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Skutterudite Derivatives: A Fundamental Investigation with Potential for Thermoelectric Applications

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Skutterudite Derivatives: A Fundamental Investigation with Potential for Thermoelectric Applications

by

Kaya Wei

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Applied Physics
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Abstract
Thermoelectric devices allow for direct conversion of heat into electricity as well as solid-state refrigeration. The skutterudite family of compounds continues to be of considerable interest both scientifically and technologically due to their unique physical properties, in particular as promising thermoelectric materials. In this thesis, the basic thermoelectric phenomena and some background history on skutterudites will be reviewed. Rhombohedral derivatives of the cubic skutterudite CoSb$_3$, namely Co$_{4-x}$Fe$_x$Ge$_6$Se$_6$ with x=0, 1, 1.5 (p-type) and rare-earth filled Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$ and Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$ (n-type), were synthesized and their synthesis and low temperature transport properties will be discussed.

Reitveld refinement and elemental analysis were used to identify the structure and stoichiometry of these compositions. Both Fe substitution and rare-earth filling reduced the thermal conductivity compared with Co$_4$Ge$_6$Se$_6$ skutterudite derivative. In addition the electrical and thermal properties of these compounds are greatly affected by doping. This fundamental investigation reveals new insight and is intended as part of the continuing effort to explore different skutterudite compositions and structure types for potential thermoelectric applications.
Chapter One:

Introduction

Over the last three decades, the interest in space exploration, medical applications and waste heat recovery have lead to the investigation of new and novel materials for thermoelectric power generation and refrigeration applications. In addition, since the 1990s, environmental concerns have has invigorated the interest in thermoelectrics. [1]

Thermoelectric phenomena enable the direct solid-state inter-conversion of electrical and thermal energy, thus thermoelectric devices are of great interests for cooling and power generation applications. The Seebeck and Peltier effects, discovered in the years of 1823 and 1834, respectively, set the theoretical stage for understanding such phenomena.[1-3] The understanding of these thermodynamic phenomena allows for the discovery and development of different materials systems that have good thermoelectric properties as well as increases the potential for technological applications. Thus, it is important to develop an understanding of the role of thermoelectrics before investigating to specific materials. In the first part of the thesis, the basic thermodynamic phenomena will be discussed followed by definition of the thermoelectric figure of merit, the efficiency of thermoelectric devices, and some of the different material science approaches employed to enhance thermoelectric performance from a fundamental point of view.
Definitions of Thermoelectric Materials

The behavior of a thermoelectric circuit is dependent on the Seebeck (\(S\)), Peltier (\(\Pi\)), and Thomson coefficients (\(\tau\)). [1] For a junction made with two dissimilar uniform conductors, the Seebeck effect defines the electric potential across the interface of this junction with an established thermal gradient, while the Peltier effect refers to the heat generated (or removed) at the junction when a current is made to flow through the junction.[2-3] When the current is flowing and the temperature gradient is forming, the heat generation (or absorption) flux rate is described by \(\tau\). [4] These three thermodynamic phenomena will be described in this section.

By applying a thermal gradient in a uniform conductor, the thermally excited charge carriers on the hot end will diffuse along the concentration gradient to occupy the lower energy states in the cold end, generating a voltage difference (Figure 1.1). The ratio of the voltage \(\Delta V_{ab}\) developed due to the temperature gradient \(\Delta T\) is related to an intrinsic property of a material defined as the Seebeck coefficient, \(S\), or thermopower.[2]

\[
S_{ab} = \frac{\Delta V_{ab}}{\Delta T}
\]

For metals, \(S\) is typically between 1 and 10 \(\mu\)V/K. For semiconductors \(S\) is in the range of \(10^2\) to \(10^3\) \(\mu\)V/K. In general, when electrons are the majority carriers, in n-type semiconductors for example, a potential difference is generated in the direction of the thermal gradient, resulting in a negative \(S\). When holes are the majority carriers, in p-type semiconductors for example, a positive \(S\) will be observed since the potential is generated in the opposite direction of the thermal gradient.
On the other hand, if a current is passed through the junction of two dissimilar materials, depending on the current direction, heat will be reversibly absorbed or rejected at the junction. This is the Peltier effect, discovered a few years after the discovery of the Seebeck effect.[3] The rate of thermal exchange at the junction is given by

\[ Q_p = S_{ab}IT = \Pi_{ab}I \]  

(2)

where \( I \) is the current through the junction at temperature \( T \) and \( \Pi_{ab} \) is the Peltier coefficient.

Figure 1. Seebeck effect for an isolated metal in a uniform thermal gradient. Electrons (solid circle) diffuse from the hot end to the cold end leading to a voltage difference between the ends of the metal.
While the Seebeck and Peltier effects define the thermoelectric properties observed in the junction of two dissimilar conductors, the Thomson effect defines a thermoelectric property of a single material. That is, a current passing through a homogeneous material in a thermal gradient will result in a reversible flow of heat, defined by the Thomson coefficient,[4]

$$\tau = \frac{1}{I} \frac{dq}{dx} \left( \frac{dT}{dx} \right)^{-1}$$  \hspace{1cm} (3)

where $\frac{dq}{dx}$ is the rate of heating per unit length and $\frac{dT}{dx}$ is the temperature gradient. The equations

$$\tau_a - \tau_b = T \frac{dS_{ab}}{dT}$$  \hspace{1cm} (4)

and

$$\Pi_{ab} = S_{ab} T$$  \hspace{1cm} (5)

describe the Kelvin relations and relate the three fundamental thermoelectric phenomena to each other, and the link between thermoelectric cooling and thermoelectric power generation.

**Figure of Merit ZT**

In general, the ratio of the rate of heat extraction from the source to the rate of expenditure of electrical energy gives the coefficient of performance for thermoelectric refrigeration, [5]

$$\phi = \frac{Q_c}{W} = \frac{(S_p - S_n)IT_c - K\Delta T - \frac{1}{2}I^2R}{I[(S_p - S_n)\Delta T + IR]}.$$  \hspace{1cm} (6)
$T_C$ ($T_H$) is the temperature of the cold (hot) side, $\Delta T = T_H - T_C$, $K$ is the total parallel thermal conductance, and $R$ is the total series resistance of the couple. In the absence of irreversible effects $\phi = T_C / \Delta T$, the inverse of the Carnot limit.

Similarly the efficiency of a thermoelectric power generator can be defined as

$$\eta = \frac{W}{Q_H} = \frac{I[(S_p - S_n)\Delta T - IR]}{K\Delta T + (S_p - S_n)IT_H - \frac{1}{2}I^2 R}$$  \hspace{1cm} (7)$$

where $W$ is the power delivered to an external load and $Q_H$ is positive for heat flow from the source to the sink. The value of $I$ that maximizes $\eta$ depends upon the ratio of the cross-sectional area ($A$) to the length ($L$) of each thermoelectric segment. [1]

These relative dimensions can also be used to optimize the thermoelectric figure of merit for the couple, $Z = \left(\frac{(S_p - S_n)^2}{RK}\right)$, by minimizing the product of $RK$ in Equation (8):

$$\frac{L_nA_p}{L_pA_n} = \left(\frac{\rho_p\kappa_n}{\rho_n\kappa_p}\right)\frac{1}{2}.$$  \hspace{1cm} (8)$$

The figure of merit, $Z$, then becomes

$$Z = \frac{(S_p - S_n)^2}{\left[(\rho_p\kappa_p)^{1/2} + (\rho_n\kappa_n)^{1/2}\right]}.$$  \hspace{1cm} (9)$$

The efficiency of thermoelectric devices can also be characterized by the dimensionless thermoelectric figure of merit $ZT$, 

where $\sigma$ is the electrical conductivity ($\sigma = 1/\rho$, where $\rho$ is the electrical resistivity) and $\kappa$ is the thermal conductivity. This equation indicates that an ideal material system for thermoelectric applications will be one with good electrical properties (large $S$ and $\sigma$) together with poor thermal conduction (small $\kappa$). Since both of $S$ and $\sigma$ are related to the electrical properties, $S^2\sigma$ is typically defined as the power factor.

As shown below in Figure 1.2, the power factor for semiconductors can be maximized only within a certain carrier concentration range, therefore, in order to achieve high $ZT$ values, the reduction of $\kappa$ is one approach to increase $ZT$.

Figure 2. Optimal electrical properties for thermoelectric applications.
Reprinted from Reference 9.
The thermal conductivity is typically understood as the sum of the electronic and lattice contributions,

$$\kappa = \kappa_E + \kappa_L,$$  \hspace{1cm} (11)

where $\kappa_E$ is the electrical thermal conductivity and $\kappa_L$ is the lattice thermal conductivity.

The electronic component of the thermal conductivity, $\kappa_E$, can be estimated using the Wiedeman-Franz relation,

$$\kappa_E = L \sigma T$$  \hspace{1cm} (12)

where $L$ is the Lorentz number. $L$ varies for different materials and with temperature. The ideal Lorentz number can be written as

$$L = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2$$  \hspace{1cm} (13)

where $k_B$ is Boltzmann’s constant, and $e$ is the charge of an electron. Since $\kappa_E$ is proportional to $\sigma$, efforts to reduce $\kappa$ should focus on reducing $\kappa_L$. Therefore, an approach that has the potential for significantly reducing $\kappa_L$ for a particular material system is of great interest.

The dominant thermal conduction mechanism in non-metals is typically $\kappa_L$. The development of a theoretical model to understand the behavior of $\kappa_L$ was not simple and required that it be in strong agreement with experimental results. Dulong and Petit specified the high temperature limit to the heat capacity in order to try to describe temperature dependent thermal behavior from a statistical mechanics point of view.[14-15] By employing Planck’s blackbody radiation model Einstein did not obtain good agreement with the known experimental data at low temperatures.[14-15] Eventually Debye developed a method to describe the low temperature
limit by modeling solids as an interacting continuous medium. This is different than the Einstein model which considers a solid to be as a series of noninteracting atoms.[14-15]

In the Debye model $\kappa_L$ is given by the integral

$$
\kappa_L = \frac{k_B}{2\pi^2\nu} \left( \frac{k_B T}{\nu} \right)^3 \int_0^{\theta_B/T} \frac{x^4 e^x}{\tau_C^{-1}(e^x - 1)^2} \, dx
$$

(14)

where $x = h\omega/k_B T$ is dimensionless, $\omega$ is the phonon frequency, $\theta_B$ is the Debye temperature, $\nu$ is the speed of sound, and $\tau_C$ is the phonon scattering relaxation time. Considering only the terms with dominant contributions, $\tau_C^{-1}$ can be written as a sum of different specific phonon scattering terms, each defines a particular phonon scattering mechanism. In this thesis, as will be described in Chapter 2, four different terms for $\tau_C^{-1}$ will be described such that

$$
\tau_C^{-1} = \frac{\nu}{L} + A\omega^4 + B\omega^2 T \exp\left(-\frac{\theta_D}{3T}\right) + \frac{C\omega^2}{(\omega_0^2 - \omega^2)^2}
$$

(15)

where $L$ is the grain size, $\omega_0$ is the resonance frequency, and the coefficients $A, B,$ and $C$ are fitting parameters. The four terms on the right side of the equation represent grain boundary scattering, point-defect scattering, Umklapp scattering and resonance scattering, respectively. Grain boundary scattering inhibits the low temperature (longest) wavelength phonons. For polycrystalline specimens $L$ gives an average grain size of the specimen. Point defect scattering is caused by defects or impurities resulting in a decrease in crystal periodicity and thus scatters phonons. The introduction of disorder in the crystal structure will also have an affect on $A$, as will be discussed in Chapter 2. Umklapp scattering represents phonon-phonon scatterings. It
refers to the interaction of two phonons giving rise to a third. Thermal resistance results when the total wave vector of this third phonon is greater than the reciprocal lattice.[8] At high temperatures this scattering mechanism is significant as phonon-phonon interactions are common and all phonon modes are excited.[8] The last term in the equation, resonance scattering, is essential for modeling loosely-bound atoms inside a crystal lattice, or Einstein soft modes, as will be discussed in Chapter 2.

**Thermoelectric Devices and Applications**

One application of the thermoelectric effect is for the measurement of temperature. [2-5] By the late 1950s research on semiconducting thermocouples was underway and semiconducting thermoelectric devices were employed in terrestrial cooling and power generation applications. Later, NASA realized thermoelectric energy conversion was the best choice, compared with other forms of small-scale electric power generation, for space applications. By the 1990s thermoelectric refrigerators can be purchased at any local department store. Starting around 2000 thermoelectrics was used in automobiles for seat cooling and cooling passengers’ beverages.

Thermoelectric devices allow for the direct conversion of heat into electricity as well as solid-state refrigeration, as described in the previous section. A typical thermoelectric device consists of pairs of n and p-type semiconducting segments, or legs, as shown in Figure 1.3. These legs are electrically in series and thermally in parallel so that sufficient heat transport will be carried through the legs by the charge carriers.
As shown in Figure 1.3(a), an electric current passing through the couple results in the transfer of thermal energy via the charge carriers, thus acting as a refrigerator. On the other hand, imposing a thermal gradient across the couple generates a thermoelectric voltage. Sourcing a current through the load, can provide power, as described in Figure 1.3(b). This is the fundamental basis for thermoelectric refrigeration and power generation.

Figure 3. Energy conversion diagrams illustrating thermoelectric (a) refrigeration, and (b) power generation. The thermoelectric module is composed of a p-type and an n-type semiconducting material connected electrically in series through contact pads and thermally in parallel between ceramics.
Considering thermoelectric cooling applications, seat cooling for automobiles for example, the advantages of thermoelectric refrigeration include compactness, weight, no moving parts, noise and environmental friendly. Other applications such as waste heat recovery and small-scale remote power generation are also of great interest for development. [1,4-5,40]

Considerable effort by NASA and other agencies has established radioisotope thermoelectric generator (RTG) as the power source for deep space missions and therefore an integral component of space exploration. The RTGs convert heat, generated by the radioactive decay of plutonium 239, into electricity thus supplying power for all the Cassini and Discovery deep space probes. This technology was used in the Voyager 1 deep space probe that was launched in 1977. It recently passed the edge of the solar system in early 2013. The planed deep space probe New Horizons will also employ RTGs for thermoelectric power generation.

**Approaches to Improve ZT**

Early studies on thermoelectric materials included three different families of compounds, \( V_2\text{VI}_3 \) compounds (based mainly on \( \text{Bi}_2\text{Te}_3 \)), \( \text{IV-VI} \) compounds (based on \( \text{PbTe} \)), and the \( \text{IV-IV} \) compounds (the SiGe-alloys). [1] The \( ZT \) value of these materials is limited to \( \sim 1 \) at their optimum temperature of operation. Since there is no theoretical limit for \( ZT \), materials with better thermoelectric performance can be expected in the future.[1]

Some of the goals of current thermoelectric materials research includes developing new materials that are either able to enhance the efficiency of thermoelectric devices (achieve higher \( ZT \)) or have the capability of operating at new and broader temperature regimes, particularly at lower temperatures such as \( T < 200 \text{ K} \) for cooling applications.
According to the definition of $ZT$, the ideal thermoelectric material will possess good electrical properties together with very poor thermal conductivity, that is, a good thermoelectric material should have thermal properties similar to that of a glass and electrical properties similar to that of a good single-crystal. This describes the Phonon-Glass Electron-Crystal, or PGEC, model. [11] As described by Slack,[11] this model material should have the following features:

(a) It should possess “loose” atoms or molecules whose translational or rotational positions are not well defined, possessing two or more metastable positions;
(b) There is no long-range correlation between the positions of the “loose” atoms or molecules and
(c) The mass of these “loose” atoms or molecules is relative large compared with the total mass of the compound.

In addition, disorder produced by point defect scattering cannot lead to glass-like thermal conductivity.

The Skutterudite family of compounds share these feature and possesses two large empty voids inside each unit cell.[1] By introducing “guest” atoms into the voids in the crystal lattice these atoms can “rattle” inside the crystal structure resulting in a dramatic reduction in $\kappa_l$.[11] These guest atoms are loosely bound within a relatively large space, they therefore can be thought to “rattle” about and strongly scatter phonons thus providing one of the features for PGEC materials, namely a glasslike thermal conductivity.[12-15]

In this thesis a fundamental investigation of the synthesis and low temperature transport properties of unfilled and partially filled rhombohedrally modified skutterudite derivatives $\text{Co}_4-x\text{Fe}_x\text{Ge}_6\text{Se}_6$ ($x= 0, 1, 1.5$) and $\text{RE}_x\text{Co}_4\text{Ge}_6\text{Se}_6$ (RE = Ce, Yb) will be described. The crystal
structure and transport properties of these materials will be discussed in detail. Since the low temperature thermoelectric properties of this group of compounds has not been previously investigated, this work is also intended as a new direction in furthering the investigation of skutterudites for potential thermoelectric power generation applications.
Chapter Two:

Introduction to Skutterudites

This chapter reviews the crystal structure of skutterudite compounds and the general approach employed to improving $ZT$ for this materials system. The ability to tune the electrical and thermal properties relatively independently makes the skutterudite material system of interest for thermoelectric applications.

From Skuterud to Skutterudites

In 1845 skutterudites were first discovered in Skuterud Mines, Modum, Buskerud, Norway. [1] They are typically opaque with a metallic luster and tin-white to silver-gray in color. Today, as an accessory mineral, they are found in many localities worldwide.

In one of the earliest studies on skutterudites, in 1980s, Braun and Jeitschko reported on structural investigations of skutterudite antimonides and indicated that “…the lanthanum atoms seem to ‘rattle’ or may participate in a ‘soft’ lattice mode inside the 12-coordinated pnictogen site in skutterudites”. [10] Later in 1994, the earliest published work on skutterudites for thermoelectric applications, G. A. Slack first predicted that “‘rattling’ atoms will strongly scatter the lattice phonons that are responsible for heat transport”. [11] These studies lead to a new direction for thermoelectric materials research since “rattling” atoms are expected to
substantially reduce $\kappa_L$. Similar approaches have resulted in an increase in $ZT$, indicating the potential skutterudites possess for thermoelectrics applications.

Figure 4. Naturally occurring skutterudite. (Rob Lavinsky, iRocks.com
(http://www.irocks.com/)-CC-BY-SA-3.0)

**Structural Features**

The basic composition of skutterudites can be described as $\text{MX}_3$. Here $M$ represents a metal atom while $X$ is a pnictide atom. Common compositions include $\text{CoSb}_3$, $\text{CoAs}_3$, $\text{CoP}_3$, $\text{RhSb}_3$, $\text{RhAs}_3$, 
RhP₃, IrSb₃, IrAs₃ and IrP₃. The crystallographic unit cell consists of eight MX₃ formula units with thirty two atoms per unit cell. They form in the body-centered cubic space group Im3. [1]

One of the features skutterudites possess, as compared to other thermoelectric materials, is a large unit cell. The unit cell volume of CoSb₃ is 687 Å³. [4] As shown in Figure 2.2, each unit cell contains two voids at the a crystallographic position. These large voids, due to the large unit cell and low atom coordination numbers, allows for the accommodation of different types of filler atoms in these voids. The composition of skutterudites can then be described as RCo₄Sb₁₂ or R₂Co₈Sb₂₄ (R: 2a(0, 0, 0); Co: 8c(1/4, 1/4, 1/4); Sb: 24g(0, y, z)) where R indicates the guest atom. [1] Studies have been done for different filling species including group-III, group-IV, lanthanide, actinide alkaline and alkaline-earth atoms. [4,9,23]

Figure 5. CoSb₃ skutterudite with no “guest” atoms inside the voids.
Another interesting structural feature is the four-membered rings, of X atoms, in MX$_3$. The rings have directional orientations, one parallel and the other perpendicular to the cubic crystallographic axes. [1,31,32] Each X$_4$ ring is orthogonal with its neighbor rings. The distance between the X atoms inside the rings has an effect on the physical properties of these materials[23-25]. As an example, along the chains of the Sb$_4$ rings in CoSb$_3$, the distances between two neighboring Sb atoms are 2.918 Å and 2.954 Å [Figure 2.3].

![Image of Sb$_4$ ring in CoSb$_3$.](image)

**Figure 6.** Representation of the Sb$_4$ ring in CoSb$_3$.

**Filled Skutterudites versus Unfilled Skutterudites**

Skutterudites have large unit cells, heavy constituent atom masses and large carrier mobilities due to their covalent bonding. This matches one of the expectations for good thermoelectric materials, that is, complex structures made up of atoms that have heavy masses. [1] Since Slack predicted that “rattling” atoms will contribute to low $\kappa_l$, [11] different approaches have been initiated in an effort to increase this rattling effects. One successful path is filling the voids of skutterudites with heavy rare earth atoms while replacing M atoms with Fe, Os or Ru. As an example, $\kappa_l$ of CeFe$_4$Sb$_{12}$ is compared with unfilled skutterudites CoSb$_3$ and IrSb$_3$, in Figure 2.4,
from reference 12. $\kappa_E$ was calculated using the Wiedemann-Franz relation (Equation 7) and $\kappa_L$ was calculated by subtracting $\kappa_E$ from the measured $\kappa$ values. As seen from this figure, the room temperature $\kappa_L$ values for CeFe$_4$Sb$_{12}$ was reduced by nearly an order of magnitude as compared with the unfilled skutterudites due to the presence of Ce in the lattice. The model is that Ce atoms “rattle about” inside the voids to scatter the phonons that are responsible for the heat transfer. Thus $\kappa$ was lower compared with the compositions with empty voids.

Figure 7. Thermal conductivity of polycrystalline CeFe$_4$Sb$_{12}$, CoSb$_3$ and IrSb$_3$.

Reprinted from reference 12.
Different Fillers

The size of the voids and the filler species will have a large impact on phonon scattering, and therefore $\kappa_L$. Voids of small size will limit the dynamic disorder, related to the atomic displacement parameter (ADP), of the guest, or filler atoms.[1] As an example, $\kappa_L$ of filled skutterudites with different fillers ($\text{Ir}_4\text{LaGe}_3\text{Sb}_9$, $\text{Ir}_4\text{SmGe}_3\text{Sb}_9$, and $\text{Ir}_4\text{NdGe}_3\text{Sb}_9$) are compared with that of unfilled $\text{IrSb}_3$ in Figure 2.5. [13] By introducing filler atoms into the voids rare earth filled skutterudites show a reduction in $\kappa_L$. Since the $\text{Nd}^{3+}$ and $\text{Sm}^{3+}$ ions have smaller radii than $\text{La}^{3+}$ they possessed a larger thermal mean-square displacement amplitude (therefore a large ADP). This enables the atoms to interact with lower-frequency phonons thereby reducing $\kappa_L$ further as compared with that for the La filled compound. Moreover, the fact that the ground state of $\text{Nd}^{3+}$ ions split into more energy levels than $\text{Sm}^{3+}$ ions means $\text{Ir}_4\text{NdGe}_3\text{Sb}_9$ is more capable of scattering a larger spectrum of phonons than the Sm-filled skutterudite even though $\text{Sm}^{3+}$ is smaller than $\text{Nd}^{3+}$ in skutterudites. [14] As a result $\text{Ir}_4\text{NdGe}_3\text{Sb}_9$ has the lowest $\kappa_L$ among the three compounds shown in Figure 2.5.

From these studies, introducing guest atoms into the voids in order to scatter phonons resulted in a promising approach to improve the thermoelectric properties of skutterudites. Many different atoms have been introduced into the voids of skutterudite, including lanthanides, actinides, alkaline-earth, alkali, thallium, and group-IV elements. [15] The following question then arises: Which of the filler species will have the greatest affect on $\kappa_L$?
Figure 8. Temperature dependence of $\kappa_L$ for La, Nd, and Sm-filled skutterudites as compared with that of the unfilled skutterudite IrSb$_3$. The dashed line indicates the minimum $\kappa_L$ values for IrSb$_3$ based on calculations from reference 26. Reprinted from reference 13.

**Introduction to Atomic Displacement Parameters (ADPs)**

ADPs measure the mean-square displacement amplitude of an atom about its equilibrium position within its crystallographic position. In general, the heavier and smaller the guest atoms, the smaller $\kappa_L$. For instance, the ADP values for Yb is relatively large compared with all other rare earth atoms (presumably except Lu) due to its small size. As a result, Yb fillers create strong phonon scattering centers that affect phonon propagation substantially. The room temperature ADP values can be used to estimate the Einstein temperature $\theta_E$, or soft (“rattle”) mode, when static disorder is small and $\theta_E$ is less than 300K. Analyses of ADPs can also
determine the Debye temperature $\theta_D$ (from data in the temperature range up to $\theta_D$), the velocity of sound, the mean free path of phonons and $\kappa_L$, [14-15] as will be discussed below.

If we treat the rattling atoms as harmonic oscillators, that is assume that all the rattlers are vibrating independently of each other, the displacement amplitude can be written as

$$U_{iso} = \langle u^2 \rangle = \frac{h}{(8\pi^2 mv)} \cdot \coth\left(\frac{hv}{2k_B T}\right)$$

(16)

where $m$ is the mass of the rattler, $v$ is the frequency of the vibration, $h$ is the Plank constant and $k_B$ is the Boltzmann constant.[14] At high temperatures, $2k_B T >> hv$, Equation (12) can be reduced to

$$U_{iso} = k_B T / K = \frac{h^2 T}{(4\pi^2 mk_B \theta_E^2)}$$

(17)

where $K$ is the spring constant of the oscillator and the $\theta_E$ is the Einstein temperature expressed as $\theta_E = hv / k_B$. As shown in Figure 2.6, $\theta_E$ can then be estimated from the slope of $U_{iso}$ at high temperatures.

If we take into consideration the correlation of the vibration of different atoms, the Debye model can be applied to quantitatively describe the lattice vibrations, particularly at low temperatures where only long wavelength phonons are excited. When the temperature is higher than $\theta_D$, $U_{iso}$ can be written as

$$U_{iso} = \left[3h^2 / (4\pi^2 mk_B \theta_D^2)\right]T.$$  

(18)

Assuming that all the phonons have the same velocity, the speed of sound can be written as

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

(19)

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Figure 9. Temperature dependence of ADPs of La, Ce, Yb, Fe, and Sb in $\text{RFe}_4\text{Sb}_{12}$ (R=La, Ce, and Yb). Reprinted from Reference 14.

where $n$ is the number of atoms per unit volume. Given that the maximum wave number is

$$K_D = (6\pi^2 n)^{1/3},$$

(20)

the vibration frequency can be calculated using $\omega_b = \nu K_D$. By applying the expression adapted from the kinetic theory of gases,

$$\kappa_L = \frac{1}{3} C_v \nu_s l$$

(21)

where $C_v$ is the heat capacity per unit volume and $l$ is the mean free path of the heat carrying phonons, $\kappa_L$ can be estimated.
As evidence of the success of this approach, the temperature dependence of the ADPs values for LaFe₄Sb₁₂, shown in Figure 2.6, predicts a Debye temperature of 299 K while the experimentally measured value is 308 K.[14] Since the ADP values can sometimes be the initial information for a new crystalline compound, they can be used as a guide in searching for crystalline materials with unusually low $\kappa_L$. This can be particular useful in the design of materials with improved thermoelectric properties such as skutterudites.

**Filling Fractions**

Adding rattlers in the voids inside a skutterudite will reduce $\kappa$. [1-4,16,17] However it is of interest to understand what is the best filling fraction that will lead to the largest ZT values. Figure 2.8 shows $\kappa_L$ as a function of temperature of La-filled CoSb₃ skutterudites with different filling fractions. [18]

As shown in Figure 2.8, [18] although all the specimens with nonzero filling fractions achieve lower $\kappa_L$ values compared with CoSb₃, the largest decrease does not correspond to 100% filling. This suggests that together with the effect of “rattling”, point-defect scattering by the partial, random, distribution of the filler atoms in the voids results in the scattering of a larger spectrum of phonons as compared with fully filled compositions. To be more specific, when the filling fraction of La atoms increases from 0 to 0.31, $\kappa_L$ decreases. However, when the filling fraction increases above 50%, $\kappa_L$ begins to increase again. The maximum filling level here, $x=0.9$, shows a higher $\kappa_L$ than that of the mid-range $x=0.31$ filled skutterudite.
Figure 10. Temperature dependence of $\kappa_L$ of skutterudites with different filling fractions. The dotted and dashed lines are calculated $\kappa_L$ values for CoSb$_3$ with 4 and 7 $\mu$m grain sizes, respectively. Reprinted from Reference 18.

In partially filled skutterudites the random distribution of the fillers and the voids inside the crystal structure introduces additional phonon scattering, as described above. When half of the voids are occupied, the mass difference between the empty voids and the filled voids reaches the optimal “concentration” for mass-fluctuation scattering.[18] What makes this phenomenon more interesting is that less than 100% filling also maximizes the power factor compared with other filling fractions, as described in a n-type filled CoSb$_3$ skutterudites study.[18] Yang et al.[19] showed that this is due to the fact that the guest atoms will move the Fermi level upwards from the top of the valence band into the conduction band. It also leads to a large DOS near the Fermi
level, mostly due to delocalized s states with large group velocity, therefore also resulting in a larger power factor. Thus the electrical properties can be optimized while simultaneously minimizing $\kappa$. Partially filled skutterudite compounds are therefore most promising for thermoelectric power generation applications.

The Challenge of P-type Skutterudites

To make high performance thermoelectric devices, both n and p-type semiconducting materials are needed for thermoelectric modules, as described in Chapter 1. The effective mass of electrons is an order of magnitude higher than that of the holes for skutterudites.[4] With electrons being the charge carriers, n-type skutterudites can usually be optimized at higher carrier concentrations than p-type skutterudites. Thus thermoelectric properties developments for n-type skutterudites are beyond that of p-type materials for most skutterudite compositions.

Room temperature $ZT$ values of both n and p-type CoSb$_3$ are shown in Figure 2.9. [20] The intrinsic $\kappa_L$ is from single crystal CoSb$_3$ while $\kappa_{min}$ is estimated to be 0.31 Wm$^{-1}$K$^{-1}$ at room temperature.[21] By collecting electrical properties data from published results,[21] the $ZT$ values of CoSb$_3$ are plotted over a large range of carrier concentrations. At the optimum carrier concentration, n-type CoSb$_3$ yields a $ZT$ value twice as large as that of p-type CoSb$_3$. Thus for p-type skutterudites there is larger potential for further improvement.
Introduction to Skutterudites Derivatives

The skutterudite family of compounds includes a large number of different isostructural compositions. By substituting the atoms on the pnicogen sites, skutterudites with slightly different structural features, or skutterudite derivatives, can be formed. These are of great interest in investigating the fundamental properties of new skutterudites, as well as research towards potential thermoelectric power generation applications. For instance, group IV and VI elements substituted for Sb in CoSb$_3$ leads to compounds with smaller mobilities [22] and larger $S$ values and band gaps. [21] Since the physical properties of similar compounds are very sensitive to their compositions, it is of interest to investigate the structure-property relationships in these material
systems. Taking these reasons into consideration, fundamental studies of the synthesis and low temperature transport properties of unfilled and partially filled rhombohedrally modified skutterudite derivatives are the focus of this thesis. The investigation of CoGe$_{1.5}$Se$_{1.5}$ based skutterudites, including filling with Ce and Yb and substituting on the metal site with Fe, will therefore be discussed in the following sections.
Chapter Three:
Sample Preparation and Measurement

For this thesis, two groups of specimens were prepared for investigation of p-type (group I) and n-type (group II) CoGe\(_{1.5}\)Se\(_{1.5}\) based skutterudite derivatives. By substituting for the Co site with different concentrations of Fe, Group I contains the compounds (a) CoGe\(_{1.5}\)Se\(_{1.5}\), (b) Co\(_3\)FeGe\(_6\)Se\(_6\), and (c) Co\(_{2.5}\)Fe\(_{1.5}\)Ge\(_6\)Se\(_6\) with holes being the majority carriers. By incorporating fillers into the crystal structure, Group II contains the compounds (d) Ce\(_{0.13}\)Co\(_4\)Ge\(_6\)Se\(_6\) and (e) Yb\(_{0.14}\)Co\(_4\)Ge\(_6\)Se\(_6\) with electrons as the majority carriers. These compounds are compared with p and n-type CoGe\(_{1.5}\)Se\(_{1.5}\). [21] The affect of Fe doping and Ce and Yb filling on both the electrical and thermal properties will be described below.

Solid State Synthesis

All the skutterudite compounds were prepared by solid state reaction of the elements. Co powder (99.998 %, Alfa Aesar), Ge pieces (99.9999 %, Alfa Aesar), Se powder (99.999 %, Alfa Aesar), Fe powder (99.9 %, Alfa Aesar), Ce powder (99.9%, Alfa Aesar), and Yb chunks (99.9 %, Ames Labs) were used for the syntheses. The elements were loaded into silica ampoules according to the desired stoichiometric ratios of each specimen inside a nitrogen-filled glove box to minimize oxidation. The quartz tubes with the ampoules inside were then quickly transferred to a sealing station. Nitrogen gas was used to flush out the air inside the tubes. The tubes were then sealed under vacuum by using an oxygen/hydrogen fuse to melt the open end of the tube with a quartz
sealing cap. The furnaces used were profiled before the quartz tubes were loaded to ensure accuracy of the reaction and annealing temperatures, as described in Table 3.1.

After the initial reaction, the specimens were removed from the furnace, cooled down to room temperature slowly, ground to 325 mesh, cold pressed into pellets and then placed back into the furnaces for annealing. This annealing step was repeated once more to ensure homogeneity. The resulting pellets were again ground to fine powders inside a nitrogen atmosphere glove box and loaded into graphite dies for densification.

Table 1. Sample preparation procedures for (a) CoGe$_{1.5}$Se$_{1.5}$, (b) Co$_3$FeGe$_6$Se$_6$, (c) Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$, (d) Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$, and (e) Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Temperature (K)</th>
<th>Time</th>
<th>Condition</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
<td>(d)</td>
</tr>
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<td>1073</td>
<td>1073</td>
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<tr>
<td>Hot Press</td>
<td>973</td>
<td>973</td>
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</tr>
</tbody>
</table>

**Densification and Analyses**

Densification of all the specimens was accomplished by hot pressing at 973 K and 160 MPa for 3 hours under nitrogen flow resulting in dense, polycrystalline pellets. The densities of the pellets were then determined by measuring their dimension and mass. As a result, densities higher than 96% of the theoretical values were obtained for all specimens.
X-ray diffraction (XRD) and energy dispersive spectroscopy (EDX) were used to examine the purity, homogeneity, and chemical composition of the specimens. Powder XRD data were collected with a Bruker D8 Focus diffractometer in Bragg-Brentano geometry using Cu Kα radiation and a graphite monochromator. (Figure 3.1) The XRD data were examined by the Rietveld method using the GSAS suite of programs. [5] EDX analyses were accomplished with an Oxford INCA X-Sight 7582M equipped scanning electron microscope (JEOL JSM-6390LV). The homogeneity of the specimens was investigated from at least twelve data sets obtained from random positions across the dense pellet for each specimen, as well as from XRD analyses. The EDX analyses corroborated the stoichiometries from the refinement results, as will be discussed in the next chapter.

**Transport Properties Measurements**

After densification, polycrystalline specimens were cut into 2 x 2 x 5 mm³ parallelepipeds for low temperature transport properties measurements (ρ, S, and κ). Data were collected from the Novel Materials Laboratory’s custom-built transport properties measurement system from 12K to 300K.[41]

The surface of the specimens were polished using 800 SiC and 1200 SiC polishing papers. A number 80 drill bit (0.3429 mm diameter) was then gently and vertically touched one surface of each specimen twice, ~3mm apart, in order to make two divets for the differential thermocouples.
Figure 12. Powder XRD patterns for (a) CoGe$_{1.5}$Se$_{1.5}$, (b) Co$_3$FeGe$_6$Se$_6$, (c) Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$, (d) Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$, and (e) Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$ after hot pressing. An asterisk (*) indicates the GeSe impurity phase and the pound sign (#) indicates the Fe$_7$Se$_8$ impurity phase.

Ohmic contacts were achieved with 0.001” bare copper wires, on the nickel plated portions of each specimen. Following rinsing thorough with distilled water, an anodized aqueous solution nickel pen (Hunter Products) deposited a thin nickel metal layer over the negatively biased specimen, covering the intended electrical contact areas. A final DI water rinse was used to clean the remaining aqueous solution.
The nickel-plated areas were tinned using a Weller WES51 soldering iron, a custom 1/64” conical tip, acid-free flux, and Ostalloy 281 solder (42% Sn / 58% Bi alloy). This solder has a low solidus temperature, 138° C, thus providing quick and convenient soldering/desoldering of contact wires. It was used for soldering all the electrical contact wires.

A differential thermocouple and specimen thermocouple were made by arc melting Omega Engineering, Inc. 0.001” bare chromel and bare constantan wires in acetone to prevent oxidation. For the preparation of the heater, a 10 kΩ thick metal film ceramic resistor measuring 1.0 x 0.5 x 0.35 mm³ was first sanded with 800 SiC sand paper, removing the film contacts on the bottom face, before four 0.001” bare copper wires were soldered to the tinned contacts on longitudinally opposing sides of the specimen heater to provide the heater with current contacts and voltage contacts. This specimen heater was then mounted to the free end of the specimen. Thermocouples and the heater were mounted to the specimen by connecting with wet thermally conductive and electrically insulating Stycast Epoxy and drying in an oven under 100 °C for one hour.

After measuring the effective lengths, the difference in length between the two tips of the differential thermocouple and between the voltage leads, the specimen was mounted onto the measurement system that was in excellent contact with the custom-designed sample holder by indium foil. The specimen lead wires were then soldered to their respective pins using Ostalloy 281 solder. [41]
Figure 13. Illustration of the position of the contact wires and the specimen holder. The red wires represent the current input sourced by a Keithley 2400 SourceMeter, the blue wires represent the voltage output detected by a Keithley 2001 MultiMeter, and the green wires indicate the thermocouple wires.

**Resistivity**

The $\rho$ values of each specimen was measured using a four-probe method in which one pair of copper wires sources current through the specimen and a separate pair of copper wires measures the corresponding voltage drop. This eliminates discrete voltage contributions from lead wires and sample contacts. At each temperature the $\rho$ values are calculated by the equation

$$\rho = \frac{V}{I \cdot l_o}$$  \hspace{1cm} (22)
where $V$ is the measured voltage drop, $I$ is the current sourced through the sample, $A$ is the cross-sectional area of the specimen and $l_o$ is the effective length between the two voltage leads. Typically $l_o$ is set to $l_o \leq l - 2w$, where $l$ is the length of the specimen and $w$ is the thickness of the specimen, in order to ensure a homogeneous current flow where the voltage is measured. A 3% experimental uncertainty is estimated at room temperature.[41]

### Seebeck Coefficient

The $S$ values for each specimen was measured by relating the thermoelectric voltage to its imposed temperature gradient

$$ S = \frac{\Delta V}{\Delta T} = \frac{V_H - V_C}{T_H - T_C}, \quad (23) $$

where $V_H$, $T_H$, and $V_C$, $T_C$ are the voltages and temperatures of the hot side and cold side, respectively. The heater on the free end of the specimen generated a thermal gradient while the other end, soldered to the contact pad, served as the heat sink (recall Figure 1.3). At each stabilized temperature of interest, the heater then applied a small thermal gradient ($\Delta T = 2\%$ to $5\%$ of the stabilized specimen temperature) across the specimen. The potential difference was read by a Keithley 2001 Multimeter and then recorded as a function of the thermal gradient. As a result, the slope yielded $S$. The measured values included both the sample contribution as well as the contact wire contribution, which was subtracted from the measured value ($S_{\text{Specimen}} = S_{\text{Chromel}} - S_{\text{Measured}}$). The estimated uncertainty in $S$ is 6% at room temperature.[41]
**Thermal Conductivity**

Using our low temperature transport properties measurement system, when the temperature of the specimen is stabilized at the desired value, the temperature difference between the differential thermocouple represents the contribution from the specimen heater. Thus $\kappa$ is given by

$$\kappa = \frac{P}{\Delta T} \frac{l_o}{A} = \frac{I^2 R}{\Delta T} \frac{l_o}{A},$$

(24)

where $P$ is the power applied to the specimen by the heater which can be determined by the sourced current $I$, and the resistance of the heater $R$, $\Delta T$ is the thermal gradient, $l_o$ is the effective length between the two voltage leads, and $A$ is the cross-sectional area of the specimen.

Two heat shields were used to cover the specimen while employing the steady-state technique to determine $\kappa$. There are however losses involved in the measurements that should be accounted for or minimized.[42] Thus $\kappa$ is related to the true power that through the specimen responsible for the temperature gradient

$$\kappa = \frac{P}{\Delta T} \frac{l_o}{A} = \frac{P_{\text{total}} - P_{\text{loss}}}{\Delta T} \frac{l_o}{A}.$$ 

(25)

All the specimens showed a very small difference before and after estimating this radiation loss, an indication of the small heat loss in our system. The uncertainty of $\kappa$ was estimated to be 8% at room temperature.[41]
**Chapter Four:**

**Results and Discussion**

**Group I p-type specimens Co$_{4-x}$Fe$_x$Ge$_4$Se$_4$ with x=0, 1, and 1.5**

Although the atomic mass and ionic radius of Co and Fe are similar, Fe substitution for Co in CoSb$_3$ can affect the transport properties, including an reduction of $\kappa_L$.\cite{27, 28} Fe substitution for Co therefore becomes the main route for obtaining p-type skutterudites. Thus we investigated Fe doping in CoGe$_{1.5}$Se$_{1.5}$ skutterudite derivatives, to the best of our knowledge for the first time, as part of the continuing effort to explore different compositions of these skutterudite structure types.

This group of specimens was prepared as described in the previous section (Table 3.1). Reitveld refinement and elemental analyses were used to identify the structure and stoichiometry of the compositions. The refinement results indicated that the Ge sites in Co$_4$Ge$_6$Se$_6$ are partially occupied (95% occupancy). However, these crystallographic sites for the Fe containing compositions were fully occupied to over 99% occupancy. The observed and calculated XRD patterns and difference profiles for each specimen are given in Figure 2.11. As the Fe content increases there is a larger amount of the Fe$_7$Se$_8$ impurity phase present resulting in a larger difference between the observed and calculated XRD patterns.
Figure 14. Powder XRD data for (a) \( \text{Co}_4\text{Ge}_6\text{Se}_6 \), (b) \( \text{Co}_3\text{FeGe}_6\text{Se}_6 \), and (c) \( \text{Co}_{2.5}\text{Fe}_{1.5}\text{Ge}_6\text{Se}_6 \) including profile fit, profile difference, and profile residuals from Rietveld refinement.

Figure 4.2 shows the crystal structure of \( \text{CoGe}_{1.5}\text{Se}_{1.5} \) from the powder XRD refinement as an example. The small octahedral are formed by Ge and Se atoms. The Co atoms are located at the center of these octahedra, eight octahedra per unit cell, with two octahedral sharing a corner where the Ge or Se atom are located. The void in the center of the unit cell, surrounded by these octahedra, can contain filler atoms, as will be described in the second section of Chapter 4.

Figure 4.3 shows \( \kappa \) of \( \text{CoGe}_{1.5}\text{Se}_{1.5} \), \( \text{Co}_3\text{FeGe}_6\text{Se}_6 \), and \( \text{Co}_{2.5}\text{Fe}_{1.5}\text{Ge}_6\text{Se}_6 \) as a function of temperature. As expected, by introducing Fe substitution \( \kappa \) was reduced by Fe substitution.[27]
In order to identify the mechanism for such a reduction, the Debye approximation was used to fit the $\kappa_L$ data.

Figure 15. Crystal structure of CoGe$_{1.5}$Se$_{1.5}$ from powder XRD refinement. The figure on the right represents the unit cell of CoGe$_{1.5}$Se$_{1.5}$.

Figure 16. Thermal conductivity as a function of temperature for CoGe$_{1.5}$Se$_{1.5}$ ( ), Co$_3$FeGe$_6$Se$_6$ ( ), and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$ ( ).
The Debye model assumes an “elastically isotropic” and continuous solid, for example the atomic bonding is the same in all directions.\[29\] It further assumes that the cut off for elastic waves is limited to $3N$, where $N$ represents the degrees of freedom. This is reasonable since the longer wavelengths are dominant at low temperatures.\[29\] In the Debye model $\kappa_e$ is given by Equation (14) and $\tau_C^{-1}$ by Equation (15).

As described in Chapter 1, the terms in Equation (15) represent grain boundary scattering, point defect scattering, Umklapp scattering, and resonance scattering, respectively, however, since this group of specimens do not possess filler atoms no resonance scattering is possible here. The solid lines in Figure 4.4 are theoretical fits to the experimental data using this approximation. The fitting parameters were uniquely defined using a minimization of best sequence fit function, as compared to the data, yielding results with strong agreement with the experimental data.

![Figure 17. Lattice thermal conductivity as a function of temperature for CoGe$_{1.5}$Se$_{1.5}$ (○), Co$_3$FeGe$_6$Se$_6$ (□), and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$ (☑). The solid lines are fits to the data using the fitting parameters shown in Table 2.2 based on Equation (22) and (23).](image-url)
The fit parameters are uniquely defined using a minimization of the best sequence fit function, as compared to the data. The strongest agreement with the experimental data is presented in Table 4.1. All the specimens in this group were prepared under similar conditions. Thus the fitting resulted in similar grain sizes after densification, as indicated by the grain size parameter $L$ and confirmed using EDS. By substituting Fe for Co, disorder was introduced into the crystal structure. As a result the point defect scattering parameter $A$ for the Fe substituted specimens was an order of magnitude larger than that of $\text{CoGe}_{1.5}\text{Se}_{1.5}$. A higher Fe content corresponds to stronger disorder therefore stronger point defect scattering. This can be seen in Table 4.1 by the fact that the $A$ parameter for $\text{Co}_{2.5}\text{Fe}_{1.5}\text{Ge}_6\text{Se}_6$ is two times larger than that for $\text{Co}_3\text{FeGe}_6\text{Se}_6$.

There is no information on the Grüneisen parameters for these skutterudite derivative compounds therefore the effect of Fe substitution on $B$ is not clear. However, the $B$ values for the three specimens are in the same order of magnitude.

Low temperature $\rho$ measurements for $\text{CoGe}_{1.5}\text{Se}_{1.5}$, $\text{Co}_3\text{FeGe}_6\text{Se}_6$, and $\text{Co}_{2.5}\text{Fe}_{1.5}\text{Ge}_6\text{Se}_6$ are shown in Figure 4.5. The $\rho$ values decrease with increasing temperature for $\text{Co}_4\text{Ge}_6\text{Se}_6$ indicating typical thermally activated semiconductor behavior, while the $\rho$ values for $\text{Co}_3\text{FeGe}_6\text{Se}_6$ and $\text{Co}_{2.5}\text{Fe}_{1.5}\text{Ge}_6\text{Se}_6$ indicate a metallic temperature dependence, particularly below 150 K. Although $\rho$ for $\text{CoGe}_{1.5}\text{Se}_{1.5}$ is too large to be considered for thermoelectric applications, by introducing Fe substitution $\rho$ was reduced by approximately two orders of magnitude at room temperature, and even more at low temperatures, due to an increase in carrier concentration.
Table 2. Values of $k_1$ fit parameters as defined by Equation (18) and (19) for CoGe$_{1.5}$Se$_{1.5}$, Co$_3$FeGe$_6$Se$_6$, and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>L (μm)</th>
<th>A ($10^{-45}$ s$^3$)</th>
<th>B ($10^{-18}$ s/K)</th>
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<tr>
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</table>

Figure 18. Resistivity as a function of temperature for CoGe$_{1.5}$Se$_{1.5}$ ( ), Co$_3$FeGe$_6$Se$_6$ ( ) and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$ ( ).

Figure 4.6 shows the measured $S$ values of CoGe$_{1.5}$Se$_{1.5}$, Co$_3$FeGe$_6$Se$_6$ and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$. The Ge deficiency in Co$_4$Ge$_6$Se$_6$, determined from XRD refinement, and the Fe substitution in Co$_3$FeGe$_6$Se$_6$ and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$ increases the number of holes in the valance band. The $S$ values for Co$_4$Ge$_6$Se$_6$ increase rapidly with temperature above 200 K, a behavior that is similar to that observed previously,[21] while the $S$ values for Co$_3$FeGe$_6$Se$_6$ and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$ have a
linear dependence with temperature. At room temperature, $S$ decreases with increasing Fe content due to the increase in carrier concentration. Consistent with the $S$ data, Hall measurements indicated that holes are the majority carriers for all specimens, with room temperature carrier concentrations ($\rho$) of $2 \times 10^{18}$/cm$^3$ for CoGe$_{1.5}$Se$_{1.5}$, $9 \times 10^{19}$/cm$^3$ for Co$_3$FeGe$_6$Se$_6$ and $2 \times 10^{20}$/cm$^3$ for Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$. Together with the room temperature $\rho$ data, we estimate a carrier mobility of $5 \times 10^{-3}$ cm$^2$/Vs, $2 \times 10^{-2}$ cm$^2$/Vs and $1 \times 10^{-2}$ cm$^2$/Vs for CoGe$_{1.5}$Se$_{1.5}$, Co$_3$FeGe$_6$Se$_6$ and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$, respectively.

![Figure 19. Seebeck coefficient as a function of 1/T dependence for CoGe$_{1.5}$Se$_{1.5}$ (○), Co$_3$FeGe$_6$Se$_6$ (□), and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$ (△), with room temperature of 142 $\mu$V/K, 64 $\mu$V/K and 30 $\mu$V/K, respectively.](image)

In a single parabolic band model $S$ and $\rho$ are given by [37]

$$S = \pm \frac{k_B}{e} \left( \frac{(2 + r)F_{1+r}(\eta)}{(1 + r)F_r(\eta)} - \eta \right)$$

(22)
and

\[ p = \frac{4\pi(2m_e k_B T)^{3/2}}{h^3} \left( \frac{m^*}{m_e} \right)^{3/2} F_{1/2}(\eta) \]  \hspace{1cm} (23)

where \( r \) is the exponent of the energy dependence of the electron mean free path, \( \eta (= E_F / k_B T) \) is the reduced Fermi energy, \( E_F \) is the Fermi energy, \( F_r \) is the Fermi integral of order \( r \), \( m^* \) is the carrier effective mass, and \( m_e \) is the free electron mass.\,[38,39] The \( \pm \) signs in Eq. (1) are for holes (+) and electrons (–). For scattering from lattice vibrations (acoustic phonons) \( r = 0 \) and for ionized impurity scattering \( r = 2 \). In our estimate of \( m^* \) we used the intermediate value \( r = 1 \). From the room temperature \( S \) and \( p \) values we obtained \( m^* = 0.1 \ m_e \) for CoGe\(_{1.5}\)Se\(_{1.5}\), and \( m^* = 0.3 \ m_e \) for Co\(_3\)FeGe\(_6\)Se\(_6\) and Co\(_{2.5}\)Fe\(_{1.5}\)Ge\(_6\)Se\(_6\). These \( m^* \) values are approximately an order of magnitude smaller than that of the n-type rhombohedral skutterudite derivatives \,[21\] and are similar to what reported for skutterudite antimonides.\,[20\]  

Theoretical studies indicate that CoX\(_{1.5}\)Y\(_{1.5}\), with (X,Y) = (Ge,S), (Ge,Se), (Ge,Te), (Sn,S), (Sn,Se), and (Sn,Te), have relatively larger band gaps as compared with CoSb\(_3\)[23] due to splitting of the bands caused by the different chemical nature and electronegativity difference of the group 14 and 16 atoms. As a result, p-type skutterudite derivatives have \( m^* \) values in the range of 0.1 \( m_e \) to 0.2 \( m_e \).[23] The effective mass estimated for our CoGe\(_{1.5}\)Se\(_{1.5}\) specimen agrees with these theoretical calculations.\,[23] The relatively large band gaps also contribute to the low mobility and high \( S \) values for these materials. The fact that the Fe substituted specimens possessing higher \( m^* \) and carrier mobility is also in agreement with previous studies.\,[14-15, 44]
**Group II n-type specimens Ce_{0.13}Co_4Ge_6Se_6 and Yb_{0.14}Co_4Ge_6Se_6**

As discussed in the beginning of Chapter 2, one of the most interesting aspects of the skutterudite family of compound is the fact that they contain relatively large voids in their crystal structures. By incorporating guest atoms inside these voids, $\kappa_L$ can be reduced due to the introduction of phonon scattering centers. We studied the low temperature transport properties of Ce_{0.13}Co_4Ge_6Se_6 and Yb_{0.14}Co_4Ge_6Se_6 in order to investigate the fundamental properties of these partially filled skutterudite derivatives.

This group of specimens was prepared by the procedure described in the section 3(Table 3.1). Reitveld refinement and elemental analyses were used to identify the structure and stoichiometry of the compositions. According to the refinement results, Ce is partially occupied (13%) in Ce_{0.13}Co_4Ge_6Se_6, while the other sites are fully occupied. The Yb sites as well as both Ge sites have partial occupancy for the Yb-filled composition. The two Ge crystallographic sites refined to 98% occupancy while the Yb site refined to 14% occupancy in Yb_{0.14}Co_4Ge_6Se_6. The observed and calculated XRD patterns and difference profiles for each specimen are given in Figures 4.7.

As an example of the refinement results for the n-type group of specimens, Figure 4.8 shows the crystal structure of Yb_{0.14}Co_4Ge_6Se_6. Compared with Figure 4.2, the center of the unit cell here is occupied by Yb. In addition, by introducing fillers into the crystal structure the Ge-Se rings had smaller angles thus “tilting” the octahedra even more compared with unfilled specimens.
Figure 20. Powder XRD data for (a) Ce_{0.13}Co_{4}Ge_{6}Se_{6} and (b) Yb_{0.14}Co_{4}Ge_{6}Se_{6} including profile fit, profile difference, and profile residuals from Rietveld refinement.

Figure 21. Crystal structure of Yb_{0.14}Co_{4}Ge_{6}Se_{6} from powder XRD refinement. The figure in the right represents the unit cell of Yb_{0.14}Co_{4}Ge_{6}Se_{6}. 
Temperature dependent $\kappa_L$ for Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$ and Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$ are shown in Figure 4.9 together with that for unfilled CoGe$_{1.5}$Se$_{1.5}$. The solid lines are theoretical fits to the experimental data using the same approximation for the p-type group of specimen. The fitting parameters are shown in Table 4.2.

![Graph showing temperature dependent $\kappa_L$ values for Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$ and Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$, as well as that of the unfilled ternary composition. The solid lines are fits based on Equation (14) and (15). Reprinted from Reference 33.]

As shown in Table 2.3, the grain size parameter $L$ for these three specimens is very similar due to the fact that they were synthesized and densified using the same approach. The point defect scattering parameter $A$ is 5 or 6 times larger for the Ce and Yb-filled compositions than that of
CoGe$_{1.5}$Se$_{1.5}$, indicating strong mass fluctuation scattering due to disorder on the rare earth (RE) site. In addition, parameter $A$ for the Yb-filled composition is larger than that for the Ce-filled composition although the RE filler atom concentrations are similar. This is presumably due to the Ge vacancies in Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$. The fact that the Yb atom is heavier than the Ce atom may result in larger mass fluctuation between the RE and the lattice vacancy as compared to Ce, as also shown in a previous investigation. [20] Again, since no data for $\theta_B$, $\nu$, and the Grüneisen constant exist for these types of compositions the effect of RE filling on $B$ is not clear. The $C$ parameter is similar for both RE compositions. Because of the smaller atomic size and heavier mass of Yb compared to Ce, the “rattle” frequency $\omega_0$ of Yb in Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$ is smaller than that of Ce in Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$.

Compared with the reported $\omega_0$ values for RE$_x$M$_4$Sb$_{12}$ (RE = La, Eu, Yb and M = Co) and Yb$_x$Co$_4$Sb$_{12-y}$Sn$_y$, the $\omega_0$ value for both of these two specimens is relatively large.[20,34] The longest Sb-Sb distance in CoSb$_3$ is 6.70 Å,[35] much larger than that of Ge$_6$Se$_6$ (Ge-Ge 6.14 Å and Se-Se 6.36 Å) in CoGe$_{1.5}$Se$_{1.5}$. Thus it is clear that the RE atoms have more room to move in the Sb$_{12}$ “cage” as compared to that for the Ge$_6$Se$_6$ framework. As a result, Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$ and Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$ have larger $\omega_0$ values.

Temperature dependent $\rho$ data, shown in Figure 4.10, indicates that Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$ and Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$ have lower $\rho$ values than that of unfilled CoGe$_{1.5}$Se$_{1.5}$ due to their higher carrier concentration. Over the entire temperature range the $\rho$ values decrease with increasing temperature for both the Ce and Yb-filled specimens, indicating typical thermally activated semiconductor behavior. The solid line is a fit to the highest temperature data using $\rho = \rho_0 \exp(E_a / k_B T)$ where $E_a$ is the activation energy and $k_B$ is the Boltzmann constant. The fitting
results indicate that $E_a$ values are 0.07 eV for $\text{Ce}_{0.13}\text{Co}_4\text{Ge}_6\text{Se}_6$ and 0.05 eV for $\text{Yb}_{0.14}\text{Co}_4\text{Ge}_6\text{Se}_6$, and imply an activation energy ($E_g \sim 2E_a$) of 0.14 eV and 0.10 eV for the Ce and Yb-filled compositions, respectively. These estimated activation energies are relatively small compared with the reported values for $\text{CoGe}_{1.5}\text{Se}_{1.5}$ (0.34 eV), and close to that of $\text{CoSb}_3$ (0.10 eV).[21,36]

The negative sign for the $S$ values in Figure 4.11 for these two specimens indicates $n$-type conduction. Consistent with the $S$ data, Hall measurements indicated that electrons are the majority carriers for both specimens, with room temperature electron concentrations ($n$) of $5.0 \times 10^{19}/\text{cm}^3$ for $\text{Ce}_{0.13}\text{Co}_4\text{Ge}_6\text{Se}_6$ and $6.1 \times 10^{20}/\text{cm}^3$ for $\text{Yb}_{0.14}\text{Co}_4\text{Ge}_6\text{Se}_6$. These values are naturally higher than that of unfilled $\text{CoGe}_{1.5}\text{Se}_{1.5}$ ($3.5 \times 10^{18}/\text{cm}^3$).[21] From refinement results there are vacancies on the Ge sites in $\text{Yb}_{0.14}\text{Co}_4\text{Ge}_6\text{Se}_6$. Although the filling fractions of $\text{Yb}_{0.14}\text{Co}_4\text{Ge}_6\text{Se}_6$ and $\text{Ce}_{0.13}\text{Co}_4\text{Ge}_6\text{Se}_6$ are very similar there are more electrons per unit cell for the Yb-filled specimen. Together with a larger electron concentration, the vacancies on the Ge site may also contribute to lowering the mobility of $\text{Yb}_{0.14}\text{Co}_4\text{Ge}_6\text{Se}_6$ (0.51 cm$^2$/Vs at room temperature) as compared to that for $\text{Ce}_{0.13}\text{Co}_4\text{Ge}_6\text{Se}_6$ (1.13 cm$^2$/Vs at room temperature).

<table>
<thead>
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<th>specimens</th>
<th>L (μm)</th>
<th>A ($10^{-44} \text{s}^5$)</th>
<th>B ($10^{-18} \text{s/K}$)</th>
<th>C ($10^{-33} \text{s}^5$)</th>
<th>$\omega_0$ (THz)</th>
</tr>
</thead>
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<tr>
<td>$\text{CoGe}<em>{1.5}\text{Se}</em>{1.5}$</td>
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<td>4.7</td>
<td>6.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Ce}_{0.13}\text{Co}_4\text{Ge}_6\text{Se}_6$</td>
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<td>5.8</td>
<td>4.5</td>
<td>15</td>
</tr>
<tr>
<td>$\text{Yb}_{0.14}\text{Co}_4\text{Ge}_6\text{Se}_6$</td>
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<td>30</td>
<td>4.8</td>
<td>4.8</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 3. Values for the lattice thermal conductivity fit parameters as defined by Equation (18) and (19) for $\text{CoGe}_{1.5}\text{Se}_{1.5}$, $\text{Ce}_{0.13}\text{Co}_4\text{Ge}_6\text{Se}_6$ and $\text{Yb}_{0.14}\text{Co}_4\text{Ge}_6\text{Se}_6$. 
Figure 23. Temperature dependent electrical resistivity of Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$ and Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$, together with that of the unfilled ternary composition and CoSb$_3$.[21,36] The solid lines are fits of the form $\rho = \rho_0 \exp(E_a/k_B T)$ to the highest temperate data. Reprinted from Reference 33.

By using Equation (22) and (23), $n$ can also be used in Equation (23), $m^* = 2.7 \, m_e$ for Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$ and $m^* = 3.8 \, m_e$ for Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$ were obtained. These estimates indicate that the $m^*$ values for these compositions are relatively large, in agreement with previous reports.[9,21]
Figure 24. Temperature dependent Seebeck coefficient for $\text{Ce}_{0.13}\text{Co}_4\text{Ge}_6\text{Se}_6$ and $\text{Yb}_{0.14}\text{Co}_4\text{Ge}_6\text{Se}_6$, as well as the unfilled ternary composition. [21] Reprinted from Reference 33.

In conclusion, by introducing guest atoms into the crystal lattice, the electrical properties and the thermal conductivity were affected due to an increase in carrier concentration as well as an increase of both point defect scattering and filler-atom disorder scattering of phonons. This study indicates that the transport properties are tunable in filled variants of these skutterudite derivatives, and indicates possible potential interest for thermoelectric applications.
Chapter Five:
Summary and Future Work

Three p-type rhombohedral skutterudite derivatives, Co$_4$Ge$_6$Se$_6$, Co$_3$FeGe$_6$Se$_6$ and Co$_{2.5}$Fe$_{1.5}$Ge$_6$Se$_6$, and two n-type rhombohedral skutterudite derivatives, Ce$_{0.13}$Co$_4$Ge$_6$Se$_6$ and Yb$_{0.14}$Co$_4$Ge$_6$Se$_6$, were synthesized and their structure and low temperature transport properties were investigated. Fe substitution for Co as well as rare-earth filling greatly affected the transport properties, partly due to an increase in carrier concentration. The thermal conductivity was investigated by employing the Debye model with different phonon-scattering parameters. As a result, by introducing disorder into the crystal structure, the thermal conductivity of these compositions was reduced.

A combination of metal-site substitution together with guest fillers may be of interest for future work. A larger reduction in the thermal conductivity has been reported for multiple fillers as compared to single filler skutterudites. This is also to be expected here. In addition, the Ge-to-Se ratio in these compounds has a large affect on the transport properties, indicating another approach to further investigate materials with similar compositions for potential thermoelectric applications. This work was initiated in furthering an understanding of the underlying physics behind these compositions, and can thus impact other thermoelectric materials research.
References


