Chapter 6: CoSb₃ and Other Thermoelectric Materials with Optical Evidence of Multiple Bands

6.1 - Introduction

As has been a theme in previous chapters of this thesis, many of the best thermoelectric materials contain multiple valence and/or conduction bands. In this chapter, we will investigate a few examples where these features are directly observable in the optical properties. The first example of this will be for $CoSb_3$, which exists in a well-studied class of thermoelectric materials known as the skutterudites. Skutterudites have received a lot of attention in recent literature due to their ability to accommodate filler atoms, which can drastically lower their thermal conductivities (many authors attribute this to rattling of the atom within its cage). Combined with reasonable electronic properties, these materials have achieved good zTs of up to ~1.0 for p-type and 1.5 for n-type—resulting in a significant amount of academic and commercial interest. In this chapter, I explore Yb filled n-type $CoSb_3$ optically, electronically, and using *ab-initio* calculations to provide an alternative explanation for their good performance which utilizes multiple conduction bands that participate in transport (increasingly so at high temperatures), similar to the features observed in the IV-VI materials (Chapter 4). This is contrary to many literature reports which attribute the high zTs mainly to thermal conductivity reduction, while the electronic properties are not generally understated.

Beyond CoSb₃, one other group of materials have yielded optical evidence of multi-band behavior. Zintl compounds, which have inherently low thermal conductivity due to their structural complexity, show optical evidence of multiple band features. Unfortunately, in this case the electronic properties do not reflect this fact, but this is likely because the secondary bands are too far away to access at reasonable temperatures. However, this section indicates the presence of multiple bands and opens the door for future band engineering studies in this class of materials.

$6.2 - CoSb_3 - The Electronic Origin of High zT$

6.2a - Introduction

Among the best thermoelectric materials, *n*-type filled skutterudites have been widely studied after it was found that the addition of filler atoms (La, Ce, and others), which can be filled into the one void site per primitive cell, can lead to high *zT* by reducing the thermal conductivity while simultaneously doping the material [270-272]. The CoSb₃ skutterudite structure is the Im3 (space group 204) which has the general formula AX₃ where A=Co, Rh, Ir and X=P, As, Sb. In this structure, the metal atom is octahedrally coordinated by 6 X atoms, the arrangement of which in 3D space leads to interstitial sites that can be filled with an additional atom [273]. This interstitial site can be filled as in the case of LaFe₄Sb₁₂, which maintains charge balance by compensating the change from Co to Fe (which has one fewer electron) by inserting the interstitial lanthanum atom. In this chapter, I will discuss the binary CoSb₃, which is semiconducting as synthesized, but can be doped n-type by partially filling the interstitials with filler atoms. This filling is then accompanied by a reduction in thermal conductivity, leading to good thermoelectric performance.

Since the 1990's, there has been much progress in the field of *n*-type filled skutterudites as thermoelectric materials resulting in high *zT* values of around 1.3 (and up to 1.7) at 850 K for single filling (with filler atoms being La [274], Na [275], In [276-278], Yb [279, 280], Nd [281], and others) and multiple filling (In+Ba [282], In+Pr [283], In+Nd [284], Ba+Yb [285], Ba+La+Yb [286]) respectively. The excellent thermoelectric performance of skutterudites at intermediate temperature ranges (400-600 °C) and their superior mechanical properties [287-289] make them ideal candidates for heat-recovery applications in the automobile industry [290]. High *zT* in skutterudites is mostly attributed to the addition of the filler atoms and subsequent reduction in thermal conductivity [291-293]. These reductions are thought to be a result of the filler atom rattling within the interstitial space that it occupies [274]; however, at least part of the reduction is believed to be due to point-defect scattering of phonons [274]. With regards to the good performance in these materials, the increased *zT* is often attributed to the beneficial thermal properties as a result of filling, whereas the influence of the intrinsic electronic structure is often understated or ignored completely. Band engineering approaches to enhancing *zT* have been a theme of this thesis; it has become increasingly apparent that complex band structures including multi-valley Fermi surfaces [16, 21, 34], convergence of bands (PbSe as shown in Chapter 4 for Pb_{1-x}Sr_xSe [25], Mg₂Si [26], or PbTe [16]), or even threads of Fermi surface connecting band extrema (which will be discussed further in Chapter 7) [294, 295], are key features of many good thermoelectric materials.

Regarding the electronic structure in $CoSb_3$, Singh et al. has shown that valence band of $CoSb_3$ is very light with approximately linear (rather than the usual parabolic) character. The light bands explain the high mobility in lightly doped p-type $CoSb_3$ [296], but this does not explain why n-type $CoSb_3$ has substantially higher *zT* than p-type. For *n*-type $CoSb_3$ skutterudites, the non-parabolic (Kane) band concept has been borrowed to explain the apparent increase in effective mass measured by Seebeck coefficient (m_s^* as defined in previous chapters) as a function of doping level [271, 275, 281, 297-300]. However, I will show evidence of why the increasing effective mass cannot be due to non-parabolic bands, and that the effect is instead the result of multiple conduction bands.

While good thermal properties certainly contribute to the thermoelectric performance in $CoSb_3$, I show in this work that the electronic structure in $CoSb_3$ is also conducive to high *zT* for many of the reasons mentioned previously regarding band convergence and band engineering. In this chapter, I thoroughly investigate the electronic properties of Yb filled $CoSb_3$ in the context of complex conduction band behavior. I show both electronic and optical evidence of the existence of a second, multi-valley conduction band which increases the effective valley degeneracy. This band is also observed to shift as a function of temperature, resulting in its convergence towards

the conduction band minimum as temperature increases, resulting in important contributions to the performance of *n*-type filled skutterudites.

I would like to acknowledge contributions to this work from Yinglu Tang (Caltech Snyder Group), who will be an equally contributing first author on this paper once it is submitted, and from Luis Agapito (University of North Texas).

6.2b - Multi-conduction Band Behavior in *n*-type CoSb₃ Skutterudite

Multiple band effects in CoSb₃ materials are observable through several methods, both experimental and theoretical, as presented in Figure 6-1. A clear demonstration of complex band behavior is seen in the doping dependent Seebeck coefficient (Pisarenko plot at 300K) shown in Figure 6-1a. At low carrier concentrations (n_H less than ~1 × 10¹⁹ cm⁻³) CoSb₃ shows light mass behavior ($m_S^* \sim 0.7 m_e$); as the carrier concentration increases, the system transitions to a much heavier mass, requiring a second band with $m_S^* = 4.8 m_e$ in the heavily doped regime (larger than 3×10^{20} cm⁻³). In the degenerate limit the relationship between *S*, m_S^* , and *n* can be described by the degenerate limit of the Mott relation [301]:

$$S = \frac{2k_B^2 T}{3e\hbar^2} \left(\frac{\pi}{3n}\right)^{2/3} m_S^* (1+\lambda)$$
 Equation 6-1

where λ is the scattering parameter ($\lambda = 0$ for acoustic phonon scattering, which is quite common above 300K and is most appropriate for CoSb₃) and m_s^* is the density of states (DOS) effective mass obtained from Seebeck measurements using the single parabolic band (SPB) model (method detailed in Chapter 2). By considering two conduction bands and one valence band in a three-band transport model with a conduction band offset (ΔE) of ~0.08 eV, consistent with optical measurements in this work, we capture the behavior of both the lightly and the heavily doped regions (Black line in Figure 6-1a). In addition to the 300 K Seebeck coefficient, several other experimental and theoretical results indicate multi-band behavior [302-307].







Figure 6-1: a) Pisarenko plot of Seebeck coefficient vs Hall carrier concentration at 300K. Black line is a twoband model with density of state effective mass for the light and heavy bands being 1.1 m_0 and 3.9 m_e , respectively. Orange and red lines are for single parabolic band models with the individual band masses. b) The DFT calculated electronic band structure for CoSb₃. c) Fermi surface calculation for Fermi levels 0.12 eV above the conduction band edge. d) Room temperature optical absorption measurement (Kubelka Munk function) with estimated joint density of states from DFT.

The calculated electronic band structure is consistent with an m_s^* that becomes gradually heavier as long we consider not only the primary conduction bands (Γ point), but also the bands higher in energy (labelled CB₂ in Figure 6-1b) for heavily doped CoSb₃. In CoSb₃, the *ab-initio* density functional theory (DFT) calculated band structure (Figure 6-1b) shows a direct band gap at the Γ point ($E_{g,\Gamma-\Gamma} = 0.23 \text{ eV}$), which yields a triply degenerate (N_v =3) conduction band edge. As a result of the heavily doping (and relatively low mass for CB_{Γ}), the Fermi level quickly moves deep into the conduction band, allowing a large population of electrons to develop in secondary conduction bands, i.e., CB₂. Our calculations show that this secondary conduction band (CB₂) begins about 0.12 eV above the conduction band edge along the $\Gamma - N$ line. The calculated isoenergy Fermi surface for a Fermi level just inside of CB₂ (Figure 6-1c) is also consistent with previous Fermi surface calculations by Chaput et al which show a highly degenerate Fermi surface with ~12 pockets (although they do not discuss its significance to the electronic properties beyond the Hall coefficient, r_H) [308]. Regarding the CB₂ ($\Gamma - N, N_v = 12$) minima, only PbTe, which reaches a maximum zT of ~2 [16], has such a high value of N_v ; this high degeneracy is also found to play a crucial role in the high temperature Seebeck and zT values. Modeled zT in Figure 6-4c shows that much of the zT is due to this high valley degeneracy band, which will be discussed later in this work.

Additional conduction band minima observed along $\Gamma - F$ (N_v =24, 0.012 eV above CB₂) and $\Gamma - H$ (N_v =6, 0.034 eV above CB₂) have high degeneracy and likely also contribute to thermoelectric transport. Even though Chaput et al. presented Fermi surfaces that show the formation of threads (along the $\Gamma - F$ direction) connecting the $\Gamma - N$ pockets (as shown in Figure 6-1c), this second region of complexity is generally not plotted in DFT calculations because the *F* point is not a common symmetry point in the $Im\overline{3}$ space group's Brillouin zone. A third set of bands at the *H*-point (triply degenerate each with N_v =1) lays ~0.08 eV above the $\Gamma - H$ minimum. Other DFT calculations from Puyet et al. suggest a secondary conduction band, but they show a qualitatively different conduction band structure (with the primary minimum at *H*) [305, 306]. Despite the complex secondary conduction band structure, simply considering two conduction bands (CB_{Γ} and CB₂) with their appropriate degeneracies seems to qualitatively capture the Seebeck Pisarenko behavior (Figure 6-1) and the optical results.

In support of thermoelectric transport and DFT calculations, multi-band features in CoSb₃ can be directly observed by IR optical absorption. Optical absorption edge spectra for a nearly intrinsic sample of CoSb₃ ($n_H = 1.7 \times 10^{17} cm^{-3}$) shows two distinct features (Figure 6-1d). The lower energy transition (which begins at ~0.16 eV optically and is computed to be 0.23 eV from DFT) is likely associated with the direct, $\Gamma - \Gamma$ transition; the second transition (which begins at ~0.3 eV optically, 0.34 eV from DFT) indicates the onset of a $\Gamma - CB_2$ transition. While direct transitions often result in more than 10x as strong of absorption when compared to indirect ones

[48], it is important to remember that the transition rate is also proportional to the density of states. Because both VB_{Γ} and CB_{Γ} are extremely light (see density of states in Figure 6-1b, right panel), the $\Gamma - \Gamma$ transition, despite the fact that it is a direct transition, may occur with a lower intensity than the $\Gamma - CB_2$. I roughly estimate the strength of all transitions by calculating the joint density of states (JDOS, inset Figure 6-1d), which shows reasonable agreement with the two slopes observed in the optical measurements.

Other possibilities exist for the two distinct absorption edges which should be considered. First, a shallow absorption feature before the primary gap can be observed either in the case of intrinsic disorder/alloying in the sample (Chapter 4, PbSe/SrSe alloys showed long Urbach edges) or by intrinsic defect states which lay in the gap. However, because optical measurements were performed on the undoped sample that showed nearly intrinsic behavior, we do not expect the effects due to alloying or disorder. The possibility of a deep, intrisnic defect state laying within the band gap is possible; to exclude this as a possibility a series of lightly doped samples was also measured. I measured both extrinsically doped (filled with Yb or Na) and intrinsically doped (Co rich, Sb rich, Co poor, Sb poor) to encourage any intrinsic or extrinsic defect states to grow in number. Absorption edge measurements indicated no appreciable change in the strength of transition 1 relative to transition 2 that was not consistent with the addition of free carriers into the sample alone; therefore, I conclude that transition 1 is not a result of defect states.

Historically, optical measurements in the skutterudite system have been limited to Ackermann and Wold, who report an optical band gap for CoP₃ of 0.45 eV; they note that CoSb₃ and CoAs₃ do not show an absorption edge [309]. This was likely because the lowest light frequency that they had measured was 0.4 eV (our results suggest a lower band gap). Other optical measurements have focused on very low frequencies (<0.1 eV) in order to probe optical phonons [310, 311]—just missing the frequency range important for interband transitions. One recent thesis report by Ni shows that photoacoustic measurements on undoped CoSb₃

compounds can yield an absorption edge around 0.3 eV [312] (although he is not able to detect the absorption due to transition 1 that we observe here). In skutterudite systems other than CoSb₃, the literature has been sparse regarding optical absorption edge data, although Slack did publish a result for IrSb₃ which suggested a large optical gap (more than 1 eV) [313]. Optical measurements have also been performed over a wide range of frequencies by Matsunami et al. on Ce-filled skutterudites (with Fe, Ru, and Os rather than Co); these show band gaps within 0.2-0.3 eV, although additional analysis regarding other the nature of these interband transitions near the fundamental absorption edge is not discussed [314].

6.2c - Effective Mass in Systems with Non-parabolic Bands

The unexpectedly high thermopower at high carrier density in Yb_xCo₄Sb₁₂ observed in the Pisarenko plot of Figure 6-1a can also be represented as an increase in m_s^* (the Seebeck effective mass) as a function of carrier concentration as shown in Figure 6-2a. This apparent increase in effective mass with doping has previously been attributed to highly non-parabolic (Kane) bands [281, 315, 316] rather than multi-band effects. A non-parabolic dispersion (shown in Figure 6-2b, Equation 6-2) can arise as a result of interaction between the valence and conduction bands, which is common in narrow gap semiconductors, which can be described using $k \cdot p$ perturbation theory [58, 63, 64] (As mentioned in Chapter 2 and 3). Such bands are often described by the dispersion relation where the band is approximately parabolic (with band edge effective mass m_0^*) near the band edge, but becomes more linear as the electron energy, *E*, become larges large relative to the band gap *E*_q.

$$E\left(1+\frac{E}{E_g}\right) = \frac{\hbar^2 k^2}{2m_0^*}$$
 Equation 6-2

here *k* is the electron wave vector. This relation is expressed in terms of dimensional quantities, unlike the non-parabolic models in previous chapters which the dimensionless: $\beta = \frac{k_B T}{E_g}$ and $\epsilon = E/k_B T$. For non-parabolic bands, effective mass is not well defined because it can be derived from a number of classical relationships. In non-parabolic transport theory the commonly used energy dependent effective mass, derived from the electron momentum, is

$$m_P^*(E) = \hbar^2 k \left(\frac{dE}{dk}\right)^{-1} = m_0^* (1 + \frac{2E}{E_g})$$
 Equation 6-3

This is a different definition than that found in most solid state physics textbooks $m^* = \hbar^2 \left(\frac{d^2 E}{dk^2}\right)^{-1}$, which relates the effective mass to the band curvature directly. Many common semiconducting materials are reported to show $m^*(E)$ increasing with energy (Fermi level, E_F), including InSb [317], InAs [318], GaAs [319], PbTe [320], and others in a variety of different measurements, including electrical susceptibility (measured using optical reflectance) [320, 321], Shubnikov-De Haas/De Haas-Van Alphen oscillations [322], Faraday rotation [317, 318], and combined galvano thermomagnetic measurements (Seebeck and Nernst coefficients) [323]. In general these measurements are able to provide an estimate of the effective electronic mass, which is then compared to $m_P^*(E)$ of Equation 6-3 to determine the degree of non-parabolicity.



Figure 6-2: Effective mass calculation (equivalent single parabolic band effective mass) in a) n-type CoSb3 computed for experimental data along with the three-band model. The two individual band masses are also plotted to show the transition between them. b) Parabolic and Kane dispersions plotted with the same band edge effective mass showing the increasing effective mass (as the Kane band becomes linear). c) Seebeck Pisarenko plot for both Kane and Parabolic bands (full, Fermi integral calculation) illustrating that the Pisarenko mass actually decreases for Kane bands at high carrier concentration.

For thermoelectric materials we frequently define $m_S^*(E)$ from measurements of Seebeck coefficient and Hall carrier concentration ($n_H = 1/eR_H$) as the equivalent parabolic band mass that would give the measured Seebeck coefficient with the measured n_H (assuming $\lambda = 0$ from acoustic phonon scattering commonly observed in TE materials at 300K and above). In CoSb₃, this carrier concentration dependent effective mass $m_s^*(E)$ is observed to increase in both *n*-type (Figure 6-2a) and *p*-type materials, which is commonly attributed to band non-parabolicity using Equation 6-2 and Equation 6-3 [271, 315, 316, 324]. However, we must realize that these are two distinct definitions of effective mass that, in this case, are both qualitatively and quantitatively different. The degenerate limit of the Seebeck coefficient for a material whose bands display a Kane dispersion (the equivalent of Equation 6-1 obtained by applying Equation 6-2) can be expressed as [301, 325]:

$$S = \frac{2k_B^2 T}{3e\hbar^2} \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} m_P^*(E)(1+\lambda-\phi)$$
 Equation 6-4

where and additional correction factor, $\phi = \frac{\frac{4E}{E_g} \left(1 + \frac{E}{E_g}\right)}{\left(1 + \frac{2E}{E_g}\right)^2}$, has been added to the equation for that of a

parabolic band (Equation 6-1). For a general scattering mechanism, Equation 6-4 can be simplified upon substation of $m_P^*(E)$:

$$S = \frac{2k_B^2 T}{3e\hbar^2} \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} m_0^* \left(\lambda \left(1 + \frac{2E}{E_g}\right) + \frac{1}{1 + \frac{2E}{E_g}}\right)$$
 Equation 6-5

In the case where $\lambda = 0$, as is commonly found in TE materials, the m_s^* mass in a Kane band should actually decrease according to:

$$m_S^*(E) = \frac{m_0^*}{1 + \frac{2E}{E_a}}$$
 Equation 6-6

Thus the Seebeck mass, as computed from most thermoelectric studies, does not necessarily increase with doping or Fermi level as the momentum mass. The Seebeck effective mass is

derived by inspection when comparing Equation 6-5 for the non-parabolic band and the expression for the parabolic band (Equation 6-1).

The η -dependent Seebeck effective mass can also be derived for alternative scattering mechanisms as presented in Figure 6-3a. Here, we can see that only for the case of acoustic phonon scattering does the mass decrease in the degenerate limit. All other scattering mechanisms show an increase. In this sense, it is not difficult to understand why Equation 6-3 is so widely used to show increasing effective mass with chemical potential over a wide range of measurement techniques (which includes thermomagnetic and thermoelectric measurements, such as the Seebeck coefficient). While I do not dispute the fact that measurements that probe the conductivity effective mass (m_c^*) should increase with reduced Fermi level because the density of states for a Kane band is in fact larger (as evidenced by the lower curvature in Figure 6-2b at higher energies), I am saying that this effect is cancelled out when considering the Seebeck coefficient and the m_s^* (Figure 6-2c and Figure 6-3a) in the acoustic phonon scattering ($\lambda = 0$) case. If we consider some literature data for systems that are known to show Kane-like behavior, we can observe this trend. The m_s^* is extracted using (zero field) Seebeck Pisarenko data (S vs $n_{\rm H}$) from several sources in InSb [64, 326] and InAs [64], and the results are plotted in Figure 6-3b. It has been observed that the primary mechanism for scattering in these materials is by polar optical phonons that have an $E^{1/2}$ energy dependence ($\lambda = 1$), indicating that the effective mass should increase as shown in Figure 6-3a. In fact, experimental results show that the mass does increase with doping level and that Equation 6-5 works reasonably with the substituted room temperature band gaps of 0.35 and 0.18 eV and band edge effective masses of 0.03 and 0.018 m_e for InAs and InSb, respectively. In order to investigate the hypothesis of whether m_s^* increases with increasing chemical potential, we should consider a system where acoustic phonon scattering dominates.

Doping dependent m_s^s is also considered for PbTe, PbSe, and SnTe, which are known to show acoustic phonon scattering at room temperature, as shown in Figure 6-3c. n-type PbTe and PbSe both show a doping-dependent effective mass that does not change too much with doping level (PbTe shows ~10% increase, while PbSe stays relatively constant). SnTe and p-type PbTe, however, show a decreasing mass with doping. These materials show a mass that decreases from ~0.2 and ~0.5 m_e in the lighter doped samples to to 0.1 m_e and 0.32 in the more heavily doped samples in SnTe and PbTe respectively (before the effects of the second bands are reached). As shown in Chapter 4 of this thesis, both p-type SnTe and PbTe are known to exhibit multi-band behavior with a secondary valence band about 0.4 and 0.12 eV below the primary at room temperature, respectively; however, in this plot, I have compiled data where the Seebeck coefficient still decreases with doping. These results seems to support our claim in Equation 6-6 that the Seebeck effective mass does decrease with doping level, although it is not clear why ntype PbTe and PbSe do not obey the same trends. In order to confirm the result, this analysis should be extended to other systems, but it is difficult to find quality Seebeck data across a range of doping for materials that show both Kane band behavior and acoustic phonon scattering. However, as more information is gathered, this effect could be investigated further.





Figure 6-3: a) Calculated theoretical effective mass (ratioed to the value for reduced Fermi level at the band edge) derived using the Mott relation for different scattering mechanisms (Equation 6-5); the dashed line indicates an energy independent effective mass. A $\beta = \frac{k_B T}{E_g}$ value of 0.083 (consistent with PbTe at 300K) was used. b) Calculated SPB Seebeck effective mass (m_s^*) versus the reduced chemical potential calculated using the SPB model (η_{SPB}) for experimental examples at 300 K (InAs [64] and InSb [64, 326]) which are believed to be dominated by polar scattering. c) m_s^* versus η_{SPB} for n-type PbTe [28], p-type PbTe [34], n-type PbSe [65], and p-type SnTe [128]. The solid lines in B and C indicate the best fit of the band edge mass along with the appropriate scattering mechanism plugged into Equation 6-5.

Even though $m_p^*(E)$ increases with energy in a Kane band, I have shown that in CoSb₃, we expect that the Seebeck coefficient and $m_s^*(E)$ should actually decrease relative to that of a parabolic band in the degenerate limit, as shown in Figure 6-2c. This may be surprising because, according to the Mott relation (Figure 6-1), a higher density of states leads is often expected to result in a higher Seebeck coefficient. Instead Equation 6-6 shows that the Kane band dispersion, and linear bands in general, does not benefit thermoelectric performance relative to a parabolic band with the same band-edge effective mass. For CoSb₃, Equation 6-6 demonstrates that the increasing m_s^* in Figure 6-2a is not evidence of Kane-type behavior, but rather that multiple conduction bands are necessary to explain the properties of CoSb₃ (as evidenced by the fitting performed in Figure 6-1a where 2 parabolic conduction bands are considered).

6.2d - Band Convergence in CoSb₃—High Temperature Transport Properties

We have shown evidence that a second band is required to explain the room temperature transport and optical properties. However, it is at high temperatures that the performance of CoSb₃ excels. At high temperatures, the electronic structure of CoSb₃ is expected to be even more exceptional as optical absorption edge measurements indicate that the two conduction bands approach each other with an extrapolated $T_{cvg} \approx 900 \, K$. The effective valley degeneracy is further increased as a result of the multi band behavior (even below 900 K) to $N_v \approx 12 - 15$. The optical absorption measured from 20 – 450 °C clearly shows the stronger Γ – CB_2 absorption edge decreasing in onset energy (Figure 6-4a). The extrapolated absorption edges (Figure 6-4b) indicate that the primary ($\Gamma - \Gamma$, direct) transition does not shift as much with temperature (~- 0.6×10^{-4} eV/K, and actually is overtaken by free carrier absorption at high temperatures), while the secondary band $(\Gamma - CB_2)$ shows a clear temperature dependent decrease in energy at a rate of $\sim -2.0 \times 10^{-4}$ eV/K. Depending on the method of extrapolation, the resulting estimations of the band gap were slightly different, which resulted in a range of possible values for the primary (Γ – Γ) and secondary ($\Gamma - CB_2$) transitions indicated by the error bars in Figure 6-4b (the details of which are described in the methods section). Figure 6-4b shows that as the temperature increases, CB_{Γ} and CB_2 are becoming closer in energy. As the two bands, CB_{Γ} and CB_2 , become closer in energy (i.e., differ by less than 2 $k_B T$ for T>400 K), both bands will contribute significantly to thermoelectric transport and improve the thermoelectric quality factor and zT in the same way that band convergence enables high zT in p-type PbTe [15, 16].

The high temperature zT reflects this conclusion; Figure 6-4c shows the carrier concentration dependent zT for a series of Yb-doped samples at 800 K along with the calculated results of a three-band model (two converged conduction bands, assuming $\Delta E \approx 0$). From this plot, we can see the benefits that having a second conduction band allows, resulting in a significantly higher zT than the primary conduction band at Γ can provide alone. If we consider

both the primary (CB_{Γ} , N_{v} =3) and the secondary band (CB_{2} , $N_{v} = 12$) in the context of band engineering and the quality factor $B = \frac{2k_{B}^{2}h}{3\pi} \frac{N_{v}C_{L}}{m_{c}^{*}E_{def}^{2}\kappa_{L}}T$ ($m_{\Gamma,d}^{*} \approx 0.7$, $m_{CB_{2},d}^{*} \approx 4.8$ at 300 K), we can see that B_{CB2} is about four times that of B_{Γ} (as indicated by the much larger maximum zT in Figure 6-4c at 800 K). Because CB_{Γ} and CB_{2} are converged at high temperatures ($\Delta E = 0.2 k_{B}T \approx 0$ for 800 K), the overall quality factor is enhanced by the presence of a second band since both pockets can be thought to conduct in parallel, thereby increasing the electrical conductivity without being detrimental to the Seebeck coefficient (in the limit of converged bands, $B_{eff} = B_{1} + B_{2}$ [327]). At 800 K, bipolar effects are significant as a result of the highly mobile valence band and relatively narrow gap—reducing the overall zT, especially at the lower carrier concentrations. Future studies regarding CoSb₃ might build on this understanding by attempting to shift these bands together at lower temperatures to provide a further zT enhancement, as was the case for PbSe/SrSe alloys shown in Chapter 4.





Figure 6-4: a) Temperature dependent optical absorption edge spectrum for $CoSb_3$ from 25 to 400°C. b) Temperature dependent extrapolated band gap for the direct $(E_{g,\Gamma-\Gamma})$ and indirect $(E_{g,\Gamma-CB_2})$ transitions, error bars represent a range of possible values depending on the extrapolation technique, dashed line is a continuation of the low temperature behavior of the direct gap which is overcome by free carriers for T>200°C. c) Experimental data represents zT (at 800 K) vs. room temperature n_H, along with the corresponding results for the three band model $(\Delta E = 0)$ shown as the black line. The individual band contributions from CB_{Γ} and CB_2 are computed as shown in the methods section.

Temperature-dependent optical absorption spectra in lightly doped samples can also yield other interesting information in the form of absorption due to inter-conduction band transitions [116, 127, 328-330]. Temperature-dependent absorption spectra were measured for a lightly Ybdoped (Co₄Yb_xSb₁₂, x=0.0025, $n_{H,300K} = 6.8 \times 10^{17} \text{ cm}^{-3}$) sample as presented in Figure 6-5. Here, the small amount of doping allows a small population of electrons in the primary conduction band which can participate in interband transitions to the secondary conduction band, CB₂. This feature is not observable upon further Yb doping because the free carrier absorption from intraband transitions increases too much. The free carrier contribution (which is expected to decay with $(\hbar\omega)^{-2}$ as discussed in Chapter 3), is fit using a power law (dashed lines in Figure 6-5a). This feature is subtracted to show the growing interband contribution as temperature increases in Figure 6-5b. Following Spitzer and Fan [329], I also consider the possibility that these features may arise from transitions to or from in-gap defect states. If we consider the free carrier absorption from the intrinsic sample (Figure 6-4a) at high temperatures, we might expect to see some of these features. At high temperatures, the intrinsic sample does indicate a small bump between 0.1 and 0.15 eV (where valence-conduction band transitions occur) relative to the decaying free carrier absorption. Another feature is observed in the intrinsic sample at 0.05 - 0.1 eV which exists even at room temperature (above the relatively flat free carrier background) and grows larger as temperature increases; however, it is difficult to resolve the difference between this feature and the growing free carrier absorption. To confirm the character of the intrinsic sample's features, better resolution at lower photon energies would be preferred (0.01 - 0.2 eV). These measurements have been performed to investigate optically active phonon modes in the Far IR (100-400 cm⁻¹, 0.001 – 0.05 eV) by Kliche et al [310], and it is possible that the 0.05-0.1 eV feature is related to these phonon modes.





Figure 6-5: Temperature-dependent absorption edge measurements in a lightly Yb-doped (x=0.0025) CoSb₃ sample from 100-400°C. a) Raw Kubelka Munk transformed absorption data an arrow indicates the possible interconduction band absorption feature. Dashed lines indicate a power law fit for the free-carrier absorption. b) Resulting spectra after subtracting the free carrier contribution (FC) and normalizing, and an that arrow indicates the growing inter-band contribution.

6.2e - Conclusion

A unified picture explaining the extraordinary thermoelectric properties of skutterudites has emerged from a combined analysis of transport measurements, optical absorption, and theoretical calculations on a series of Yb_xCo₄Sb₁₂ samples. The primary light conduction bands at Γ , and have a good thermoelectric quality factor, but they are significantly aided by a secondary conduction band with extremely high valley degeneracy $N_v = 12$. At high temperatures these two bands converge, enabling the extraordinarily high zT > 1 that is observed in many CoSb₃ based skutterudites with a variety of filling and doping elements. The contribution of band convergence to the performance at high temperatures suggests that band engineering methods to converge the two conduction bands at lower temperatures would improve the low temperature zT. The analysis of linear and Kane bands presented here suggests that such non-parabolic band dispersions do not lead to an increase in thermopower (Seebeck coefficient) and are not beneficial to thermoelectric performance.

6.2f - Methods

Sample Synthesis

Samples were prepared by a process of melting and quenching followed by annealing at various temperatures for one week in order to achieve the equilibrium state, with details described previously [331] (and in Chapter 2 of this thesis). Phase purity was checked with SEM and SEM analysis in the same way as described in previous work [252, 276, 331]. Annealed samples were hot pressed according to the procedure outlined in Chapter 2.

Electrical transport properties, including electrical conductivity (σ) and Seebeck coefficient (*S*) were measured using the ZEM-3 (ULVAC Co. Ltd.) apparatus under a helium atmosphere from 300 to 850 K. Thermal conductivity (κ) was calculated using $\kappa = dD_T C_P$, with the thermal diffusivity D_T measured along the cross-plane direction by the laser flash method (Netzsch LFA 457) under argon flow with the Cowan model plus pulse correction. The specific heat capacity C_P was determined using the Dulong - Petit law $C_P = 3k_B$ per atom throughout the temperature range 300K to 850K.

Optical Absorption Edge

DRIFTS measurements were performed both at room temperature and high temperature for a series of CoSb₃ samples according to the details outlined in Chapter 2 of this thesis. Different extrapolation techniques led to different values of the band gap, hence the error bars in Figure 6-4b. First, regarding transition 1 (believed to be the direct gap, $\Gamma - \Gamma$ transition), several extrapolation techniques were considered. Linear regions were obtained for the three extrapolation techniques direct (α^2), indirect ($\alpha^{1/2}$), and forbidden [43] ($\alpha^{2/3}$) transitions, each giving a slightly different value of the band gap, the direct being the largest at around 0.23 eV. Because PbX (Chapter 4) also showed linear absorption regions for both direct and indirect transitions, I concluded that the direct gap extrapolation should be used (Figure 6-4b orange circles). The error bars in the figure correspond to the actual onset of absorption (as determined through linear extrapolation to the minimum), which should give a good lower bound for the value of $E_{g,\Gamma-\Gamma}$. With increasing temperature, the estimate for the direct gap did not change much (approximately constant at 0.22 eV). At high temperatures (T>200°C), the optical absorption spectra contained a considerable amount of free carrier absorption which overshadowed the first transition (as indicated by the dashed line above these temperatures). The free carrier absorption was fit to a power law and subtracted from the Kubelka Munk function in order to perform the absorption edge extrapolation fitting.

Regarding Transition 2, it was fit after subtracting both the free carrier absorption and either the direct extrapolation or linear extrapolation from transition 1 from the spectrum. This transition was fit as an indirect gap using either Tauc method, $(\alpha\hbar\omega)^{1/2}$, or simply $\alpha^{1/2} \propto$ $(\hbar\omega - (E_g \pm E_{ph}))$ (both gave similar results for the gap). This method yielded two slopes which, according to theoretical analyses, indicate the onset of phonon absorption (-*E*_{ph}) and phonon emission (+*E*_{ph}) [43]. The band gap was extracted as either half-way between the absorption and emission intersections or simply as the emission intersection (as indicated by the symbols and error bars respectively in Figure 6-4b).

The joint density of states (JDOS) was computed numerically using the density of states (Figure 6-1b, right side). The JDOS was estimated using $JDOS(\hbar\omega) = \int \int \sqrt{D_{VB}(E_{VB})D_{CB}(E_{CB})}\delta(E_{CB} - E_{VB} - \hbar\omega) dE_{VB}dE_{CB}$ where $D_{VB,CB}$ is the density of states of the conduction or valence band respectively and δ is the Dirac delta function (selecting only energies where the valence and conduction band energies are separated by the desired photon energy).

Band Model

Here I consider transport properties of $Yb_xCo_4Sb_{12}$ using a rigid band approximation [332], meaning that the conduction band structure does not significantly change with doping (Yb content) from that of unfilled CoSb₃. Experimentally, similar electronic properties are obtained whether CoSb₃ is doped through filling or by substitution on the Co or Sb sites [281, 333] (both showing optimum thermoelectric performance at about 3×10^{20} cm⁻³ or 0.5 electrons per unit cell) [286, 334, 335] which justifies the use of the rigid band model. In other thermoelectric materials such as PbTe, rigid band models have been used quite successfully and have been confirmed theroetically [105]. Filled Yb_xCo₄Sb₁₂ is shown theoretically to be an essentially rigid band up to *x*=0.25 (0.5 electrons per unit cell [335]) although deviations appear at higher concentrations and for different fillers [305, 306].

In this work, a three band transport model was used to calculate the thermoelectric properties for CoSb₃ at *T*=300 and 800 K. The properties were calculated assuming acoustic phonon scattering [58] for all bands by solving the chemical potential dependent Boltzmann transport equations detailed in Ravich's appendix [58] for non-parabolic bands (parabolic bands were modelled assuming $\beta = 0$). The appropriate transport integrals were computed numerically (Python) to determine the η -dependent Seebeck, mobility, carrier concentration, etc. for each band [24]. The overall properties computed using conductivity weighted averages given by Putley et al. (as detailed in Chapter 2 for multi-band semiconductors) [62] for a system of two conduction bands (*CB*_r and *CB*₂) and one valence band.

We determine the room temperature density of states effective masses of CB_{Γ} and CB_2 to be 0.7 and 4.8 m_e with deformation potentials of 37.2 and 20.4 eV, respectively, and a band offset of 0.08 eV. The valley degeneracies for these bands were assumed to be 3 and 12, respectively. The anisotropy factor was assumed to be 5.0 for CB_{Γ} to reflect the three widely varying effective masses of the converged bands at the conduction band minimum. Including the valence band in the calculations was necessary (particularly at high temperatures); the best fit of its parameters were found to be: $N_{\nu} = 1$ (valence band maximum exists at Γ), $m_d^* = 0.6 m_e$, $\beta = 0$ (parabolic), and $E_{def} = 7.8$ eV with a band gap of 0.22 eV. At high temperatures (800K), the conduction band offset was taken to be $\Delta E = 0.0 \text{ eV}$, in accordance with the optical observation of band convergence. The density of states effective masses were fit to 0.42 and 2.88 m_e with deformation potentials of 44.5 and 24.4 eV for the CB_{Γ} and CB_2 , respectively. The valley degeneracy and anisotropy parameters were taken to be the same as at 300 K. The valence band parameters were adjusted at these high temperatures to accommodate for the much larger bipolar effect; the effective mass was taken to be 0.6 m_e with a deformation potential of 20 eV and a band gap of 0.22 eV (which is shown to be approximately constant from optical measurements). Because of the large bipolar effects, high temperature Halleffect measurements (and carrier concentrations) are not reliable; room temperature n_{H} was plotted instead (even for high temperature properties). In order compute the room temperature Hall carrier concentration for the three band model, the charge neutrality equation $N_A - N_D =$ $\sum_i p_i(\eta, T) - \sum_i n_i(\eta, T)$ was solved at high temperature to determine the intrinsic defect concentration (N_A - N_D as a function of η at 800 K), which was then projected back to room temperature (solved for an equivalent η_{300K}) from which the room temperature Hall coefficient (R_{η}) and n_{η} could be calculated.

*zT*s are plotted for each band (Figure 6-4c) assuming that the lattice thermal conductivity is equal to the value obtained where the maximum *zT* is obtained. The contribution for each individual band is computed as: $zT_i = \frac{S_i \sigma_i S}{\kappa_L + \kappa_e}$, where S_i and σ_i represent the contributions from each band and *S* is the conductivity weighted average over all bands (defined in Chapter 2) and $\kappa_e = \sum L_i \sigma_i$.

We should note that while these values yielded acceptable fits of the properties at these particular temperatures, the fits are not unique. In other words, other sets of parameters may provide adequate fits for the masses. In fact, the electronic structure calculations suggest that the states are more complicated than simply considering two conduction bands; however, we obtain

both a quantitative and qualitative fit that seems to adequately reflect the nature of both transport and optical measurements.

Ab-initio DFT calculation and ultrafine evaluation of Fermi surfaces

Ab-initio calculations were performed by a collaborator, Luis Agapito (University of North Texas, Denton). The position of the 16 atoms in the CoSb₃ unit cell (with conventional lattice constant of 9.07 Å) is relaxed using norm-conserving pseudopotentials and the Perdew-Burke-Ernzerhof [336] density functional, as implemented in the *ab-initio* package Quantum Espresso [337]. The plane-wave basis set is defined by an energy cutoff of 270 Ry.

A 9x9x9 Monkhorst-Pack sampling of the reciprocal space is sufficient to converge the DFT calculations. However, an ultrafine *k*-mesh, containing 200x200x200 *k*-points in the reciprocal unit cell, is needed in order to obtain smooth isosurfaces. Highly accurate real-space tight-binding Hamiltonian matrices are built by projecting the DFT Bloch states onto a "small" set of atomic orbitals (4*p*, 3*d*, 4*s* for Co; and 5*p*, 5*s* for Sb) while filtering out states of low projectability [338, 339]. The reciprocal-space Hamiltonian matrices are obtained by Fourier transformation and then diagonalized at each point in the ultrafine mesh to obtain the Eigen energies. The tight-binding and the actual DFT eigenvalues are numerically the same for all practical purposes. We use the parallel implementation of the method that is available in the WanT code [340]. XCrySDen [341] is used for visualizing the isosurfaces.

6.3 - Zintl A₅M₂Sb₆ Materials

6.3a - Introduction

Due to their complex crystal structures, tunable transport properties, and high temperature stability, Zintl compounds such as $Yb_{14}MnSb_{11}$ ($zT \sim 1.4$ at 1200 K), Sr_3GaSb_3 ($zT \sim 0.9$ at 1000 K), and $Ca_5ln_2Sb_6$ ($zT \sim 0.7$ at 1000 K) are promising candidates for use in thermoelectric applications [342-347]. While the complex unit cells of Zintl compounds reduce the velocity of the

optical phonon modes, which lowers the lattice thermal conductivity [348], their covalently-bonded polyanionic structures also allow them to maintain good high electronic conductivity [349]. Through doping, these phases become extrinsic semiconductors with carrier concentrations in the range of 10^{19} - 10^{21} carriers/cm³, resulting in good thermoelectric *zT*s [350].

The A_5M_2 Sb₆ Zintl phases (A = Ca or Sr, M = AI, Ga, In), which will be investigated in this section, also benefit from a complicated crystal structure and a resulting low lattice thermal conductivity. This family of compounds can be doped p-type by partial substitution of the metal site with Zn to optimize their charge carrier concentration. In this section, I will continue with the theme of this chapter, which has been identifying multi-band behavior using optical absorption edge measurements.

6.3b - Results and Discussion

Optical absorption edge measurements in Ca₅In₂Sb₆ and Sr₅In₂Sb₆ (Figure 6-6a) indicate two slopes in the absorption coefficient (similar to CoSb₃ shown in the previous section) which could be evidence of multiple band behavior. In both systems, the optical absorption edge spectra show a slow rise for energies above ~0.3 eV followed by a faster rise above ~0.55 eV and ~0.65 eV for the Sr₅In₂Sb₆ and Ca₅In₂Sb₆ variants, respectively. By examining the calculated Sr₅In₂Sb₆ electronic band structure shown in Figure 6-6b [351], we can determine which possible interband (valence-conduction band) transitions can occur that might correspond to the features in the optical absorption edge spectrum. The computed interband transition with the lowest energy corresponds to the direct band gap near the *X* point with a calculated value of ~ 0.44 eV and 0.48 eV for Sr₅In₂Sb₆ and Ca₅In₂Sb₆, respectively [351]. While the shallow rise at low energy in the optical data seems to indicate a weaker absorption feature (possibly an indirect gap or even midgap impurity states), we believe that this feature ($\hbar\omega_1$ as indicated in Figure 6-6a and b) is due to the direct *X* – *X* transition. The second increase in absorption ($\hbar\omega_2$) is possibly due to an indirect interband transition from one of several lower laying valence bands (the first of which is centered

at the Γ point) to the conduction band edge (at X). As is commonly understood, direct gaps usually yield substantially higher optical absorption coefficients than indirect ones [352]; however, in this case the density of states for the lower-laying secondary valence bands at Γ is significantly higher (by about a factor of 10) than the band edge states at X [351], similar to what was observed in CoSb₃. The (linear) extrapolation of the second absorption edge resulted in $\hbar\omega_2$ values of ~0.55 and 0.64 eV (see Figure 6-6a) for Sr₅In₂Sb₆ and Ca₅In₂Sb₆, respectively. In comparison, DFT results for the $\Gamma - X$ transition energy are ~0.73 and 0.75 eV, respectively, which shows reasonable agreement with the optical and theoretical results. We can compare the optical results with other experimental estimations of the electronic band gap. The temperature dependent resistivity approximation of the band gap calculated from $\rho \propto e^{E_g/2k_BT}$ is ~0.26 eV at low temperatures and ~0.58 eV at high, which corroborates the optical absorbance data [248]. The Goldsmid-Sharp band gap estimated from the maximum Seebeck coefficient (~380 μ V/K at 500 K for the undoped sample) using the Goldsmid-Sharp band gap: $E_g = 2eS_{max}T_{max}$ is 0.38 eV [50]. Both estimates agree approximately with the optical and DFT results [353]. It is well known that multiple-band effects can lead to excellent thermoelectric performance, as is the case in PbTe [126, 354] and PbSe (Chapter 4 of this thesis). However, for $Sr_5In_2Sb_6$ the offset between the two bands is too large to improve the properties, requiring a chemical potential of ~0.25 eV to reach the second valence band which corresponds to a carrier concentration of about 10²¹ holes/cm³ (assuming single parabolic band at T = 300 K and $m^* = 1.3 m_e$). Further investigation into whether the suggested offset is either a function of temperature or alloying, as in PbX (X = S, Se, Te) [126], can be performed to develop strategies towards band engineering in this system.

In this case, we have not thoroughly investigated the possibility that $\hbar\omega_1$ may be a result of intrinsic defect levels (as we had in CoSb₃), which might indicate that the primary gap is actually associated with $\hbar\omega_2$. However, when considering the combination of the gaps estimated from transport properties and the theoretical calculations which indicate relatively narrow gaps, we believe that the current explanation is reasonable.



Figure 6-6: a) Optical absorption edge results showing F(R) or $(\frac{\alpha}{R})$, the normalized Kubelka Munk function, for $Sr_5In_2Sb_6$ and $Ca_5In_2Sb_6$ where $\hbar\omega$ is the light energy in eV [355]. The two transitions at 0.3 eV and 0.55 eV are observed and are indicated by $\hbar\omega_n$. F(R) is the Kubelka Munk function (previously represented as $\frac{\alpha}{R}$. b) Calculated DFT band structure of $Sr_5In_2Sb_6$ with the suggested direct ($\hbar\omega_1 \sim 0.48 \text{ eV}$) and indirect ($\hbar\omega_2 \sim 0.73 \text{ eV}$) transitions indicated [351]. Both calculations indicate a difference of $\sim 0.25 \text{ eV}$ between the direct and indirect band gaps despite discrepancies in the band gap values. The peak at $\sim 0.44 \text{ eV}$ is indicative of O-H stretching vibrations consistent with some water adsorbed to the powder surface.

Additional measurements were performed over several different 5-2-6 compositions, each of which indicated semiconducting behavior [356]. Of these, Eu₅In₂Sb₆ exhibits the lowest measured band gap with an absorption edge around 0.25 eV, which agrees with previous

calculations and experimental literature [357]. While the two-slope features are less pronounced in the Eu-containing compound, it is possible that they still exist but with a smaller offset (<0.1 eV), indicating that this might be a promising compound for band engineering. Of the other compounds, each begins absorbing light at ~0.3 eV and exhibits a secondary absorption edge at a different, higher energy. This is true for each system except the Ca₅Ga₂Sb₆, which shows the largest free-carrier absorption and a resulting minimum in *F(R)* at ~0.28 eV (indicating that the first absorption edge begins at a bit lower energy). Previous literature results agrees with this finding because they show a smaller gap (estimated from electronic properties) in Ca₅Ga₂Sb₆ than the other 5-2-6 compounds [358]; the valence band offset in the Ga compound is the smallest (other than the Eu-containing compound) with a value of ~0.15 eV. Literature Seebeck data on Ca₅Ga₂Sb₆ does not show deviation from the SPB model, but careful studies have not been performed. The In and Al containing compounds have a similar offset of ~0.35-0.4 eV which, as mentioned previously, is likely too far to be accessible through doping.



Figure 6-7: Optical absorption edge measurements in various Zintl 5-2-6 compounds. F(R) is the Kubelka Munk function (previously represented as $\frac{\alpha}{k}$.

6.3c - Conclusions

Further band structure calculations of intrinsic defects might provide some insight as to whether in-gap states might arise upon substitutions/vacancies/interstitials, as was the case for ZrNiSn in Chapter 5, which might suggest whether transition 1 is in fact related to a defect state. Based on a combination of optical, electronic, and computed properties, however, this conclusion of multiple band features seems to reasonably match the results. In order to confirm these suppositions of multiple band behavior, additional doping and transport measurement experiment should be performed, particularly in the Eu₅In₂Sb₆ and Ca₅Ga₂Sb₆ compounds, which seem to have the most promising band structures to utilize these multi-band effects through band engineering.

6.3d - Methods

The $Sr_5ln_{2-x}Zn_xSb_6$ (x = 0, 0.025, 0.05, 0.1) series was synthesized using ball milling followed by hot pressing [359]. An InSb precursor was prepared using stoichiometric amounts of In shot (99.999%, Alfa Aesar) and Sb shot (99.9999%, Alfa Aesar). The elements were vacuum sealed in a quartz ampoule and heated to 900 K at a rate of 150 K/h and annealed there for 12 h, then slowly cooled to room temperature. In an argon-filled glove box, stoichiometric quantities of InSb, Sb, dendritic Sr (99.9%, Sigma Aldrich), and Zn foil (99.99%, Alfa Aesar) were weighed and placed in a stainless-steel vial with two 0.5 inch diameter stainless-steel balls. The Sr was cut into 1-3 mm pieces before it was weighed. The samples were then ball milled using a high energy SPEX Sample Prep 8000 Series Mixer/Mill for one hour. Each resulting powder was loaded into a high-density graphite die (POCO) with a 12 mm inner diameter and hot pressed in an argon environment at 823 K for 2 hours under 110 MPa of pressure. The samples were then cut into 1 mm thick disks.

Optical measurements were obtained and analyzed as outlined in Chapter 2. Absorption edges were extrapolated to the zero (or previous transition) in order to estimate the transition onset energies. Both direct (n=2) and indirect (n=1/2) extrapolations: $(F(R)\hbar\omega)^n \propto (\hbar\omega - E_g)$ were considered, each of which produced a linear region over which to fit (for each absorption edge). Because both direct and indirect extrapolations each yielded reasonable fits, we use the calculated band structure to help us determine which interband transitions are likely responsible for the absorption edge features.

6.4 - Conclusions

Multiple transitions can be observed optically in a variety of systems as shown in this chapter. CoSb₃ is particularly interesting because of its widespread use in commercial applications. While the electronic structure of CoSb₃ is not generally touted as one that is conducive to great thermoelectric properties, in this chapter I show that a multiple band transport is required to indicate the increasing Seebeck effective mass. We have fit the band parameters for the second band based on both optical measurements, and the behavior is consistent with a two conduction band transport model at both room and high temperature. Temperature dependent optical measurements indicate a decreasing energy of the second transition ($E_{g,\Gamma-CB_2}$), suggesting that, at high temperatures, the offset between the primary and secondary bands becomes even smaller until the bands are converged. We attribute a portion of the good thermoelectric performance to the shifting band structure and multi-band behavior, in addition to the reduction in lattice thermal conductivity upon Yb filling the voids in the CoSb₃ structure.

In addition to the CoSb₃ system, which shows multi-band behavior which is measurable through both the optical and electronic properties, the Zintl 5-2-6 system indicates the possibility of multi-band behavior as well. Optical measurements show two distinct absorption edges for a variety of compounds within this class of materials. In contrast to CoSb₃, the electronic properties in the Zintl compounds do not reflect a second band, likely because of the large band offset energies and large effective masses; although more studies should be performed to attempt to increase the doping concentration until the Fermi level reaches the secondary bands.

As has been a theme of this thesis, the combination of optical properties, electronic properties, and electronic band structure calculations has allowed us to develop relationships between the electronic structure and the good thermoelectric properties in CoSb₃. We provide necessary insight into the electronic structure of CoSb₃, which should provide the thermoelectrics community with a direction for further optimizing these materials. Only by understanding the electronic structure can we perform the appropriate carrier concentration optimization and band engineering to further enhance the thermoelectric properties.