Chapter 8: Conclusions and Future Directions

In this work, I have shown several examples where band engineering concepts have been utilized to understand and optimize the thermoelectric properties over a range of material systems. Band structure characterization using optical properties, electronic/thermoelectric properties (as a function of doping), and ab-initio computed band structures provide detailed description of the electronic band structure in three important material systems.

First, in the lead chalcogenides I have used optical and *ab-initio* techniques to characterize the temperature-dependent band gap. I conclude that the gap increase is due to both lattice expansion and electron-phonon interaction, and that a convergence temperature around 700 K is consistent with optical and *ab-initio* results. This realization that the convergence temperature is larger than previously believed is important and will likely lead to more well-refined temperature-dependent transport models, and it can be used to help distinguish the effectiveness of different band engineering strategies in these materials.

Second, in the half Heusler (ZrNiSn) system I have considered several estimates for the band gap using optical, electronic, and *ab-initio* techniques. The optical absorption edge results allow us to obtain the true band gap value (0.13 eV), which we can use to resolve the weighted mobility ratio (A=5) between electrons and holes. I explain the excellent high temperature zT in n-type ZrNiSn by suppressed bipolar effects due to the low weighted mobility for holes in the system. I develop a chart to quickly determine the deviation of the Goldsmid Sharp band gap as the A value is varied. Future work can apply what was learned from the large A value in ZrNiSn, particularly with respect to how it affects the estimate of the Goldsmid Sharp band gap, to rank bipolar suppression strategies in other classes of materials.

$CoSb_3$ is an important thermoelectric material with excellent thermoelectric properties upon filling of the internal voids. In this thesis, I have shown a series of Yb-filled $CoSb_3$ skutterudite

samples, which displayed a rapidly rising carrier concentration dependent effective mass (as obtained from the Seebeck coefficient). I have explained this rise in the context of multiple conduction band transport, which is supported by optical results that show two distinct absorption edges and *ab-initio* electronic structure calculations that show a high valley degeneracy (N_v=12) secondary conduction band. Further, these bands are found to shift together with temperature, resulting in convergence for T>700 K. While skutterudites are not often explored in detail for their electronic structure, this work suggests that the high degeneracy secondary conduction band plays a critical role in the electronic transport in filled $CoSb_3$, particularly at high temperature. Future directions from this work will likely involve engineering the conduction band structure (possibly through alloying); $CoSb_3$ shares many similar traits to other IV-VI materials where band engineering strategies have led to successful *zT* improvements.

Lastly, the Fermi surface complexity factor ($N_v^* K^*$), as computed from Boltztrap results (and effective mass estimates), is a simple way to obtain an estimate of the Fermi-level dependent effective valley degeneracy (N_v^*). Further, complex Fermi surface features (such as threads or tubes) also manifest themselves by increasing the effective anisotropy factor (K^*). This section provides an alternative to traditional presentation of computed Boltztrap data that is independent of the assumed scattering mechanism and directly reflects the electronic structure. I believe that this alternative is a better way to compare materials from a band structure perspective in a high-throughput sense.

While optical properties measurements in the thermoelectrics community are not commonplace, this thesis provides several important examples where they are critical in determining the band positions. By combining electronic, optical, and *ab-initio* computed properties, multiple band effects can be identified and ultimately utilized to improve the thermoelectric properties. Band engineering and multiple bands are a viable route towards improving *zT*, and future material enhancements will likely utilize these features.