and mid-range temperatures. For the La and Yb-filled skutterudite series, the lattice thermal conductivity is most effectively reduced at the low and mid-range temperatures, but we also see an additional though smaller reduction at the higher temperature range. These results were overall favorable and to be expected, but don’t produce enough of an improvement in the lattice thermal conductivity to give us a significant increase in the ZT value.

Results that were surprising came from both of the Ce-filled skutterudite series. Again most of the changes in the lattice thermal conductivity was again seen in the low and mid-range temperatures, but in these instances the lattice thermal conductivity was actually systematically increased with an increase of incorporated nanoparticles. The
expectation was for the nanoparticles to act as point scatterers for the phonons. The increase in lattice thermal conductivity is both surprising and unexplainable.

6.1.3 - Double filling

Double filling with Ce and Yb produced positive results. The addition of the Ce increased the Seebeck coefficient and reduced the electrical resistivity, thereby improving the Power Factor by a factor of 6.5 at room temperature. The double filling also produced a reduction in lattice thermal conductivity over single filling. Amount of double filling did not affect the thermal conductivity. Over the variation of the Ce filling the lattice thermal conductivity was reduced by roughly 30% at room temperature.

Adding the 5 weight % nanoparticles produced results similar to that discussed in the earlier series. The electrical properties remained relatively intact only producing a very slight decrease in the Power Factor. The lattice thermal conductivity was reduced further but again the different amounts of Ce filling all produced approximately the same reduction down to 2 Wm\(^{-1}\)K\(^{-1}\) at room temperature.

6.1.4 - Conclusions

Positive results were seen for the La and Yb filled skutterudites. For both of these series the Seebeck coefficient was improved. At the same time both series showed a reduction of the lattice thermal conductivity with increase in nanoparticle concentration throughout the entire temperature range. Unfortunately these same results are not seen for the Ce filled skutterudite series.
This hydrothermal nano-plating technique, in which nanoparticles are grown directly onto the bulk matrix in a homogeneous manner, shows some favorable results in the thermoelectric properties of filled skutterudites. Unfortunately the behavior is complicated and not necessarily predictable, especially in the electrical properties. Although not a good method on its own, used in conjunction with other favorable methods, such as doping or void filling, nano-plating could be a viable method to improve ZT.

6.2 - Future Work

Future work in these materials would include using a newly acquired SPS instead of hot pressing in order to further improve the density of these materials. Although these materials generally have densities greater than 90, increasing the density of nanoparticle incorporated samples even further would remove a possible contribution to the electrical resistivity and thermal conductivity. Both of these variables are affected by the density, generally decreasing with decreasing density.

More Ce filled skutterudite series should be grown in order to understand the behavior of these systems with the incorporation of nanoparticles. The incorporation of nanoparticles was expected to increase grain boundaries, therefore decreasing the thermal conductivity with increase of nanoparticles. This behavior was seen for all series, except the Ce filled systems, which showed the exact opposite behavior. Ce filled series should be attempted in both p and n type series. In this study both series were p type, therefore seeing if the same behavior is found in the n type system would be informative.
Another study of benefit would be optimizing the nanoparticle incorporation. From these studies it is seen that best concentration would lie between 2 and 5 weight %. Optimizing the nanoparticle concentration, would allow skutterudites to be studied without having to study long series of samples making the process quicker.

The final study I would suggest and would love to have had the opportunity to attempt would be to try making the nano-plating barrier out of more complex skutterudites. Recent studies have reported Fe doped solvothermally grown skutterudite nanoparticles. In time, filled skutterudites may be grown by the same method. Instead of double filling skutterudites, one filled skutterudite can be grown as the parent compound and a different filled skutterudite could be nano-plated as the barrier. This may be a way to possibly have more control over double filling of the skutterudite.
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