Toward Improved Computational Tools for Electronic Transport Analysis and their use in the Development of Materials for Energy Applications

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Toward Improved Computational Tools for Electronic Transport Analysis and their use in the Development of Materials for Energy Applications

by

Maria Stoica

A dissertation presented to the Graduate School of Arts and Sciences of Washington University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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Maria Stoica

Washington University in Saint Louis
December 2014
Dedicated to the Earth.
ABSTRACT OF THE DISSERTATION

Toward Improved Computational Tools for Electronic Transport Analysis and their use in the Development of Materials for Energy Applications

by

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Doctor of Philosophy in Computational Materials Science, Energy Engineering

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With the rapid rise in computational speed and capacity of massively parallel computing clusters in recent years, theoretical screening of large, previously unexplored sets of complex compounds to find materials with a given set of desired properties is quickly becoming a reality. In order to maximize the predictive ability of these large-scale computations, it is desirable to develop accurate post-processing algorithms that can efficiently manipulate electronic structure data to produce theoretical predictions of experimentally observable quantities. To address this need, the work of this dissertation has been to expand existing ab initio methods for determining electronic properties of bulk complex structures to allow for the characterization of both n- and p-type semiconducting materials. Although previous methods have successfully characterized carrier transport in n-type materials which obey the spherical parabolic band approximation, these methods have failed for p-type materials for which band warping results in asymmetry of carrier transport. As part of this work, we develop a generic algorithm for determining the curvature of semiconductor bands near the band edge, and use the results to process band data and derive electronic properties such as
effective masses, electronic conductivity, and Seebeck coefficient. To illustrate the flexibility and utility of the methods developed, we apply them to a variety of bulk systems and show how such analysis can help not only to identify potentially successful materials, but also to gain insight into the relationship between electronic structure and material properties. Specifically, we study metallic atom filled skutterudites and their electronic properties in context of thermoelectric theory and gain knowledge about a secondary electronic structure that forms a resonance lattice within the skutterudite lattice that leads to enhanced electronic conductivities. We also study a new group of potentially transparent conducting oxide spinels and quantify the improvement of electronic properties that results from enhanced valence band curvature. We also introduce the effective mass wheel, and use this technique to visualize deviation from spherical parabolicity for the valence bands of compounds of increasing levels of complexity: Si, GaAs, Cu$_2$O, and a ternary spinel oxide. Lastly, we present an extension to the work performed here through the reformulation of the effective mass problem in a more widely applicable form. We hope that this work helps to advance the ability of materials screening in identifying potentially successful materials for a variety of applications in electronic materials science and solid state energy technologies.
Chapter 1

Introduction

Computational screening of experimentally unexplored compounds for electronic device applications has in recent years become a possibility with the advent of electronic structure calculations on massively parallel, large-scale computing clusters. With these powerful computational tools, it is now possible to perform electronic structure calculations on hundreds of atomic permutations of a single structure quickly and efficiently. Although electronic structures contain all the information necessary about a given arrangement of atoms, that information is not readily available in quantitative form by a simple analysis of the band data. Therefore, it is desirable to have available fast post-processing algorithms that can manipulate electronic structure band data to produce theoretical complements to experimentally observable quantities. Additionally, values derived from quantum theory can better describe the carrier transport in small-scale devices where quantum effects begin to dominate and a completely classical approach to device characterization is no longer adequate. These values can be used to derive the carrier mobility and diffusion coefficient that describe carrier transport in the drift-diffusion approach.

The drift-diffusion equation

\[ J_n = qn \mu_n E + qD_n \nabla n \]  

(1.1)

has in the past been sufficient for describing carrier transport in semiconductor devices. Here, \( n \) denotes that the majority carriers are electrons; an analogous equation exists for hole drift-diffusion characteristics. This equation is a “sister” equation of other common transport equations derived from continuity equations; its parent equation is known as the convection-diffusion equation, and it can be used to describe the transport of particles or
energy. Equation 1.1 comprises a drift term and a diffusion term, which are dependent on the carrier mobility, $\mu_n$, and the carrier diffusivity, $D_n$, respectively. For macroscopic devices, these properties can be measured experimentally, and are not dependent on the short-range interactions of electrons as at this level electrons can be treated classically, and the overall device properties are determined through a Boltzmann distribution statistical averaging of randomly moving point-charges. However, in small scale devices such as thin films and highly ordered nanostructured systems, the short-range interactions (i.e., with the lattice, other electrons, or due to applied potentials) of carriers become very important. For such systems, we must employ quantum theory to determine carrier lifetime distributions and diffusion coefficients. In this work, we focus specifically on computing the characteristics of a lattice that determine carrier mobility; namely, we compute the carrier group velocity, $v_g$, and effective mass, $m^*$. $m^*$ is a mathematical construct that allows us to express the acceleration of carriers in a semiconductor in terms of Newton’s laws, where the forces applied to the carrier may be external, such as applied electric fields, or internal.

For this dissertation work, we develop an automated means of deriving the complete effective mass space and the optical (i.e., momentum) matrix elements that determine $v_g^1$. We start off by laying the foundation for the post-processing algorithm that processes electronic structure results of the \textit{ab initio} calculation and devising the first computational building blocks necessary for the effective mass model. We modify the first principles calculation code to output the necessary optical matrix elements, which are synonymous with the carrier momenta; these are the values that can be plugged into the electronic property equations derived from the Boltzmann Transport Equation (BTE) using the relaxation time approximation (RTA). The resulting BTE expressions are phenomenological, and apply even when the RTA condition doesn’t hold, or for not spherically parabolic bands, such as those found in p-type materials. We use this modified code to analyze a set of new thermoelectric systems, metallic atom filled skutterudites, and we illustrate the power of using such property calculations to analyze systems at the first principles level, instead of simply analyzing charge distribution and band structure character. We also analyze a set of new transparent conducting systems, based on the spinel structure, using advanced electronic structure derivation algorithms.

\footnote{The algorithms developed in this work are intended to serve as a foundation for higher level calculations of electronic properties from first principles. As the effective mass surface plays a key role in the electronic relaxation time, regardless of the dominant mechanism for carrier scattering, this calculation is transferable to more complex systems that have intricate carrier scattering effects. Additionally, since the derivation of the effective mass is performed directly on band data and is thus a \textit{post-processing} algorithm, the method is independent of the electronic structure minimization algorithm used, and should thus be applicable to more advanced band structure calculation algorithms as well.}
Lastly, we develop a model for deriving the effective mass surface from the same data set used for transport properties to obviate the need for doing separate costly first principles calculations. This effective mass surface data can then be used to derive momentum-dependent electronic relaxation times that are then plugged into the BTE derived property equations to more accurately determine properties based on carrier transport behavior. To illustrate the effect of the $k$-dependent effective mass, we compute the electronic relaxation time population distributions for carriers within the Fermi distribution region for the Si and GaAs systems at low temperatures when ionized impurity scattering is the dominant scattering mechanism. To demonstrate the insight that can be achieved with these new calculations, we apply the effective mass surface analysis to the technologically important Si, GaAs, and Cu$_2$O systems, as well as to our theoretically derived spinel structure, and we develop a new means of plotting the effective mass surface which helps us visualize the deviation from spherically parabolic behavior.

The following five chapters will outline the computational tools that were developed as part of this dissertation, and will also present specific case studies that illustrate the insights that can be provided by these post-processing algorithms. Chapter 2 presents the background of the theoretical foundation necessary; namely, we review Density Functional Theory (DFT) and the derivation of the electronic property equations from the BTE in the RTA. Chapter 3 illustrates the application of the BTE with the constant RTA (cRTA) to calculating the thermoelectric properties of skutterudites. Chapter 4 illustrates the application of the same BTE derived equations to highly correlated oxide spinel systems using the hybrid DFT method to properly handle the correlation interactions. Chapter 5 describes the automation of the effective mass surface determination on a rectangular transport property calculation grid. In Chapter 6, we apply the effective mass surface calculation to the technologically important Si, GaAs, and Cu$_2$O systems, as well as to the new oxide spinel structure. Finally, in Chapter 7 we review our results and present possible further extensions and next steps for the effective mass methods presented here.
Chapter 2

Background

In this section we give a brief overview of the theories and foundational principles on which the work described in this dissertation is based. First, we review computational methods for obtaining electronic densities of solid state materials, and provide a rationale for why the chosen methods have been used to analyze the systems studied. Further computational details about parameters used for the different systems are outlined in the respective chapters. Then, we review the derivation of the Boltzmann Transport Equation (BTE) and outline the assumptions and simplifications that have been used for this dissertation work. We follow this derivation with a list of the property equations derived from the BTE within the relaxation time approximation (RTA), as well as a definition of the Figure of Merit of the material, which helps us determine the ability of a certain materials for a desired application. In Section 2.2 we present a brief introduction to the theory of the two application technologies we look at in this work, thermoelectric generators and transparent conductors.

2.1 Theoretical Framework

2.1.1 Computational Methods for Solving Electronic Densities

Density Functional Theory (DFT) is the most widely used optimized algorithm for determining the ground state electronic structure of periodic solids. Instead of minimizing the total energy of a system by solving the Slater determinant of electronic wave functions like its predecessor, Hartree Fock (HF) Theory, DFT minimizes the electronic density, a function that describes the probability of finding an electron at any given coordinate. The charge density distribution function simplifies the numerical computations since it only depends on the
three spatial coordinates (for a time-independent system) while the wave function depends on 4N coordinates, where N is the number of electrons in the system, and each electron has a distribution dependent on position and momentum. According to the Hohenberg-Kohn Theorems, this electronic density distribution completely and uniquely determines a given system (spatial arrangement of a given set of atoms), and can thus be used to extract any desired information about the electronic system characteristics, such as its ground state energy. Specifically, DFT algorithms attempt to find the minimum ground state energy, $E_0$, by minimizing the electronic density distribution, $\rho$, for an N electron system using the equation

$$E_0 = \min_{\rho \rightarrow N} \left( F[\rho] + \int \rho(r) V_{Ne} dr \right)$$

where $F = T + J + E_{ncl}$, the sum of the kinetic energy, classical Coulombic electronic interactions and the nonclassical interactions functionals, and $V_{Ne}$ is the nuclear-electronic interaction functional. Unfortunately, the kinetic energy and nonclassical electron-electron interactions are not known and must be either estimated, ignored, or empirically determined. Kohn and Sham derived reasonable assumptions for these two terms by defining the kinetic energy as equal to that of a non-interacting system, and lumping the remaining unknown quantities into a so called exchange-correlation potential functional. This functional is most commonly determined from the free electron gas model, with the exchange derived by Bloch and Dirac, while the correlation is determined from Monte Carlo simulations and either a direct relationship to the density (LDA) or a relationship to the gradient of the density (GGA). For systems without much correlation, these DFT calculations are speedy and accurate. Therefore, we choose to use DFT calculations for our skutterudite semiconductor systems (Chapter 3). However, for highly correlated systems, the correlation energies are incorrectly determined, leading to band gap underprediction and thus large errors in band character in the electronically active region near the valence and conduction band edges; in some cases, the band gap disappears altogether. Therefore, for the oxide systems of Chapter 4, and the semiconducting systems of Chapter 5, a different method had to be chosen that would better be able to predict band gaps and thus band curvatures near the band edges. For these highly correlated systems we select the hybrid functional approach. This approach involves using the DFT correlation potential and a weighted exchange potential comprising the Hartree Fock short-range exact exchange correlation potential and both the short and long range DFT exchange potential.
Of particular interest in this work are the electronic wave function descriptors, indexed by spatial and crystal momentum coordinates, that can be extracted from the charge density distribution function, and can then be used in conjunction with the BTE to derive the electronic properties of the system. By applying the momentum operator to these descriptors, we can derive the momenta of the carriers. The main problem addressed in this work is how to use the band energy and momentum data to derive the group velocities and effective masses of carriers.

### 2.1.2 The Boltzmann Transport Equation

The semiclassical Boltzmann transport equation is an electronic transport model that can be derived from a balance of the carrier distribution function in a region of position-momentum phase space. The distribution \( f \) balance equation reads

\[
\frac{\partial f}{\partial t} + v \cdot \nabla_k f + F \cdot \nabla_p f = \frac{\partial f}{\partial t}_{\text{coll}} + s(r,p,t)
\]

(2.2)

The second and third terms on the left hand side of Equation 2.2 represent the net inflow to position and momentum space, respectively, due to the diffusion of carriers through phase space. The terms on the right hand side of the equation represent the generation-recombination flows. The collision term is a pseudo-generation term and results from collisions in other regions of phase space that instantaneously change a carrier’s momentum but not its location. These scattering events may include the interaction of electrons with other electrons, defects, or lattice phonons. The \( s \) equation describes actual generation recombination terms that describe the generation or annihilation of a carrier through photogeneration or defect formation. When all terms are uniformly zero, there is no scattering and the system is at a perfect steady state. For the purpose of this work, we do not consider the effect of the generation-recombination factor \( s \), and focus solely on collision in and out scattering. The BTE models how the distributions of electrons in the system varies from its equilibrium form.

In order to derive the transport coefficient equations, we adopt the relaxation time approximation, which states that for the conditions of a small applied field, the perturbation in
the distribution function is small, so that the collision term can be estimated as a linear dependence, \( \frac{f-f_0}{\tau} \), where \( f_0 \) is the equilibrium distribution,

\[
f_0(\varepsilon) = \left[ \exp\left( \frac{\varepsilon - \varepsilon_f}{k_B T} \right) + 1 \right]^{-1}, \tag{2.3}
\]

and \( \tau \) is the electronic relaxation time constant. The relaxation time approximation is not always valid; however, it turns out that the resulting equations for the fundamental quantities \( v_g \) and \( m^* \) are phenomenological, and they are valid whether or not the RTA is true or whether the carrier bands are non-parabolic. The relaxation time constant is dependent on the effective mass of the carriers since the scattering rates of carriers intrinsically depend on their effective masses. Therefore, our main goal for this work is to achieve a systemic way of describing carrier transport in terms of carrier group velocities and effective masses by providing a means of performing quick, 3-dimensional fitting of the band curves in the region of carrier transport. By solving for the carrier group velocities,

\[
v_{i,k} = \frac{1}{\hbar} \frac{\partial E_{i,k}}{\partial k}, \tag{2.4}
\]

and the carrier effective mass, \( m^* \),

\[
\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E_{i,k}}{\partial k^2}, \tag{2.5}
\]

using quantum theory we can compute the solutions to the constant RTA-BTE for electronic properties entirely from first principles. Here, \((i, k)\) denotes the eigenvalue-band index, and \( k \) is the reciprocal lattice vector. Equations 2.4 and 2.5 are derived using the free electron energy assumption for mobile carriers within the semiconductors,

\[
E_k = \frac{\hbar^2 k^2}{2m_e}. \tag{2.6}
\]
Equations 2.4-2.5 tell us we can approximate $v$ and $m^*$ of an electron at the $\Gamma$ point using the derivatives of the band structure. In Chapter 7 we will extend these equations to the generic form that does not make the spherical parabolic band approximation. One problem with this approach is that many DFT software packages output the band structure in the form of an array organized by increasing energy, without band distinction. Thus, errors may arise in the computation of the electrical conductivity, particularly at band crossings around the Fermi level, even when Fourier transformations are used [1]. A different approach is desirable in complex systems, when numerous band crossings are present.\(^2\)

The momentum matrix method rectifies this issue by relying directly on the wavefunction descriptors. We can express the computed electron group velocities as follows [2]:

$$v_{\alpha\beta}(i, k) = \frac{1}{m} \langle \psi_{\alpha\beta}(i, k) | \hat{p} | \psi_{\alpha\beta}(i, k) \rangle$$

(2.7)

Here, $v$ are the velocities, $\psi$ are the wavefunctions, $m$ is the electron mass, and $\hat{p}$ is the momentum operator. $\alpha\beta$ denote the directional coordinates. The resulting matrix of velocities indexed by energy and $k$-point is called the optical matrix. Although this equation may be used to determine group velocities from exact wavefunction descriptions, the projector augmented wave (PAW) approach to electronic structure determination used in this work requires the addition of an augmentation factor to account for errors arising from the pseudization of the wavefunctions around the atomic cores [3, 4].

In Chapter 5 we outline a path forward to determining $m^*$ without the use of the free electron model approximation, which is currently the only method in use in the literature, but which inherently contradicts the non-parabolic band fitting scheme. In the following sections, we delve into how bulk electronic and optical properties can be derived from $v_g$ and $m^*$, and how these properties can in turn be used to assess the functionality of a material for a desired application through the figure of merit ($z$), a value that can help us quantify how well a material will perform for a desired application.

**Figure of Merit Definitions** One quantity that is commonly used to characterize the thermoelectric strength of a material (Equation 2.8) or of a p-n junction (Equation 2.9) is

\footnote{In addition, in Chapter 7, we will show that by using the momentum method that follows, we can also use the more generic expression of the group velocities in terms of the momentum to more accurately determine group velocities and effective masses outside the spherically parabolic region.}
the thermoelectric figure of merit [10], $z$:

\[ zT = \frac{S^2 \sigma}{\kappa} T = \frac{S^2}{\rho \kappa} T. \quad (2.8) \]

\[ zT_{p-n} = \frac{(S_p - S_n)^2}{[(\rho_n \kappa_n)^{1/2} + (\rho_p \kappa_p)^{1/2}]^2} T, \quad (2.9) \]

Here, $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity (with $\rho$ being its inverse, or the electrical resistivity), and $\kappa$ is the thermal conductivity. We aim to maximize $S$ and $\sigma$ and minimize $\kappa$ for optimal thermoelectric performance. Equation 2.8 suggests that for every increase in the Seebeck coefficient, $\Delta S$, there is a corresponding increase, $(\Delta S)^2$, in $zT$. $\sigma$ and $\kappa$ are directly and inversely proportional to $zT$, respectively. In Chapter 3 we will focus on optimizing the electrical transport properties of skutterudites by characterizing $S$ and $\sigma$. Equation 2.8 can be used to evaluate the figure of merit of a bulk material, whereas Equation 2.9 is used to evaluate the figure of merit of a junction. The subscripts denote the property of the p or n part of the junction. In practice, $zT$ is the preferred quantity as it is dimensionless. In both equations, $\kappa = \kappa_e + \kappa_L$, is the sum of the thermal conductivity due to the electronic and lattice components. Looking at the relationship between the figure of merit and the efficiency in terms of the temperature at the cold junction, $T_c$, and the temperature at the hot junction, $T_h$, it is determined that the figure of merit should be maximized if it is desired to maximize the efficiency,

\[ \eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + T_c/T_h}. \quad (2.10) \]

Thus, we would like to maximize $S$ and $\sigma$, and minimize $\kappa$. This equation suggests that the Seebeck coefficient has a strong influence on $zT$ as for every increase in the Seebeck coefficient, $\Delta S$, there is a square increase, $(\Delta S)^2$, in $zT$.

The figure of merit of a transparent conductor can be related to its electrical and optical properties by[11],

\[ z = \frac{\sigma}{\alpha}. \quad (2.11) \]
The relationship between the figure of merit and the efficiency is complex in this case, but in general it has been shown that one would need a figure of merit above $1 \Omega^{-1}$ for efficient device performance. The efficiency curve levels off as the figure of merit increases, and the ceiling for the efficiency depends on the device integration technique (see Figure 2.1).

In a separate work, Ref. [12] defines the figure of merit as:

$$\phi_{TC} = \frac{T^x}{R_s}$$

(2.12)

where $T$ is the (optical) transmission (i.e., inverse of absorbance) of a sheet of thickness $t$, $R$ is its resistance, and $x > 0$. Here we do not define the figure of merit as $zT$ since the $T$ in this methodology is in fact the transmission and not the temperature. In terms of the electrical conductivity $\sigma$, the absorption coefficient $\alpha$, and the film thickness that maximizes $\phi_{TC}$, the equation is transformed into:

$$\phi_{TC} = \sigma t \exp (-10\alpha t)$$

(2.13)

and

$$t_{max} = \frac{1}{10\alpha}$$

(2.14)

We use the dark/DC electrical conductivity to determine the figure of merit[11], although for characterization studies it is also instructive to look at the electrical conductivity as a function of radiation frequency. The electrical conductivity is calculated the same way as previously described.
Electronic Properties  The most important coefficients which determine electronic properties in thermoelectric theory and for transparent conductors are the Seebeck coefficient, $S$, and the electronic conductivity, $\sigma$. For brevity, we present expressions for these properties as derived from the BTE, but skip the derivations, which can be found in many textbooks such as [5]. It is helpful to express $S$ and $\sigma$ in terms of the density of states distribution function, $g(\varepsilon)$, and the probability distribution function, $f_0(\varepsilon)$[6].

$$\sigma = \frac{e^2}{T} K_0 \quad (2.15)$$

$$S = \pm \frac{1}{eT} \left( \varepsilon_f - \frac{K_1}{K_0} \right) \quad (2.16)$$

$$K_y = - \frac{2T}{3m^*} \int_0^\infty g(\varepsilon) \tau e^{\varepsilon+1} \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} d\varepsilon \quad (2.17)$$

Here, $T$ is the temperature, $e$ is the electron charge, $\varepsilon_f$ is the fermi energy, and $\tau_e$ is the electron relaxation time constant.

Boltzmann transport theory is then used to derive the following nested equations that enable us to determine $\sigma$ and $S$ in terms of the group velocities[1]:

$$\sigma_{\alpha\beta}(i,k) = e^2 \tau_{i,k} v_\alpha(i,k) v_\beta(i,k) \quad (2.18)$$

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N} \sum_{i,k} \sigma_{\alpha\beta}(i,k) \frac{\delta(\varepsilon - \varepsilon_{i,k})}{d\varepsilon} \quad (2.19)$$

$$\sigma_{\alpha\beta}(T;\mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[ - \frac{\partial f_\mu(T;\varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (2.20)$$

$$\nu_{\alpha\beta}(T;\mu) = \frac{1}{eT\Omega} \int \sigma_{\alpha\beta}(\varepsilon) (\varepsilon - \mu) \left[ - \frac{\partial f_\mu(T;\varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (2.21)$$

$$S = \frac{\nu_{\alpha\beta}(T;\mu)}{\sigma_{\alpha\beta}(T;\mu)} \quad (2.22)$$

Here, $N$ is the number of $k$-points, $\delta$ is the unit impulse function, $\Omega$ is the volume of the primitive cell, and $f$ is the Fermi-Dirac distribution for an electron gas (Equation 2.3) evaluated at $\varepsilon_f = \mu$.

Equations 2.20-2.22 yield second-rank tensors. To quantify these properties as scalars, the trace of each matrix is usually evaluated in the literature. In Chapter 5 we describe how the new concept of radial effective mass is more helpful, and how to relate this back to the tensorial values of the traditional effective mass.
Optical Properties To determine the figure of merit of transparent conductors, we also need to know the optical properties; therefore we calculate the absorption spectrum from first principles. The absorption coefficient is a function of light frequency. It can be determined from the real and imaginary parts of the frequency dependent dielectric constant [7]:

\[
\alpha(\omega) = \sqrt{2\omega \left[ \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2}}. \tag{2.23}
\]

The dielectric function is directly related to the optical matrix elements through [8, 9]

\[
\begin{align*}
\varepsilon_2(\omega) & = \frac{4\pi^2e^2}{\Omega N} \sum_{c,v,k} 2\delta(\varepsilon_{ck} - \varepsilon_{ek} - \omega) \times \langle u_{ek} | u_{ek} \rangle \langle u_{ck} | u_{ek} \rangle^* \\
\varepsilon_1(\omega) & = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_2(\omega')\omega'}{\omega'^2 - \omega^2} d\omega'. \tag{2.24}
\end{align*}
\]

Here, \(c\) denotes the conduction bands, \(v\) denotes the valence bands, and \(\langle u|u\rangle\) denote the optical matrix elements. Therefore, the last element denotes the transition energy from the valence band to the corresponding conduction band.

2.2 Application to Energy Capture and Conversion Technology

2.2.1 Waste Heat Capture and Conversion

Thermoelectric materials can be used for solid state power generation in a variety of applications, including automotive power generation [13, 14] and solar energy capture and conversion [15]. Such devices operate without the need for moving parts, and can be incorporated into most current energy generation technologies to capture waste heat and increase conversion efficiency. Current thermoelectric devices are relatively inefficient (\(\approx 18\%\) [10]) but with recent advances in nanostructuring concepts, it has been shown that more efficient devices may be attainable [16].
**Thermoelectric Theory**  A thermoelectric device is comprised of a p-n junction as depicted in Figure 2.2. Thermoelectricity can be described in terms of the Seebeck, Peltier, and Thomson effects. The following descriptions are adapted from William Lucke’s “Brief Survey of Thermoelectric Theory” (1962). The Seebeck effect is the observable voltage drop across a junction of two dissimilar conductors held at different temperatures. The Seebeck coefficient \( S \) is defined in terms of the voltage drop \( V \) and the temperature difference:

\[
S = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T}.
\] (2.26)

This effect is reversible. The observed transfer of heat \( Q \) when a current \( I \) is applied across a junction of two dissimilar conductors is known as the Peltier effect. In this case, the direction of the current determines whether the heat is released or absorbed:

\[
\frac{dQ}{dt} = \Pi I.
\] (2.27)

The proportionality constant \( \Pi \) is the Peltier coefficient. This effect is also reversible.

The Thomson effect is unlike the other two effects since it can be observed in a stand alone conductor. This effect is observed when heat is absorbed by a current flowing up a...
temperature gradient. In mathematical terms, the Thomson coefficient \((\tau)\) relates the rate of heat absorption or evolution \(\left(\frac{dQ}{dx \, dt}\right)\) to the temperature gradient \(\left(\frac{dT}{dx}\right)\) in an elemental length \((dx)\) of conductor.

\[
\frac{d}{dx} \left(\frac{dQ}{dt}\right) = \tau I \frac{dT}{dx}.
\] (2.28)

The total heat loss or absorption rate can be obtained by integrating along the length of the conductor. By applying classical thermodynamics laws to a junction circuit, one can obtain the relationships between the three coefficients:

\[
S_{12} = \frac{\Pi_{12}}{T} \quad (2.29)
\]

\[
\tau_1 - \tau_2 = -T \frac{dS_{12}}{dT} \quad (2.30)
\]

Here the subscripts 1 and 2 denote the two conductors in the junction. Since the three coefficients are interrelated by the temperature gradient, only one need be determined. The most frequently encountered value when talking about thermoelectric materials is \(S\), and this value is used to determine the figure of merit of a material.

**Skutterudites** Skutterudites are relatively newly discovered materials and particularly attractive for thermoelectric applications because of their large unit cell and strong electronic properties. The crystal structure consists of eight \(\text{TM}_6\) octahedron groups, one in each corner of the cubic unit cell, where, for this study, \(T=\text{Co, Rh, Ir}\) and \(M=\text{P, As, Sb}\). Each M atom belongs to two adjacent octahedra and the T atoms are at the center of the octahedra. These octahedra are arranged in such a way that they create a cage-like void in the center of the unit cell. These voids are large enough to incorporate large atoms which, when present, have the ability to lower the thermal conductivity of the material by “rattling” about within the void, dispersing phonons, and thus shortening the phonon mean free path.

Previous research has shown that the filling of naturally occurring voids within the skutterudite lattice with heavy element atoms, such as Lanthanides, leads to a considerable
reduction in the thermal conductivity[18, 19]. In general, it is recommended that ideal filler atoms should be small, heavy, and have electrons that can readily hybridize with the conducting electrons in the lattice[20]. Recent studies have also indicated that the filling of the lattice voids with smaller or lighter atoms with more metallic properties, such as Ba[21], Na[22] or In[23], leads to an increase in the figure of merit compared to that obtained from filling with La. This is in part due to a smaller reduction, sometimes even enhancement, in the electronic properties as compared to heavier atoms. Furthermore, it has been shown that further enhancement in thermoelectric performance can be achieved through double element filling[24]. In Chapter 3 we present the results of our electronic properties analysis on a new set of skutterudite system that are fractionally filled with the light metal atoms Au and Ag.

2.2.2 Improving Solar Cell Efficiency For Energy Capture

Solar cells capture the sun’s energy, mostly the visible wavelength portion, and convert it to a direct current. They are generally complex and comprise several layers, as shown in Figure 2.3. The core of the solar cell is the p-n junction of complementary semiconductors. These are sandwiched between electrodes that carry the current to the load. The cell is then covered with an antireflective coating, a transparent adhesive, and a glass enclosure. Each of these layers is necessary for proper device function and longevity, but the complexity means that each individual component must be optimized so as not to adversely affect the overall efficiency.

\[3\] Image obtained from Atlantatech Solar Inc. website, no express permissions, [http://www.atlantechsolar.com/how_are_solar_panels_made.html](http://www.atlantechsolar.com/how_are_solar_panels_made.html)
A common means of increasing the amount of electromagnetic radiation that can reach the surface of the absorbing semiconductor is to use transparent conductors (TCs) as electrodes. By far the most frequently used TCs are those in the indium tin oxide (ITO) family. ITOs are transparent and have excellent electronic transport properties. However, the major drawback of indium compounds is that they are costly, toxic, and difficult to recycle.

Zinc oxides are a class of compounds that has shown recent potential in replacing ITOs. As shown in Figure 2.4, zinc oxide crystallizes in one of three forms: cubic zincblende, hexagonal wurtzite, or cubic rocksalt. In the first two structures, the $sp^3$ co-ordination of the lattice suggests covalent character. However, zinc oxide exhibits significant ionic behavior that results in a relatively large band gap. Wurtzite is stable at ambient conditions, and the zincblende form can only be grown on a cubic substrate[25].

By a combination of nanostructuring, alloying, and doping, this class of materials, when deposited in sufficiently thin layers, is transparent and can have a high electrical conductivity. However, there are a large number of dopants and combinations of layering with other types of oxides, especially in ternary and quartenary combinations, that could potentially have significantly improved electrical properties. Figure 2.5 shows just a small portion of the sample space for possible combinations of transparent oxides and promising dopants. The dopant space has largely been studied experimentally already, over the course of many years. However, the alloy phase space is still largely unexplored. It would be desirable to have a reliable computational method that could be used to sample the space of possible alloy permutations and ratios to find and recommend only those that show promising theoretical values. In Chapter 4 we investigate a previously unexplored region of the spinel ZnO.
Figure 2.5: Possible sample space for ternary oxide compounds (left) and promising zinc oxide dopants (right). Reproduced from Refs. [26] (left) and [27] (right) with permission from Cambridge University Press.

alloy phase space as an example. With the aid of large computing clusters, the algorithms developed in this work could be applied to many more systems in an automated way to generate material properties for a broad range of alloys.
References


Chapter 3

Electronic Transport in Skutterudites with Metallic Filler Atoms

Thermoelectric materials are a particularly interesting area of research because they can be used for solid state power generation without moving parts, and can be incorporated into most current energy generation technologies to increase efficiency by capturing waste heat. Examples of use include car engines [1, 2] and solar cells[3]. Current thermoelectric devices are inefficient and are thus only utilized on a small scale. However, the rise of nanostructuring methods to develop novel materials in the past two decades has given new hope to the possibility of devising more efficient thermoelectric devices in the future. With sufficient improvements, thermoelectric devices could be used effectively to either improve efficiency in power generating devices that produce excessive waste heat, or could be used to directly harness heat generated from the sun’s rays through devices such as solar thermal collectors or hybrid solar cells, and convert it to electricity.

In this study, we focus specifically on skutterudite materials, which are attractive for thermo-electric applications because of their large unit cells and high intrinsic electrical properties. The skutterudite unit cell consists of eight $\text{TM}_6$ octahedral groups – one in each corner of the cubic unit cell – where $T$ is a transition metal (e.g., Co, Rh, or Ir) and $M$ is a metalloid or nonmetal (e.g., Sb, As, or P) (Figure 3.1). Each $M$ atom belongs to two adjacent octahedra and each $T$ atom is at the center of the octahedral group. These octahedra are arranged in such a way that a cage-like void is created in the center of the unit cell. These voids are large enough to incorporate certain atoms (X) that, when present, have the ability to lower the thermal conductivity of the material by “rattling” about within the void, decreasing the phonon mean free path, and thus, increasing phonon dispersion.
Figure 3.1: Skutterudite (CoM$_3$) unit cell structure. The top unit cell shows the sixfold coordinated Co atoms (blue). The bottom unit cell shows a filler atom (gold) inserted in the center void. The second void in the unit cell is located at the corners.

Previous studies have shown that filling the naturally occurring voids within the skutterudite lattice with heavy element atoms, (e.g., Lanthanides La, Ce, and Eu), leads to a considerable reduction in the thermal conductivity [4, 5]. In general, ideal filler atoms are described as small and heavy, with electrons that can readily hybridize with the conducting electrons in the lattice [6, 7]. These hybridized electrons may help prevent large reductions in electronic properties that might otherwise occur through void filling. Recent studies have indicated that the filling of the lattice voids with smaller or lighter atoms with more metallic properties, such as Ba [8], Na [9] or In [10], leads to an increase in the thermoelectric figure of merit compared to that obtained by filling with La. This is in part attributable to the enhancement of electronic properties from metallic fillers as compared to heavier Lanthanides. Furthermore, it has been shown that double element filling may further enhance thermoelectric performance [11] compared to single element filling, though this is outside the scope of the present work.

In this study, we test the accuracy of density functional theory (DFT) calculations, following the Projector Augmented Wave (PAW) approach, for predicting electrical transport properties for skutterudite thermoelectric materials; we use the momentum matrix method in
Table 3.1: Filler characteristics

<table>
<thead>
<tr>
<th>Filler</th>
<th>Size (pm)</th>
<th>Atomic weight (amu)</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>144</td>
<td>108</td>
<td>1.9</td>
</tr>
<tr>
<td>Au</td>
<td>135</td>
<td>197</td>
<td>2.4</td>
</tr>
<tr>
<td>La</td>
<td>195</td>
<td>139</td>
<td>1.1</td>
</tr>
</tbody>
</table>

conjunction with PAW (PAW-MM) and compare our calculated results to previously published experimental results. Many previous theoretical investigations into skutterudites have utilized the full-potential linearized augmented plane wave (FLAPW) approach to calculate electronic properties, but we are specifically interested in PAW for its computational speed and efficiency. These qualities are desirable when screening a large group of prospective materials for a specific application. We calculate the thermoelectric properties for both well-characterized and previously uncharacterized skutterudites. We emphasize that the computational method employed is a simplified calculation for ideal bulk crystal systems that does not take into account grain boundary effects or the dependence of the electronic time relaxation constant, $\tau_e$, on temperature. Therefore, only trends and relative magnitudes of properties are demonstrated here.

We also aim to determine the effect of filler size, atomic weight, and electronegativity on the resulting electrical transport properties of filled Co-based skutterudites. A summary of filler properties is presented in Table 3.1. We hypothesize that Au is a promising metallic filler atom due to its small size and large mass, and because its valence electron configuration is similar to that of La, which has been previously shown to be a successful filler. Both Au and La have similar core electronic structures and valence shells composed of all but one filled orbitals and one unpaired electron in the highest energy orbital; they differ only in that the unpaired electron in La is a $d$ electron and that in Au is an $s$ electron. Furthermore, Au is heavier (atomic weight is 197 amu) and smaller (atomic radius is 135 pm) than La (atomic weight is 139 amu, atomic radius is 195 pm). Both of these desirable characteristics should result in improved thermoelectric properties for Au filled skutterudites. We also study Ag as a candidate filler, since Ag has a similar electronic structure compared to Au, but is lighter (atomic weight is 108 amu) and larger (atomic radius is 144 pm). From size considerations, we would expect that the size of the filler atom to be important if the atom is large enough to interact with the void boundaries; otherwise, the heaviness of the atom is likely to be more important for phonon dispersion. Finally, we note that the electronegativities of Ag, Au, and La are 1.9, 2.4, and 1.1, respectively, and those of P, As, and Sb are 2.1, 2.0, and
1.9, respectively. We expect that larger differences in electronegativity between the filler and host (M) atoms would improve electron transport in filled skutterudites. All of these effects will be explored in the calculation of the thermoelectric strength of Ag, Au, and La filled Co-based skutterudites.

### 3.1 Methods

The electrical transport properties of fractionally filled Co-based skutterudites – specifically, CoSb$_3$, CoAs$_3$, and CoP$_3$ with Ag, Au, and La filler atoms – were evaluated. La was chosen for its previously demonstrated ability to increase the thermoelectric figure of merit of filled skutterudites; thus, La will serve as a baseline for comparison to the previously uncharacterized Ag and Au fillers.

All calculations of electronic wavefunctions were performed using DFT, as implemented in the Vienna Ab Initio Simulation Package (VASP) [12, 13, 14, 15]. PAW potentials [16, 17] were used to maintain a balance between high accuracy and reasonable computational costs. The generalized gradient approximation of Perdew, Burke, and Ernzerhof [18, 19] was used to represent the exchange-correlation energy. All calculations were performed using the blocked Davidson iterative matrix diagonalization algorithm[20] to optimize the orbitals. The tetrahedron method with Blöchl corrections was used to determine partial occupancies. The first Brillouin zone was sampled with 100 $k$-points, and the kinetic energy cutoff for the plane wave basis set was set to 270eV after extensive $k$-point convergence tests. The resulting wavefunctions are used in the momentum matrix equation 2.7, with a PAW potential correction to determine the group velocities as noted in Section 2.1.2. Equations 2.18-2.22 are then used to determine the thermoelectric properties from the group velocities with a code developed in MATLAB [21].

As shown in Figure 3.1 there are two voids per unit cell, so that only a limited number of filling fractions ($x \in \{0.5, 1\}$) may be explored. In order to obtain a larger sampling set of filling fractions, a $2 \times 2 \times 2$ supercell containing 16 voids was constructed. Voids were filled in pairs until the structure was fully filled. Table 3.2 shows the resulting highest symmetries used for the filled systems, $X_x$CoM$_3$)$_4$. $S$, $\sigma$, and $S^2\sigma$ values were calculated for $x \in \{0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, 1\}$; a denser sampling of filling fractions would be difficult to achieve given computational limitations and may not yield significantly
<table>
<thead>
<tr>
<th>Filling Fraction</th>
<th>Chemical Formula</th>
<th>Highest Computed Symmetry</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>CoM$_3$</td>
<td>Im$\bar{3}$</td>
<td></td>
</tr>
<tr>
<td>0.125</td>
<td>X$_{0.125}$(CoM$_3$)$_4$</td>
<td>Im$\bar{3}$</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>X$_{0.25}$(CoM$_3$)$_4$</td>
<td>R$3$</td>
<td></td>
</tr>
<tr>
<td>0.375</td>
<td>X$_{0.375}$(CoM$_3$)$_4$</td>
<td>Im$\bar{3}$</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>X$_{0.5}$(CoM$_3$)$_4$</td>
<td>Pm$3$</td>
<td></td>
</tr>
<tr>
<td>0.625</td>
<td>X$_{0.625}$(CoM$_3$)$_4$</td>
<td>Im$\bar{3}$</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>X$_{0.75}$(CoM$_3$)$_4$</td>
<td>Cmmm</td>
<td></td>
</tr>
<tr>
<td>0.875</td>
<td>X$_{0.875}$(CoM$_3$)$_4$</td>
<td>Im$\bar{3}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>X(CoM$_3$)$_4$</td>
<td>Im$\bar{3}$</td>
<td></td>
</tr>
</tbody>
</table>

Different trends in the resulting data. All calculations were performed at the following temperatures: $T \in \{300, 400, 500, 600, 700, 800, 900\}$ K.

Calculations were first performed on the unfilled CoSb$_3$ system and the La filled, Fe doped CoSb$_3$ system at different carrier concentrations, and compared to previously published experimental data. Doping was mimicked using the rigid band model (i.e., moving the Fermi energy on a fixed band structure) to simulate different electron carrier concentrations, $n_e$, and hole carrier concentrations, $n_h$. These carrier concentrations were determined using the density of states, $g(\varepsilon)$:

$$n_e = \frac{1}{V} \sum_{\varepsilon = \varepsilon_p}^{\infty} g_c(\varepsilon) \cdot f(\varepsilon) \cdot \Delta \varepsilon$$ \hspace{1cm} (3.1)

$$n_h = \frac{1}{V} \sum_{\varepsilon = -\infty}^{\varepsilon_p} g_v(\varepsilon) \cdot (1 - f(\varepsilon)) \cdot \Delta \varepsilon$$ \hspace{1cm} (3.2)

The $c$ and $v$ subscripts denote the conduction and valence states respectively. Then, the Ag, Au, and La filled (undoped) skutterudites were screened across the range of $x$ and $T$ values in the sample space, and the electrical transport properties – $S$, $\sigma$, and $S^2\sigma$ – were calculated from the wave descriptors. Additional calculations of the electrical transport properties were performed on the most promising filled systems for a range of deviations in the chemical potential.
Table 3.3: Structural parameters for unfilled skutterudites.

<table>
<thead>
<tr>
<th>System</th>
<th>Lattice Parameter (Å)</th>
<th>Void Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Experimental</td>
</tr>
<tr>
<td>CoSb₃</td>
<td>9.0385</td>
<td>1.892</td>
</tr>
<tr>
<td>CoAs₃</td>
<td>8.2055</td>
<td>1.825</td>
</tr>
<tr>
<td>CoP₃</td>
<td>7.7073</td>
<td>1.763</td>
</tr>
<tr>
<td></td>
<td>Computed</td>
<td>1.875</td>
</tr>
<tr>
<td></td>
<td>Computed</td>
<td>1.780</td>
</tr>
<tr>
<td></td>
<td>Computed</td>
<td>1.768</td>
</tr>
</tbody>
</table>

a Experimental values from Nolas et al. [22]

3.2 Results and Discussion

3.2.1 Unfilled skutterudites

The rightmost column in Table 3.3 shows the calculated void radii as determined upon geometry optimization of the skutterudite systems. Full lattice optimizations resulted in only a +0.6% increase in the lattice parameters; thus, we allowed only the atoms to relax during geometry optimization. Smaller voids are observed in CoAs₃ and CoSb₃ and larger voids are observed in CoP₃ upon geometry optimization.

Figure 3.2 shows the band structures calculated for the three unfilled skutterudites (i.e., CoP₃, CoAs₃, and CoSb₃). CoSb₃ is a semiconductor with a small band gap of 0.3 eV, CoAs₃ has a pseudo gap of 0 eV, and CoP₃ is a conductor with an overlap at the Γ point; these results generally agree with previous findings [23, 24]. The total density of states (DOS), presented alongside the partial contributions from the Co 3d electrons and the 3p, 4p, and 5p electrons of P, As, and Sb, respectively, are also shown in Figure 3.2. The dotted horizontal lines denote the Fermi-Dirac distribution filter $(\frac{df}{d\varepsilon})$ of equations 2.20-2.21 at 300K in this and all subsequent figures.

From these plots we observe that there is significant hybridization of the valence orbitals at the Fermi level for all three bulk materials. We also notice that a majority of the DOS contribution around the Fermi energy may be attributed to the valence electrons. These DOS and band structure diagrams indicate that the valence electrons are essential in dictating the electronic properties of the compound, and fillers containing electrons that may hybridize with electrons at these energy levels can strongly impact electrical transport properties.
3.2.2 Comparison of Computational to Experimental Results

We first compare the calculated Seebeck coefficient, $S$, and electrical resistivity, $\rho$, to available experimental values for two systems – unfilled CoSb$_3$ and La filled, Fe doped CoSb$_3$. Figure 3.3 shows that the trends in both properties and the peak in $S$ are predicted correctly for unfilled p-type CoSb$_3$ at high hole carrier concentrations. By comparing our calculated values of $\rho$ to the experimental data at $T = 500$ K, we determine that the best-fit value for the electronic time relaxation constant for unfilled CoSb$_3$ is $\tau_e = 5 \times 10^{-13}$ s. For low carrier concentrations, (i.e., where the Fermi energy approaches the undoped value), our theoretical values of $S$ drop off more rapidly than the observed experimental values. At room temperature, our calculated $S$ values are correct; however, as the temperature rises, the discrepancy increases. Since we determine our band occupations from the Fermi distribution, it is possible that the deviations arise from the inclusion of conduction bands in

Figure 3.2: Band structure and partial density of states for unfilled skutterudites.
the calculation. As the temperature increases, more conduction bands are included in the computation. Furthermore, as the hole carrier concentration increases ($\varepsilon_F$ moves downward on the band structure), the Fermi distribution includes fewer conduction electrons and our estimation improves. This is a reflection of the limitations of DFT in describing conduction band characteristics, especially at band edges. Although the theoretically predicted and experimentally measured values of $\rho$ and $S$ do not always agree throughout the sampled temperature range, the trends in these properties with temperature are consistent and demonstrate that there is an optimal temperature range for high values of $S$ and low values of $\rho$.

![Figure 3.3: Comparison of theoretically computed and experimental [25] electrical transport properties, $S$ and $\rho$, for unfilled p-type CoSb$_3$, at different hole carrier concentrations, $n$.](image)

Although not directly the focus on this work, we note that there have been prior comparisons made between theory and experiment for unfilled n-type CoSb$_3$ [27, 26], so we now demonstrate that our model is flexible enough to consider both types of dopants. For n-type materials, the number of bands included in the calculation must be increased in order to ensure convergence of the behavior of the conduction bands. Figure 3.4 shows a comparison between the experimental trends and the theoretical trends for unfilled n-type CoSb$_3$. For high electron carrier concentrations, where the Fermi energy lies within the conduction band, we achieve good agreement between theory and experiment. The carrier concentration used in the theoretical calculations was obtained by fitting the computed $S$ to the experimental
Figure 3.4: Comparison of theoretically computed and experimental [26] electrical transport property, $S$, for unfilled n-type CoSb$_3$, at different hole carrier concentrations, $n$.

data at $T = 300$ K. As depicted in Figure 3.4, the shape of the computed curves does not exactly match the experimental data across the range of temperatures sampled, although the computed values of $S$ at low temperatures match within 10% of the experimental values. We attribute this discrepancy to the observation that in experimentally developed materials, the carrier concentration and transport properties will fluctuate differently with temperature, as a result of defects, than what would be expected in a defect-free model like that used in our calculations. Deviations in the steepness of the curvature of the bands are thus most likely due to the constant relaxation time estimation [26] used in our calculations. For very low carrier concentrations (not shown), where the chemical potential falls within the band gap, we observe a greater deviation from the experimental results, especially at low temperatures. Since the Fermi-Dirac distribution does not accurately describe the distribution of electrons within the band gap, we must instead increase the k-point sampling of the Brillouin zone to 5,000 points and triple the number of total bands in the calculation to achieve reasonable accuracy within the band gap. However, we again stress that for the filled systems considered subsequently in this study, the filler acts as a p-type dopant and the Fermi level is pushed into the valence band, so that only heavily doped materials are observed; therefore, such resource-intensive calculations on n-type systems are outside the scope of the present work.

The results for La filled, Fe doped skutterudites are shown in Figure 3.5. The experimental measurements are made on 90% La filled skutterudites, but given the range of filling fractions
that were computationally tractable, we relate these results to our calculated predictions on 100% La filled skutterudites. We see from these plots that the trace of the Seebeck coefficient has a flatter temperature dependence compared to the experimental trends. However, after investigating the directional components of $S$, we see that the $S_{yy}$ component exhibits a similar trend to the experimental values. As we adjust the value of $n$ to attempt to emulate 90% La filling, we notice that the values asymptotically approach the experimental results. Thus we conclude that the small discrepancy between the calculated and experimental values of $S$ is likely due to the difference in the La filling fraction. Again, we fit the calculated values of $\rho$ to the experimental data at $T = 500$ K, and determine that the best-fit value for the electronic time relaxation constant for La filled, Fe doped CoSb$_3$ is $\tau_e = 2 \times 10^{-13}$ s. From these results, it seems reasonable to estimate the electronic relaxation time constant for all of the systems considered in this study to be $\tau_e = 10^{-13}$ s, and we will use this value for all subsequent calculations.
3.2.3 Ag and Au filled skutterudites

We next explored Ag and Au filled skutterudites as potential candidates for improved thermoelectric behavior. We plotted the calculated power factor, \( S^2 \sigma \), which is the numerator of the figure of merit, as a function of temperature. For these calculations, the time relaxation constant was again assumed to be independent of filling fraction and temperature, and was approximated as \( \tau_e = 10^{-13} \) s, as described in Section 3.2.2. Figure 3.6 shows the power factors plotted as a function of temperature for the undoped compounds at the filling fractions that yielded \( \text{Im} \bar{3} \) symmetry of the unit cell. Charge compensation was not included so that the effect of composition on the thermoelectric power factor may be isolated and identified as follows:

![Graphs showing power factors for Ag, Au, and La fillers in CoSb\(_3\), CoAs\(_3\), and CoP\(_3\) skutterudites](image)

- **CoP\(_3\)**: Ag is a reasonably good filler at 100% filling fraction above room temperature. Au, however, is not a good filler in this compound. La is an excellent filler and actually enhances electronic properties for fully filled lattices.

- **CoAs\(_3\)**: Both Au and Ag are good fillers at temperatures above 500 K. The power factor for Ag(\(\text{CoAs}_3\))\(_4\) experiences a dip at 450 K because of the transition from p-type to n-type behavior, as reflected by the sign of \( S \). La is a moderately good filler.
However, completely filling the lattice with Au seems to have an enhanced effect on electrical transport properties compared to partial filling, so this system is worthwhile as the subject of future research for high temperature applications.

- CoSb$_3$: Ag is a poor filler. Au holds great promise as a filler, especially for low filling fractions at temperatures between 500 K and 800 K and for complete filling at temperatures above 700 K. Indeed, complete filling with Au exhibits the greatest enhancement of electrical transport properties at very high temperatures, even when compared with La, which is an excellent filler in fully filled systems.

Figure 3.6 indicates the potential of fillers for high-performing thermoelectric behavior, based on undoped systems. The power factors at 100% filling are markedly higher because of a multiple-fold increase in the electrical conductivity, specifically in the $\sigma_{zz}$ component. This is likely due to increased coordination between the filler atoms and the host lattice in the fully filled configuration. Ag and Au are excellent conductors, and in a fully filled skutterudite lattice, the layout of the fillers is similar to that in the pure conductors. Therefore, when the voids are fully filled, there may be resonance at the location of the fillers, so that a highly electrically conductive material would be produced. Experimentally, this is corroborated by 90% La filled CoSb$_3$ exhibiting the best performance among similar skutterudites [4].

Although the fully filled systems in general show the greatest promise, 100% filling is rarely achievable without heavy doping for charge compensation. Furthermore, a system that does not possess high power factors when undoped may still be a good thermoelectric when doped, since it is also likely that fully filled materials would exhibit high thermal conductivities without the introduction of impurities or defects. In any event, screening calculations on undoped systems, as performed here, can aid in highlighting systems where the filler acts as a dopant and enhances electrical transport properties. For the examples of solar thermal or powering electronics at mid-range temperatures (e.g., 500-600 K), fractionally filled materials, such as the Au$_{0.125}$(CoSb$_3$)$_4$ system, show the most promise for improved thermoelectric behavior.

We note that Ag performs well only for the CoP$_3$ system, while Au performs well only for the CoAs$_3$ and CoSb$_3$ systems. Thus, it appears that filler size is important only when it exceeds a threshold percentage of the void radius. Since Au is the smallest filler considered in this study, it does not fulfill this criterion for any Co-based skutterudite. La, being the largest filler considered in this study, does fulfill this criterion for all Co-based skutterudites and exhibits good performance in all cases. However, higher filler weights are important.
when considering systems with larger voids, and will likely have an even greater impact on thermal behavior.

The electronegativity of the filler may play an even greater role in determining the electrical behavior of the system. La, with an electronegativity of 1.1 on the Pauling scale, readily donates electrons to the lattice, which results in enhanced electrical properties. On the other hand, Au and Ag atoms are more selective in their willingness to donate electrons. Au has an electronegativity of 2.4 while Ag has an electronegativity of 1.9 on the Pauling scale. The electronegativity of Ag is much closer to that of the M atoms in the skutterudite (1.9-2.1 on the Pauling scale), while the difference in electronegativity between Au and the M atoms is much larger. In fact, since the electronegativity of Ag is so close to that of the M atoms, it is a poor filler in all but the phosphide skutterudites. On the other hand, Au is a good filler in arsenide and antimonide skutterudites, where the electronegativity difference is 0.4 and 0.5, respectively, but poor in the phosphides. Thus, we propose that the absolute difference in electronegativity between the filler and host atoms, combined with the atomic weight of the filler atom, are important considerations for designing improved thermoelectric materials.

We now examine in greater depth four systems that exhibit improved electrical transport properties upon filling:

- 12.5% Au filled CoSb₃
- 100% Au filled CoSb₃
- 100% Au filled CoAs₃
- 100% Ag filled CoP₃

Figure 3.7 shows the band structures and density of states for these systems. Figures 3.8-3.9 show the computed values of the Seebeck coefficient, $S$, and electrical conductivity, $\sigma$, as a function of temperature for these systems. Two observations may be made:

- From the density of states, it seems that there is no appreciable band gap in the fully filled skutterudites, Au(CoSb₃)₄, Au(CoAs₃)₄, and Ag(CoP₃)₄, so it would appear likely that these compounds would be conducting and would not make good thermoelectric materials. However, in the case of Au(CoAs₃)₄ and Ag(CoP₃)₄, the band
Figure 3.7: Band structures and partial density of states for best-performing Ag and Au filled Co-based skutterudites: 12.5% and 100% Au filled CoSb$_3$, 100% Au filled CoAs$_3$, and 100% Ag filled CoP$_3$. 
Figure 3.8: Electrical transport properties, $S$, $\sigma$, and $S^2\sigma$, as a function of temperature for 12.5% and 100% Au filled CoSb$_3$ and 100% Au filled CoAs$_3$.

structure indicates that the filler creates an indirect band gap of -0.8 eV and -0.45 eV, respectively; these indirect band gaps are seen between the $P$ and $\Gamma$ $k$-points. We expect that these materials would therefore exhibit semimetallic rather than metallic properties. The sign of the $S$ values indicate that Au(CoAs$_3$)$_4$ exhibits p-type behavior while Ag(CoP$_3$)$_4$ exhibits n-type behavior. These materials should thus be further studied to ascertain their thermal conductivities.

- Filling CoSb$_3$ with small fractions of Au does not appreciably alter the narrow band gap. In Au$_{0.125}$(CoSb$_3$)$_4$, $S$ is greatly enhanced while $\sigma$ experiences only a slight increase. The resulting undoped, Au filled compound is a p-type semiconductor with high $S$ values. To improve the values of $\sigma$, further analysis of doping was performed to determine whether enhancement of electrical transport properties is possible even at low Au filling fractions; this will be described in Section 3.2.3.
Figure 3.9: Electrical transport properties, \( S \), \( \sigma \), and \( S^2 \sigma \), as a function of temperature for 100% Ag filled CoP\(_3\).
Figure 3.10: Thermodynamic cycle indicating the thermodynamically downhill energy of formation for Au filled CoSb₃.

Figure 3.10 shows a complete thermodynamics cycle for the formation of the minimally filled Au₀.₁₂₅CoSb₃ system from CoSb₃.

- First, we calculated the total energy of unfilled CoSb₃ (-646.6 eV), and set this to be our reference point.

- Second, we calculated the total energy of 12.5% Au filled CoSb₃ (-648.9 eV).

- Third, we calculated the total energy of unfilled CoSb₃ with the same void radius as 12.5% Au filled CoSb₃, by simply removing the Au filler atom and performing an energy minimization without geometry optimization.

By subtracting the total energy of the Au filler atom (-0.1 eV) from the system, we see that the formation of the filled compound is thermodynamically favorable, with an overall energy of formation of -2.2 eV. Thus, it should be theoretically possible to synthesize partially Au filled skutterudites and experimentally characterize its properties for use in thermoelectric devices.
We also performed an analysis of the maximum filling fraction possible based on previously established methods [28]. This analysis tells us that, depending on the structure of the alternate stable phase AuSb$_2$, a maximum filling fraction of anywhere between 6% (Fm3m symmetry) to 100% (P2$_1$\bar{c} symmetry) is possible without doping. Further information about secondary phases is necessary to more accurately determine the maximum filling fraction.

### 3.2.4 Analysis of unit cell symmetry

![Symmetries of filled skutterudite systems](image)

Figure 3.11: Symmetries of filled skutterudite systems. Cubic systems have the highest symmetry, followed by rhombohedral and then orthorhombic systems.

We previously presented our calculated electrical transport properties for the filled skutterudite systems exhibiting Im\bar{3} symmetry in their unit cells, so we had omitted the 25%, 50%, 38
and 75% filling fractions in Figure 3.6. For \( \text{Au}_x(\text{CoSb}_3)_4 \), the 25% filling fraction has three possible symmetry configurations: \( \text{R}\bar{3} \), Cmmm, and Pmmm, the 50% filling fraction has five possible symmetries, and the 75% filling fraction has three possible symmetries. Since the 12.5% filling fraction had been shown in Section 3.2.3 to exhibit improved electrical transport properties, we were especially interested in exploring all of the possible symmetries for the 25% filled structure, but in the case of the 50% and 75% filled structures, we chose instead to perform calculations for only one symmetry group each, which were \( \text{Pm}\bar{3} \) and Cmmm, respectively. We note that \( \text{Im}\bar{3} \) is considered a high symmetry group, so the other symmetry groups being considered are lower in symmetry than \( \text{Im}\bar{3} \) (Figure 3.11). In Figure 3.12, we plotted the power factor, \( S^2\sigma \), of CoSb\(_3\) as a function of Au filling fraction at different unit cell symmetries corresponding to the filling fraction. We observe that visible distortions in the overall trends are indeed observed at the 25%, 50%, and 75% Au filling fractions, compared to those computed with \( \text{Im}\bar{3} \) symmetry.

Figure 3.12: Electrical transport properties, \( S \), \( \sigma \), \( S^2\sigma \), as a function of Au filling fraction, \( x \), for all symmetries computed for \( \text{Au}_x(\text{CoSb}_3)_4 \).
To quantify the effect of symmetry on electrical transport properties, the 25% Au filled system was re-optimized at all of its possible symmetries – Cmmm (orthorhombic dipyramidal), Pmmm (orthorhombic dipyramidal), and R3 (trigonal rhombohedral). From Figure 3.12, we see that the R3 symmetry for the unit cell results in the largest power factors. We conclude that the pattern in which the voids are filled is important for achieving favorable electrical transport properties, but stress that the full range of predicted values is likely to be observed experimentally when symmetry is difficult to control. Figure 3.12 also suggests that 25% Au filling at Cmmm symmetry may exhibit a higher power factor than 12.5% Au filling at Im\bar{3} symmetry, and this prediction is confirmed by the results shown in Figure 3.13 for power factor as a function of temperature.

![Graph showing power factor vs. temperature for different symmetries](image)

**Figure 3.13:** Thermoelectric power factor, $S^2\sigma$, as a function of temperature for 25% Au filled CoSb$_3$.

Figure 3.14 shows the $S$, $\sigma$, and $S^2\sigma$ values for the 12.5%, 25%, and 100% Au filled CoSb$_3$ systems at 500 K. The graphs show values for doping levels from -0.5 eV to +0.5 eV around the Fermi energy, as simulated using the rigid band model. From these graphs we note that filling with Au creates a second hump in the $S$ value which shifts further away from the Fermi energy with increasing filler concentration. This second hump also results in the highest values of $S^2\sigma$. The greatest potential for thermoelectric behavior, in terms of the $\text{tr}(S)$ value, is observed in the 25% filled compound, while directionally, it is observed for the $S_{xx}$ component in the 100% filled compound. Fully filling the lattice with Au appears to unfairly dope the host material by a suboptimal amount (i.e., too little or too much).
into the valence band, so that the power factor is compromised at 500 K. However, further improvement in the power factor may be achieved by doping the material. We conclude that low fractional filling with Au appears to induce promising p-type behavior and provides a good complement to n-type Lanthanum filled materials in p-n junction devices.

### 3.3 Conclusions

We have shown that density functional theory calculations following the Projector-Augmented Wave approach, in conjunction with the momentum matrix method for calculating electrical transport properties, may be used successfully to obtain predictive trends in the performance of Co-based skutterudites over a temperature range of 300-900 K. Au filling results in p-type behavior whereas Ag filling results in n-type behavior. When considering the properties of candidate fillers, the relative weight and electronegativity appear to affect electrical transport properties more than the absolute size of the filler atom. These properties are evident when considering that the hybridization of the filler atom’s $s$ electrons is most emphasized in the fully filled skutterudites, as demonstrated in the density of states around the Fermi level in Figure 3.7. Therefore, in these fully filled systems, a resonance quality arises in the lattice.
where the coordination of electrons results in greatly enhanced electrical conductivities; this enhancement is most notable at high temperatures. Based on our calculations, fully Au filled CoSb$_3$ would make an excellent thermoelectric material at temperatures above 600 K, but it may be difficult to synthesize this material in a cost-effective manner [29, 30] and it may even exhibit undesirable (semi)metallic behavior, as suggested by our band structure calculations. Thus, we propose that low Au filling fractions (e.g., 25% or 12.5%) offer the optimal balance between improved performance and economical value. In terms of building an efficient thermoelectric device with a p-n junction, we suggest that coupling p-type Au filled CoSb$_3$ with n-type Lanthanum (or other rare earth element) filled CoSb$_3$ would favorably result in a device with optimal performance yet minimal lattice strain at the heterojunction.
References


Chapter 4

Analysis of New Transparent Conducting Oxides

Ternary oxides, particularly doped films and compounds of oxides of tin, indium, and zinc, have long been known to possess strong transparent conducting properties [1]. Depending on the components in the compounds, ternary oxides may also exhibit magnetic properties [2, 3] and find use as dilute magnetic semiconductors (DMSs) in spintronics [4]. Many of the best-performing transparent conducting oxides (TCOs) available today are n-type, although there have been many attempts to produce p-type ZnO and CuAlO$_2$ films. Our focus is on ZnO films, as the ternary compounds of these oxides show promise for high electrical conductivities but are largely undiscovered. The oxygen vacancies and interstitial defects in ZnO have been shown to cause Fermi level pinning in these compounds, making it difficult to achieve p-type conductivities. It is this lack of highly conductive p-type materials that presents an obstacle to attaining progress in transparent electronics and spintronics. Ternary oxides, however, may prove to be the gateway to better performing p-type materials. Although many ternary oxides are insulating, they may be doped to induce semiconducting behavior. There are 140 known oxide spinels, with possibly many more structures that have yet to be synthesized. A common means of searching for ternary oxides has been to sample the triangular phase space and determine whether the most favorable structures are thermodynamically stable [5, 6]. These structure stability predictions are extremely valuable; however, improvements in computational techniques to enable accurate property predictions would facilitate the search for these new materials.
Of these ternary oxides, the zinc oxide spinels (AB₂O₄, where A = Zn) are particularly attractive due to their low cost and unique doping characteristics [7]. Specifically for p-type ZnCo₂O₄ and NiCo₂O₄, high conductivities in these materials are attributed to off-stoichiometric compositions, especially when synthesized in Zn/Ni rich environments. It has been shown that NiCo₂O₄ exhibits high conductivities, on the order of σ = 10² S/cm, in part due to self-doping through the preference of the Ni atom for the T₄ (tetrahedrally coordinated) site over the O₈ (octahedrally coordinated) site in the normal spinel structure. According to multiple theoretical investigations, ZnCo₂O₄ is a normal spinel at low temperatures. As temperature increases, so do the number of anti-site defects, and at temperatures above 800 K, the structure becomes heavily non-stoichiometric [8]. The anti-site defects create donor and acceptor states, and thus are favorable for improving the electrical conductivity of the material [9]. The compound is, however, more optically absorbent than generally desirable for transparent electronics.

In this chapter, we look at yet-to-be synthesized first-row transition metal zinc oxide spinels, and compare their electrical transport and optical properties to those of the recently characterized ZnCo₂O₄ [10]. There have been many promising results on the role of the Zn atom in these structures, and to complement these results, we would like to investigate the effect of exchanging the Co (B) atom for a higher valence atom.

The structures of the zinc oxide spinels chosen for this study are based on recent developments in accelerated materials screening and discovery. Hautier et al. [5] developed an algorithm, which combines machine learning techniques and high throughput ab initio calculations, to

Figure 4.1: Unit cell of the cubic spinel ZnB₂O₄ (left), and the high symmetry path for the corresponding first Brillouin zone (right).
build a model for predicting the structure of known ternary oxide compounds and finding new, stable compounds. Among the 209 compounds predicted by their algorithm are two first row transition metal zinc oxide spinels – ZnNi$_2$O$_4$ and ZnCu$_2$O$_4$. Spinels may have different configurations, of which the most common is the normal cubic (Fd$ar{3}$m) [11]. The distorted tetragonal ($I_4_1$/amd) structure is another common structure and phase transitions between these two structures may occur at high pressures [12, 13]. According to Hautier et al. [5], ZnNi$_2$O$_4$ is predicted to have a distorted spinel structure ($I_4_1$/amd), which has a slightly off-cubic tetragonal unit cell, while ZnCu$_2$O$_4$ is predicted to have a normal cubic spinel structure (Fd$ar{3}$m). Both structures and their Brillouin zones are shown in Figures 4.1 and 4.2. Zhang et al.[14] developed a diagrammatic separation method of classifying BA$_2$X$_4$ compounds into crystal structure types based on the tabulated pseudopotential radii of A and B; using this method, we confirm that both ZnNi$_2$O$_4$ and ZnCu$_2$O$_4$ adopt spinel crystal structures. As both compounds lie on the boundary between normal and inverse spinel structures (Figure 3 of Zhang et al.[14]), we hypothesize that they may exhibit similar properties to ZnCo$_2$O$_4$.

Figure 4.2: Unit cell of the tetragonal spinel ZnB$_2$O$_4$ (left), and the high symmetry path for the corresponding first Brillouin zone (right).

### 4.1 Focus of Study

In this study, we will calculate properties that determine the figure of merit for a transparent conductor, which we have already shown (see Section 2.1.2) depends on the conductivity, $\sigma$, and the absorption coefficient, $\alpha$, regardless of which definition is taken for the figure of merit. By calculating $\sigma$ and $\alpha$ as a function of structure and chemical composition we
will gain atomistic-level insight into how selecting the B atom may affect the performance of zinc oxide spinels; specifically, we are interested in determining whether the maximum theoretically attainable conductivities are sufficient for transparent conducting applications. We also predict the magnetic behavior of these compounds to ascertain whether they may be classified as dilute magnetic semiconductors.

4.2 Calculations

The electronic density functions and the optical matrix elements are computed with density functional theory (DFT) [15, 16], using a modified version of the Vienna ab initio Simulation Package (VASP) [17, 18, 19, 20]. Both the generalized gradient approximation (PBE) [21, 22] and the hybrid functional with an optimized screening parameter (HSE06) [23, 24, 25, 26] are used to represent the exchange-correlation term in the energy functional. Projector augmented-wave (PAW) potentials [27, 28] are used to maintain a balance between accuracy and computational costs. The blocked Davidson iterative matrix diagonalization algorithm [29] is used to optimize the orbitals, and the tetrahedron method with Blöchl corrections is used to determine partial occupancies. For the hybrid functional calculations, the range separation parameter is set to 0.2 a.u.

To determine the effect of band gap underprediction on property calculations, we apply the scissor operator to the band energies of both DFT and hybrid DFT calculation results. By artificially shifting the valence bands and conduction bands symmetrically around the midgap to match the experimental band gaps, we can quantify the effects of the difference in curvature of valence band edge states.

We use the two available methods to calculate the group velocities of electrons for the determination of material properties. The first method, implemented in the BoltzTraP package [30], applies Fourier transform expansion of the band energies to determine the gradient along the energy bands, and hence the group velocities of states. Although this method has been proven to yield accurate results across various systems, it is computationally expensive as it requires high \( k \)-point meshes for convergence.

\(^4\)Our modification directly outputs the diagonal elements of the optical matrix.
The second approach to calculating group velocities is to use the Momentum Matrix (PAW-MM) method (described in more detail in [31]) to derive the group velocities of the electrons directly from the wavefunction descriptors, which avoids band crossing errors. The velocities are computed directly by the electronic structure code, and are expressed in terms of the optical matrix elements [32] (Equation 2.7). Once the group velocities are determined, the bulk semi-classical transport properties can be calculated as a function of temperature $T$ and chemical potential $\mu$, using Boltzmann transport theory [30] (Equations 2.18-2.22). While all calculations of electronic wave functions are performed for the ground state (e.g., 0 K), electronic properties at higher temperatures are simulated by applying the Fermi distribution over electronic states, as described in Equation 2.3.

By observing the area around the Fermi level for any computed structure, we can obtain a picture of the effect of light doping on that structure. We assume that such doping can be achieved without significant distortion of the native band structure; this is the rigid band approximation (RBA).

After extensive $k$-point sampling convergence tests for the BoltzTraP method, the BZ for the Fd3m system is sampled with a $41 \times 41 \times 41$ $k$-point grid, which yields 1771 unique $k$-points in the IBZ, while the BZ for the I4$1$amd system is sampled with a $28 \times 28 \times 28$ $k$-point grid, which yields 1639 unique $k$-points in the IBZ. In order to save computational costs, we perform all calculations simultaneously with this sampling rate. The kinetic energy cutoff for the plane wave basis set is set to 520 eV. The resulting wavefunctions are used in the Momentum Matrix equation, with a PAW potential correction to determine the group velocities. Equations 2.18-2.22 are then used to determine the transport properties from the group velocities with an in-house MATLAB [33] code.

### 4.3 Structure Optimization

The results of the HSE06 structural optimizations are shown in Table 4.1. Both the cubic and tetragonal structures were evaluated for the two new compounds, ZnCu$_2$O$_4$ and ZnNi$_2$O$_4$, in three possible spin configurations (i.e., nonmagnetic (NFM), antiferromagnetic (AFM), and ferromagnetic (FM)). However, for the previously characterized compound, ZnCo$_2$O$_4$, only the known cubic structure was investigated. Only the lattice parameters of the two most stable structures for each compound are shown. ZnCo$_2$O$_4$ exhibits two possible structures,
Table 4.1: Total energy per primitive cell (14 atoms) of all systems studied. Lattice parameters are for the corresponding unit cell.

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<td>FM</td>
<td>−127.883</td>
<td></td>
</tr>
</tbody>
</table>

NFM and AFM, which suggests that this compound is not likely to possess desirable properties as a DMS. Comparison to the experimental lattice parameter of 8.0946(2) Å (JCPDS card no. 23-1390) [34] suggests that the NFM configuration is more representative of the experimentally observed structure. ZnNi$_2$O$_4$ is most stable as an AFM structure, with its FM structure being 0.3 eV less stable. ZnCu$_2$O$_4$ shows the most promise as a DMS, with the cubic and the tetragonal FM structures being equally stable. The identical total energy of these two structures suggests that fabrication method and substrate are important in determining the preferred structure formed for this compound.

Table 4.2 shows the total energy for the cubic ZnCu$_2$O$_4$ primitive cells under partial and complete inversion, and the corresponding lattice parameters of the unit cell for the most stable systems. As shown, the FM system is always the most thermodynamically stable configuration, and the inverted spinel structure is less stable than the normal spinel.

Table 4.3 shows the mean distance between the Zn and B octahedrally coordinated atoms and the corresponding O atoms. As the atomic number of B increases, so does the mean distance, independent of the structure. Inversion in the cubic ZnCu$_2$O$_4$ system leads to a decreased distance between the Cu atom and its O neighbors. Also, with the inverted systems
Table 4.2: Total energy per primitive cell (14 atoms) of cubic ZnCu$_2$O$_4$ systems under partial and total inversion. Lattice parameters are for the corresponding unit cell.

<table>
<thead>
<tr>
<th>System</th>
<th>Symmetry</th>
<th>Magnetism</th>
<th>Energy(eV)</th>
<th>lattice parameter(s) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% inversion</td>
<td>R3m</td>
<td>NFM</td>
<td>$-94.722$</td>
<td>$a=5.843, c=14.659$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AFM</td>
<td>$-96.529$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>FM</td>
<td>$-96.807$</td>
<td></td>
</tr>
<tr>
<td>100% inversion</td>
<td>Imma</td>
<td>NFM</td>
<td>$-95.286$</td>
<td>$a=5.826, a=6.103, c=8.140$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AFM</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>FM</td>
<td>$-95.577$</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3: Mean distance between octahedrally coordinated atoms, Zn and B, and the corresponding O atoms.

<table>
<thead>
<tr>
<th>System</th>
<th>Symmetry</th>
<th>Magnetism</th>
<th>Mean B-O distance (Å)</th>
<th>Mean Zn-O distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCo$_2$O$_4$</td>
<td>Fd3m</td>
<td>AFM</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>ZnCo$_2$O$_4$</td>
<td>Fd3m</td>
<td>NFM</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>ZnCu$_2$O$_4$</td>
<td>Fd3m</td>
<td>FM</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>ZnCu$_2$O$_4$</td>
<td>I4$_1$amd</td>
<td>FM</td>
<td>2.42</td>
<td></td>
</tr>
<tr>
<td>ZnCu$_2$O$_4$ 50% inversion</td>
<td>R3m</td>
<td>FM</td>
<td>2.35</td>
<td>2.52</td>
</tr>
<tr>
<td>ZnCu$_2$O$_4$ 100% inversion</td>
<td>Imma</td>
<td>FM</td>
<td>2.38</td>
<td>2.50</td>
</tr>
<tr>
<td>ZnNi$_2$O$_4$</td>
<td>I4$_1$amd</td>
<td>FM</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>ZnNi$_2$O$_4$</td>
<td>Fddd</td>
<td>AFM</td>
<td>2.33</td>
<td></td>
</tr>
</tbody>
</table>
we see that, as expected, Zn-O distances are greater than for any of the B atoms, and that increased inversion leads to O atoms being less tightly packed around the B atom. For the Co and Ni systems, we see that the most stable structures have the same mean B-O distances, regardless of magnetism. For the Cu system, we see that the tetragonal structure has greater B-O distances than the cubic structure. This will likely result in weaker hybridization of valence orbitals in the tetragonal structure than in the cubic structure.

4.4 Optical Properties

The absorption coefficient spectra for the bulk materials are shown in Figure 4.3. The absorption in the visible range (390-700 nm) is high for all three compounds. ZnNi$_2$O$_4$ exhibits an absorption coefficient similar to that of ZnCo$_2$O$_4$, although it is lower in the ultraviolet range. This would be useful in solar applications, since most solar absorbers absorb strongly in the UV range. Interestingly, the slightly less stable AFM structure has a lower absorption throughout the visible range, suggesting that if this structure could be preferentially synthesized, a more transparent compound would be formed. ZnCu$_2$O$_4$ has a much higher absorption throughout the calculated spectrum. The cubic structure has considerably lower absorption for $\lambda > 600$ nm, so again, if the synthesis could be controlled in favor of cubic lattice formation, a much more transparent compound would be formed. Cation inversion in the cubic ZnCu$_2$O$_4$ structure seems to decrease absorption at wavelengths $\lambda < 400$ nm, which may pose an option for engineering more UV-transparent spinels. However, as the percentage of inversion increases, absorption increases as well for $\lambda > 600$ nm. Therefore, should this approach be used to decrease absorption for low $\lambda$, we should consider all of these effects to account for increased absorption at higher wavelengths. It may still be possible to create very thin films of these materials, so that their optical absorption is not an impediment to transparent conducting applications.
Figure 4.3: Absorption coefficient for all systems studied.

4.5 Electronic Properties

4.5.1 Band Structures

For all systems (except ZnCo$_2$O$_4$) computed with DFT, the electronic band gap entirely disappears, so that the conduction and valence bands become entangled (see Figure 4.4). This is due to the well-known band gap underestimation caused by the incorrect treatment of electron exchange in DFT [35, 36]. As a result, the Fermi level falls within one long, extended band, and the material appears to be metallic.\(^5\) Therefore, DFT is inadequate for predicting the electronic properties of the ternary oxides under study, and is not suitable for screening these materials. Later, we will quantify whether recalculating the band gap at the $\Gamma$ point with a method that more accurately describes the exchange correlation interactions,

\(^5\)The red and green dashed lines in all band structure plots show the filter of the distribution function, (Equation 2.3), at 300 K and 800 K, respectively; these are the bands around the Fermi level that contribute to the summation in the conductivity calculation. Because of the exponential term in this expression, band energy contributions outside this distribution are zero. The filter for 300 K is much smaller than for 800 K. This result has two consequences: 1. For low temperatures, fewer bands are included in the summation, and thus a higher $k$-point mesh is necessary to obtain accurate estimations of the electrical properties, and 2. High temperature calculations are much more sensitive to errors in the determination of the band gap.
such as hybrid DFT with the HSE06 functional, and then applying the scissor operator is sufficient to correctly describe the band curvature and thus determine electronic properties.

Figures 4.5-4.10 show the HSE06 band structures and partial density of states (pDOS) for the systems under consideration with the lowest total energies. In all spin polarized pDOS calculations, the solid line represents spin up states, and the dotted line represents spin down states. For ZnCo$_2$O$_4$, the indirect band gap is 3.72 eV, which represents an increase of 2.82 eV from the DFT calculation, and an increase of 0.9 eV from the value reported by Paudel et al. [9]. From the pDOS, we see that the O 2p orbitals contribute considerably to the valence band, with a significant shallow hybridization with Co 3d orbitals and a deep valence hybridization with the Zn 3d orbitals (not shown). Spin up and spin down state populations in the AFM structure are perfectly aligned.

For the other two systems, ZnCu$_2$O$_4$ and ZnNi$_2$O$_4$, an interesting phenomenon occurs; namely, the density of states shows dependency on the spin polarization. The conduction band, which is similar in shape to the one observed in ZnCo$_2$O$_4$, is occupied by only spin down electrons in ZnCu$_2$O$_4$. In tetragonal ZnNi$_2$O$_4$, the conduction band is split between spin up and spin down states. This band is located much closer to the valence band; the calculated band gaps for the Cu and Ni compounds are significantly smaller, being 1.17 eV.
for ZnCu$_2$O$_4$ and 1.67 eV for ZnNi$_2$O$_4$. The favorable band gap and spin polarization distribution results in ZnCu$_2$O$_4$ and tetragonal FM ZnNi$_2$O$_4$ being ideal for magnetoelectronics applications.

Both the cubic and tetragonal FM ZnCu$_2$O$_4$ systems have a valence band that is populated by both spin up and spin down states, mainly of O 2p character, with some 3d hybridization from the Cu valence. This material will exhibit polarized conductivity and a variable band gap of 1.17 eV for spin down states and 5.2 eV for spin up states. Therefore, under a magnetic field, this material can be switched to exhibit properties between those of an insulator and semiconductor. The valence band states have significant curvature as compared to the ZnCo$_2$O$_4$ compound at the $\Gamma$ point, which signals low electron effective mass and potentially high p-type semiconducting behavior.

The tetragonal FM ZnNi$_2$O$_4$ system has only spin up electrons occupying shallow states of the top of the valence band and bottom of the conduction band. The spin up effective band gap is 1 eV and the spin down effective band gap is 3 eV, which makes this material attractive for applications where the material band gap needs to be dynamically tuned. In the distorted structure, the spin down electron states in the conduction band lie closer to the valence band. Whereas the valence band edge in the cubic structure is relatively flat (not shown), it shows higher curvature in the distorted spinel, which indicates high carrier
mobility. Since the conduction states lie closer in energy to the valence states, they have a strong influence on the shape of the valence states and induce enhanced curvature in these valence states. The orthorhombic AFM spinel ZnNi$_2$O$_4$ structure shows a wider indirect band gap (2.2 eV) than the other new alloys, strong curvature of the valence band, and a relatively flat conduction band edge. All of these factors make this material ideal for transparent conducting applications.

It is evident that in all of these materials, the octahedrally coordinated Zn atom is relatively inert in determining the valence electronic properties, and it is the interaction between the tetrahedrally coordinated B 3d electrons and the O 2p electrons that strongly influences these properties in the compound. With increasing atomic number of B, we notice a significant narrowing of the band gap. Additionally, we note that with increasing atomic number of B, there is less contribution from the B 3d orbitals to the shallow valence band states, resulting in a destabilization of the O 2p orbitals, and a broader hybridization energy range throughout the shallow valence states. We also notice that the curvature of the valence band also increases from ZnCo$_2$O$_4$ to ZnNi$_2$O$_4$ and ZnCu$_2$O$_4$, mainly due to the destabilized O 2p states; this would lead to lower hole effective masses and thus, higher electrical conductivities upon light p-type doping in the latter two compounds. Therefore, there is a correlation between the destabilization of O 2p orbitals and greater curvature of the valence band edge, wherein the properties of the material can be optimized with the choice of element B.
4.5.2 Cation Inversion

When synthesizing spinels, one of the most common distortions in the structure is cation inversion, or the preferential swapping of B atoms for Zn atoms. Since we have determined that the 3d electrons of the octahedrally coordinated B atom strongly influence electronic properties, it is important to study cation inversion to determine its effect on the band structure of the material. Although small fractions (i.e., < 10%) of inversion are achievable in practice, it is too computationally expensive to perform calculations for these small fractions of inversion; however, we note that the rigid band approximation we use for doping can also be used to approximate very small fractions of inversion, and can be treated as a form of light self-doping within the material. By looking at the trends from 0 to 50 to 100% inversion, we can determine the electronic characteristics of inversion, and thus, the impact on the properties of the materials.

We look at cubic ZnCu₂O₄ as an illustrative example of the effect of cation inversion on material properties. We find that, again, for 50% and 100% cation inversion, the FM structure is the most stable, so we determine that this compound is FM in the ground state regardless of atom arrangement. Additionally, by examining the band structures (see Figures 4.11-4.12), we notice that inversion causes narrowing of the band gap, and thus, a likely increase in electrical conductivity but a decrease in transparency. As indicated by the increase in
Figure 4.8: Band structure and partial density of states (pDOS) for tetragonal FM ZnCu$_2$O$_4$.

The average distance between the octahedrally coordinated Cu and Zn atoms, the hybridization peak of the transition metal 3d electrons and the O 2p electrons at the top edge of the valence band is much smaller than in the normal structure. Furthermore, inversion may possibly hinder p-type doping capabilities. Again, although such high levels of cation inversion are unlikely in practice, as corroborated by the total energy data, these computations lead us to conclude that cation inversion has adverse effects on transparency, and the occurrence of such inversion should be minimized during fabrication.

### 4.5.3 Bader Charge Analysis

Table 4.4 shows the calculated electronic charges of B and Zn atoms on their native sites in the normal spinel structure, and at a defect site, where stoichiometry of the lattice is preserved (i.e., cation inversion). The energy levels of these defects introduce donor and acceptor levels in the material, and determine whether the Fermi level is pinned [9]. We are interested in qualitatively describing what happens to the electronic structure as defects are introduced into the lattice. As indicated in Table 4.4, as the atomic number of B increases, the charge at the Zn-site also increases slightly. Thus, the added charge is dislocated towards the Zn atom, which stabilizes the charge at a deep valence state. According to this analysis,
when the B and Zn atoms swap positions and the stoichiometry of the system is maintained, the atoms also swap formal charges. This indicates that donor and acceptor levels do not compensate each other, so doping is permitted.

Table 4.5 shows a second analysis that was performed on the charge around the B and Zn atoms in the structure. In this second analysis, the stoichiometry of the structure is changed (i.e., self-doping occurs); in the first calculation one B atom was used to replace Zn and in the second calculation one Zn atom was used to replace B. As shown in the tabulated values, in these non-stoichiometric systems, the formal charge on the atoms does not change significantly when their position in the lattice changes, although there is a small change. B atoms gain some charge when located at $O_h$ sites, while Zn loses net charge at the $T_d$ site. This latter effect indicates that the stabilizing effect of Zn is negated, and thus free carrier density increases. This effect is desirable and useful when engineering a self-doped system.

### 4.5.4 Electrical Conductivity

In this section we present the conductivity values of the systems studied. The power factor, $S^2\sigma$, is shown to emphasize the fluctuations in the electrical conductivity. Calculated
Table 4.4: Electronic charges in systems with maintained stoichiometry.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atomic Number(Valence)</th>
<th>Native Location</th>
<th>Native Charge</th>
<th>Defect Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCo$_2$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>27(9)</td>
<td>$T_d$</td>
<td>7.56</td>
<td>7.56/10.52(^a)</td>
</tr>
<tr>
<td>Zn</td>
<td>30(12)</td>
<td>$O_h$</td>
<td>10.68</td>
<td>10.69/7.72(^5)</td>
</tr>
<tr>
<td>O</td>
<td>8(6)</td>
<td></td>
<td>7.05</td>
<td>7.05</td>
</tr>
<tr>
<td>ZnNi$_2$O$_4$ (I4$_1$ amd)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>28(10)</td>
<td>$T_d$</td>
<td>8.40</td>
<td>8.58/10.58(^5)</td>
</tr>
<tr>
<td>Zn</td>
<td>30(12)</td>
<td>$O_h$</td>
<td>10.69</td>
<td>10.70(^5)/8.67</td>
</tr>
<tr>
<td>O</td>
<td>8(6)</td>
<td></td>
<td>7.12</td>
<td>7.04</td>
</tr>
<tr>
<td>ZnCu$_2$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>29(11)</td>
<td>$T_d$</td>
<td>9.58</td>
<td>9.59/10.56(^5)</td>
</tr>
<tr>
<td>Zn</td>
<td>30(12)</td>
<td>$O_h$</td>
<td>10.73</td>
<td>10.73/9.80(^5)</td>
</tr>
<tr>
<td>O</td>
<td>8(6)</td>
<td></td>
<td>7.03</td>
<td>7.02</td>
</tr>
</tbody>
</table>

\(^a\)non-native site charge

Table 4.5: Electronic charges with non-stoichiometric defects.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atomic Number (Valence)</th>
<th>Normal charge</th>
<th>B on $O_h$</th>
<th>Zn on $T_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCo$_2$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>27(9)</td>
<td>7.56</td>
<td>7.56/7.73(^a)</td>
<td>7.56</td>
</tr>
<tr>
<td>Zn</td>
<td>30(12)</td>
<td>10.68</td>
<td>10.69</td>
<td>10.68/10.51(^5)</td>
</tr>
<tr>
<td>O</td>
<td>8(6)</td>
<td>7.05</td>
<td>7.04</td>
<td>7.05</td>
</tr>
<tr>
<td>ZnNi$_2$O$_4$ (I4$_1$ amd)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>28(10)</td>
<td>8.40</td>
<td>8.61/8.61(^5)</td>
<td>8.58</td>
</tr>
<tr>
<td>Zn</td>
<td>30(12)</td>
<td>10.69</td>
<td>10.71</td>
<td>10.69/10.58(^5)</td>
</tr>
<tr>
<td>O</td>
<td>8(6)</td>
<td>7.12</td>
<td>7.02</td>
<td>7.04</td>
</tr>
<tr>
<td>ZnCu$_2$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>29(11)</td>
<td>9.58</td>
<td>9.59/9.86(^5)</td>
<td>9.57</td>
</tr>
<tr>
<td>Zn</td>
<td>30(12)</td>
<td>10.73</td>
<td>10.72</td>
<td>10.73/10.53(^5)</td>
</tr>
<tr>
<td>O</td>
<td>8(6)</td>
<td>7.03</td>
<td>7.00</td>
<td>7.03</td>
</tr>
</tbody>
</table>

\(^a\)non-native site charge
Figure 4.10: Band structure and partial density of states (pDOS) for distorted orthorhombic spinel (Fddd) AFM ZnNi$_2$O$_4$.

properties are presented for 300 K, and the presented values are those obtained using the Momentum Matrix method. The BoltzTraP method yields similar curves, with a discrepancy in magnitude of less than 5%.

First, we analyze the difference in calculated properties between the DFT and HSE computational approaches. When the band gap is merely underpredicted with DFT (e.g., the ZnCo$_2$O$_4$ system), we rectify this underprediction by applying the scissor operator in the middle of the band gap to obtain the same band gap as that determined by the HSE functional. Furthermore, we also compute $\sigma$ for both the HSE and the DFT results with the reported band gap of 2.8 eV [9] to determine whether the underestimation or overestimation of this gap affects our results. $\sigma$, $S$, and the power factor, $S^2\sigma$, are shown in Figure 4.13 for the four scenarios of adjusted band gap: HSE unadjusted (HSE), DFT adjusted to match HSE (DFT-HSE), DFT adjusted to match experiment (DFT-exp), and HSE adjusted to match experiment (HSE-exp). From these results we determine that: 1. Artificially changing the band gap does not discernibly affect the magnitude and distribution of the $\sigma$ values at 300 K, 2. The curvature of the bands from the DFT calculation describes the valence states much differently from the those obtained using the HSE calculation, due to the incorrect exchange interaction factor, and 3. When the HSE calculation is corrected by manually narrowing the band gap to fit previously reported values, the conductivity values
Figure 4.11: Band structure and partial density of states (pDOS) for cubic spinel FM ZnCu$_2$O$_4$ with 50% cation inversion.

are not affected by the band gap difference. These results indicate that the distribution of states in the summation for property calculation is not dependent on the width of the band gap, as long as the conduction bands lie outside the Fermi distribution (this observation is corroborated by the previously presented band structures). The last result also means that we may calculate the electronic properties of these p-type alloys at 300 K using the HSE determined band gap, without adjustment for experiment, as long as our band gap is not over or underpredicted by an amount that would place the bottom conduction band within the Fermi distribution range filter at 300 K. Since the computed band gap deviates from the experimentally observed gap by 0.9 eV, we originally expected that the computed band curvature will not be exact. However, the HSE band curvatures are more accurate than the DFT values, as the DFT band gap is underpredicted by a much larger amount (1.9 eV), and underprediction leads to greater deviation of band curvature due to exchange interaction. Therefore, we choose the HSE method to characterize the new systems in the following analysis.

Figure 4.14 shows the $\sigma$, $S$, and $S^2\sigma$ values for AFM and NFM cubic ZnCo$_2$O$_4$. We note the first optimum doping level at -0.6 eV for p-type conductivity in this material. Assuming

\[ \text{Here, } S \text{ approaches infinity from the left and negative infinity from the right, since the material has a wide band gap and is intrinsically an insulator.} \]
Figure 4.12: Band structure and partial density of states (pDOS) for cubic spinel FM ZnCu$_2$O$_4$ with 100% cation inversion.

$\tau_e \approx 10^{-14}$ s$^7$ yields a local maximum conductivity of $1.3 \times 10^4$ S/cm with a broad average optimum conductivity of $\sigma = 1 \times 10^4$ S/cm. At 673 K, the optimum conductivity is $\sigma = 1.2 \times 10^4$ S/cm. The intrinsic conductivity at 300 K and 673 K is $\sigma = 1.5 \times 10^2$ S/cm and $\sigma = 5.5 \times 10^2$ S/cm, respectively, for the NFM structure and $\sigma = 1.6 \times 10^2$ S/cm and $\sigma = 5.8 \times 10^2$ S/cm, respectively, for the AFM structure; this is comparable to the $\sigma = 100$ S/cm reported by Paudel et al.[9] in their off-stoichiometric "doped" NiCo$_2$O$_4$. The likely computational sources for this deviation are twofold: 1. The highly off-stoichiometric character of the experimentally deposited sample, and 2. The high temperature at measurement. Both factors would increase the concentration of defects in the material and distort the electronic structure from the theoretical values. We note that the computed Fermi level lies high enough in the band gap that $\sigma$ is intrinsically far removed from its optimum value. A material with a lower lying intrinsic Fermi level would be ultimately preferable.

Figure 4.15 shows the electrical properties of cubic and tetragonal ZnCu$_2$O$_4$. Here, the cubic material is not a wide gap insulator, and hence the $S$ value does not saturate within the gap. The undoped conductivity of the material at 300 K is predicted to be $\sigma = 17$ S/cm and the first local minimum is of the same magnitude and occurs at approximately the same doping level (i.e., -0.73 eV for Cu vs. -0.65 eV for Co) as the ZnCo$_2$O$_4$ compound. However, the

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$^7$We make this assumption for all future calculations of $\sigma$ mentioned in the text.
second local maximum in ZnCu$_2$O$_4$, at $\varepsilon_F = -1.1$eV, is $\sigma = 2 \times 10^4$ S/cm, which is twice the value of the second local maximum in ZnCo$_2$O$_4$; this peak is much broader and occurs at a lower doping level than in ZnCo$_2$O$_4$. Thus, between -0.9-0 eV, the doping patterns are similar between the two compounds, but for higher doping levels, the Cu-containing compound appears to be twice as conductive as the Co-containing compound. This result confirms the prediction for higher carrier mobility due to the increased curvature of the bands. As supported by the electronic structure calculation, wide ranges of strong hybridization in shallow valence band states leads to a broader stable conductivity curve rather than a clear peak as that observed in ZnCo$_2$O$_4$. There is not a discernible difference between the cubic and tetragonal structures, so this slight adjustment to the atom locations does not have an impact on the electronic transport behavior of the overall system. Figure 4.16 shows the properties of the cubic system with cation inversion. It can be seen that the material becomes more metallic as inversion increases, and the Fermi level is brought in the midway point in the band gap; this perhaps counters the p-type dopability in these materials.
Figure 4.17 shows the electronic properties of AFM and FM tetragonal ZnNi$_2$O$_4$. The Fermi level is again located just at the edge of the valence band, and the computed intrinsic conductivities are $\sigma = 35$ S/cm and $\sigma = 18$ S/cm for the AFM and FM structures, respectively. In this compound we notice a less well-defined local maximum and a very broad maximum range, which means that dopability for optimum performance would be easy to achieve. The conductivity maximum is found at -0.6 eV and $\sigma = 7.1 \times 10^3$ S/cm for the AFM system, and -0.8 eV and $\sigma = 7.8 \times 10^3$ S/cm for the FM system.

### 4.6 Conclusions

There exists a wide range of ternary oxide materials that have yet to be discovered but may exhibit valuable electrical transport and optical properties. In this work, we have studied in depth the properties of two new materials, ZnCu$_2$O$_4$ and ZnNi$_2$O$_4$, which were previously predicted to be oxide spinels [5]. We present their properties alongside those of ZnCo$_2$O$_4$, a previously studied insulator that shows promising transparent conducting properties when defect engineering principles are applied. The two new materials both show...
spin polarization, which could be used to fine tune their properties and switch between semiconducting and insulating behavior. As shown by theoretical computations of $\sigma$, these materials also exhibit broader conductivity maxima near the valence band edge. Hence, these materials may be easier to p-dope to induce high hole mobilities. In particular, ZnNi$_2$O$_4$ and cubic ZnCu$_2$O$_4$ exhibit high electrical conductivities while maintaining acceptable optical properties. We anticipate that these findings may guide experimental design and synthesis of new materials based on zinc oxide spinels for use in applications such as transparent conductors and magnetoelectronics.
Figure 4.16: Electronic transport properties for cubic ZnCu$_2$O$_4$ with cation inversion.

Figure 4.17: Electronic transport properties for orthorhombic AFM and tetragonal FM spinel ZnNi$_2$O$_4$.
References


Chapter 5

Determining the Effective Mass Surface

The concept of inertial carrier effective mass \( m^* \) has been developed so that the motion of electrons and holes in a semiconductor may be described in terms of the Newtonian force approximation (i.e., the classical motion of particles). The acceleration of carriers under the influence of a potential field can be described in terms of the carriers’ effective masses[1], and in turn these effective masses can be used to determine electronic properties, such as the electrical conductivity, \( \sigma \) and the Seebeck coefficient, \( S \). Effective masses can be measured experimentally for high symmetry directions within crystalline systems with known surface cleavage using the cyclotron resonance technique. They can also be computed from first principles from the \( E - k \) band diagram, or from the density of states; the latter quantity is known as the density of states effective mass, \( m^*_{DOS} \) and it is an averaging of the inertial effective mass over the entire Brillouin zone and the mobile carrier states, according to[2]

\[
m^*_{DOS} = \frac{\int m^{3/2}(E')g(E')dE'}{\int g(E')dE'}
\]

where \( g \) is the density of states and the integration is performed along the carrier band states. Numerous values for effective masses have been reported for the most common semiconductors, and the spread in the measured data has been wide. In this work, we analyze the technique utilized for determining these effective masses as a function of the crystal lattice space from the \( E - k \) relationship. We show that the determined \( m^* \) value is highly dependent on the parameters used for fitting, as well as on the Brillouin zone
sampling rate, and we present a systematized approach for reporting these values so that
direct comparison can be achieved.

A complete 3D characterization of effective masses by experimental measurements is diffi-
cult; at the same time, most computational methods up until this point have utilized the
spherical band approximation for the fitting of band curvatures, and the use of this technique
has been limited to high symmetry directions within the lattice. Young et al.[3] developed a
method for describing band non parabolicity by expressing the energy instead as a function
of energy that is parabolic with respect to $k$. There have also been attempts at describing
the deviation from parabolicity with multicomponent expansions of the band components
according to band symmetry, e.g., [4], which achieve high accuracy but are system depen-
dent. Unfortunately, these methods could not be generalized completely for systems with
complicated band warping. More recently, Mecholsky et al.[5] have developed an illuminat-
ing unifying theory, linking previous radial direction fitting schemes to the radial envelope
function of the angular spherical harmonics expression that together determine the shape
of the electronic bands. By redefining the effective mass radially in terms of a set of fitted
radial polynomials with respect to the local extremum, one can then derive the envelope
that determines the non uniform energy band shape in non-parabolic energy bands, such
as the valence bands in p-type semiconductors. This is a logical result of the discontinuous
nature of the second derivative of the $E - k$ bands at the extremum when band warping
due to degeneracy occurs. Since each $k_r$-vector represents a direct lattice plane, this radial
effective mass allows us to compute direction dependent electronic relaxation times, which
in turn allow us to determine more accurately electronic properties from first principles.

In this chapter, we look at a means of automating the effective mass surface fitting scheme
in three dimensions for the purpose of computing transport properties which require sum-
mations over the BZ. We use this method in Chapter 6 to analyze the 3 dimensional effective
mass space of the widely used p-type semiconductors silicon and gallium arsenide, and we
attempt to characterize the effective mass space computationally in order to elucidate the
influence of non spherical bands on carrier motion in p-type materials. We also derive the
relationship between the traditionally used cartesian $m^*$ tensor to the scalar radial $m^*$ tensor.
5.1 Generating a Fit for the Effective Mass

For the parabolic band approximation assumption, the effective mass is defined in terms of the truncated Taylor polynomial expansion of the band energy around the local extremum. For the Γ point, this expansion is expressed as

\[ E(k) = E(0) + \left. \frac{\partial E}{\partial k} \right|_{k=0} k + \frac{1}{2} \left. \frac{\partial^2 E}{\partial k^2} \right|_{k=0} k^2 + \ldots \]  \hspace{1cm} (5.2)

where the terms of higher order than those shown are set to 0 and the second term is 0 by definition of the extremum. The resulting spherical parabolic band expression that defines the effective mass, \( m^* \), then becomes

\[ E(k) = E(0) + \frac{\hbar^2 k^2}{2m^*} \]  \hspace{1cm} (5.3)

so that

\[ \frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}. \]  \hspace{1cm} (5.4)

Here \( k \) is the magnitude of the \( k \) vector. This formulation, although it is a useful simplification, leads to complications when the band is not spherically symmetric as is often the case for the heavy and light hole bands in p-type materials. Different methods have been developed to adjust equation 5.3 to account for the non-parabolicity of this band, such as expressing the left hand side instead as \( f(E) \), where \( f \) is a parabolic function of \( E \).[6] However, upon inspection of the success of the common linear path method of fitting whereby the polynomial is expanded in individual radial directions using equation 5.3 so that \( k \) is the radial component of \( k \) in the spherical co-ordinate system, we determine that a discretization of the three dimensional space into one dimensional radial partitions will yield differentiable fits that can be used to determine \( m^* \). The parabolic band approximation can be used near the Γ point for spherically non-parabolic bands only when carriers are confined to states near the Γ point. The problem arises when the parabolicity region is very small so that carriers occupy states in the non-parabolic region; in this scenario, equation 5.2 cannot be truncated and the effective mass is no longer defined by equation 5.4. In this chapter we focus on
the development of an algorithm of radial fitting using equation 5.2 without truncation. In the Conclusion, we will explain how equation 5.4 needs to be adjusted for the non-parabolic region to accurately determine the effective mass when the higher order terms in the Taylor expansion cannot be ignored.

Since the effective mass is direction dependent within the lattice [7],[8], it is in fact not well defined by equation 5.4 for bands whose curvature is discontinuous at the extremum (e.g., have non-isotropic effective mass) and a 3D fitting with the independent variable set as $|k|$ will yield substantial errors. By decomposing the independent variable in Equation 5.2 into its x, y, and z components and splitting up the fitting space into spherical wedges, polynomial fittings that completely describe the entire effective mass space should be attainable. In order for this fitting scheme to work for any system, the wedge size should approach 0 so that the fits are performed radially; however, when performing property calculations, the Brillouin zone space is not sampled radially and so much data would have to be dropped. Therefore, by introducing the wedge method, more data can be fitted; the wedge can be defined by a $d\theta$ and a $d\phi$ term.

Even when the region of the fitting is reduced, there are still problems with the fitting for non-parabolic bands. In more recent work, the effective mass has been derived by sampling the k-space near the Γ point finely in directions of high symmetry, and defining a radius of parabolicity for a quadratic fit. This latter method, which reduces the fitting to a 1D problem has in general yielded results in much better agreement with experiment; however, such a method is sensitive to the choice of radius of parabolicity and requires a fine sampling within a range very close to the extremum to insure true parabolic behaviour. In this work, we propose a method of fitting the bands near the Γ point uniformly in all radial directions with a much larger fitting radius by using a higher order polynomial and a weighted fitting scheme that ensures that the points nearest to the Γ point are weighted most heavily during the fitting. This also allows for a better fitting of the curvature near the Γ point by including a larger sampling of k-points to determine the overall band shape. By nature of the definition of the Taylor polynomial expansion, we know that, as $r \to 0$, the fitted higher order polynomial terms (part of the ... in Equation 5.2) can be truncated to a parabolic function to yield the curvature near the extremum. By using a higher order polynomial, we are also able to perform an accurate fit for a larger radius around the Γ-point, which is useful in describing transport when carriers travel outside the parabolicity region (which in p-type semiconductors is very small, as will be shown in the next chapter).
Effectively, this method attempts to bypass the need to determine the angular spherical harmonics, $Y_{lm}(\theta, \phi)$, that describe the electronic orbitals by calculating the effective mass in every radial direction as the reciprocal of the second radial derivative. The radial effective mass is a scalar because it embodies the angular information in the direct lattice plane which it represents. To regenerate the cartesian effective mass tensor that is usually used, and that arises when a 3D fit is performed, we can determine the relationship of the second radial derivative to the respective second derivatives in cartesian coordinates. Since for each radial direction the derivatives with respect to the angular co-ordinates are 0, we can simplify these expressions. In the following expressions we use the shorthand notation $x$ for $k_x$, and similarly for $k_y$, $k_z$, and $k_r$. For the diagonal terms of the cartesian effective mass tensor, we obtain,

$$\frac{\partial^2}{\partial x^2} = \sin^2 \theta \cos^2 \phi \frac{\partial^2}{\partial r^2} + \frac{\cos^2 \theta \cos^2 \phi}{r} \frac{\partial}{\partial r} + \frac{\sin^2 \phi}{r} \frac{\partial}{\partial r}$$  (5.5)

$$\frac{\partial^2}{\partial y^2} = \sin^2 \theta \sin^2 \phi \frac{\partial^2}{\partial r^2} + \frac{\cos^2 \theta \sin^2 \phi}{r} \frac{\partial}{\partial r} + \frac{\cos^2 \phi}{r} \frac{\partial}{\partial r}$$  (5.6)

$$\frac{\partial^2}{\partial z^2} = \cos^2 \theta \frac{\partial^2}{\partial r^2} + \frac{\sin^2 \theta}{r} \frac{\partial}{\partial r}$$  (5.7)

Since the first radial derivative must be 0 at the $\Gamma$-point, at this point for a polynomial expansion $p(r)$ with the $r^2$ coefficient equal to $a$ we obtain

$$\frac{\partial^2}{\partial x^2} = 2a \sin^2 \theta \cos^2 \phi + 2a \cos^2 \theta \cos^2 \phi + 2a \sin^2 \phi = 2a$$  (5.8)

$$\frac{\partial^2}{\partial y^2} = 2a \sin^2 \theta \sin^2 \phi + 2a \cos^2 \theta \sin^2 \phi + 2a \cos^2 \phi = 2a$$  (5.9)

$$\frac{\partial^2}{\partial z^2} = 2a \cos^2 \theta + 2a \sin^2 \theta = 2a$$  (5.10)

so we see that in fact, for the parabolic band approximation we obtain the following relationship for all $k_r$. 

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Figure 5.1: Example of a 2D space, sampled in a uniform manner using cartesian coordinates (a) and sampled preferentially in the vicinity of the origin using a radial grid (b).

\[
\frac{\partial^2}{\partial r^2} = \frac{1}{3} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right). \tag{5.11}
\]

The \(m^\ast\) computation can be performed in either cartesian or spherical coordinates and, indeed, if the final values desired are the \(m^\ast\) space, then spherical coordinates would simplify the computation and reduce the fitting to a one dimensional problem in all radial directions. However, a computational inaccuracy arises with such a transformation when simultaneously performing transport property calculations that require integrations over the Brillouin zone; specifically, sampling along the radial directions would preferentially emphasize oscillations along these directions while leaving the angular space inadequately sampled [9]. Thus, sampling along radial directions would artificially emphasize oscillations very close to the \(\Gamma\) point where the sampling is denser. If the evenly spaced cartesian grid is used to sample the Brillouin zone so a proper integration can be performed, then the data must be fit in radial wedges. The fitted function would then no longer be a simple polynomial fitted to \(r\), but would also require a complex sinusoidal dependency to account for \(d\theta\) and \(d\phi\).
5.2 Methods

In order to calculate the effective mass, we sample the space around the Γ point with an equally spaced cartesian grid instead of a radial grid. We first split up the \( k \)-space into radial wedges around the Γ point. We then reduce the problem to a 2D or 1D problem, if necessary, to avoid dependencies. The fitting is performed with a weighted polynomial matrix fitting algorithm, where the weight of each \( k \)-point, \( w_k \) for fitting is computed according to

\[
 w_k = \text{norm}(2e^{-\frac{k^2}{a_1 k_{\text{min}}}}) \quad (5.12)
\]

for a more gradual dropoff of the weights, or

\[
 w_k = \text{norm}(2e^{-\frac{k^2}{2a_1 k_{\text{min}}}}) \quad (5.13)
\]

for a quicker dropoff. Here, \( k_{\text{min}} \) is the distance between the Γ point and the closest \( k \)-point in the fit, \( a_1 \) is a constant that determines the standard deviation of the normal distribution of \( w_k \), and the norm() prefix denotes the fact that the distribution is normalized by the sum of the computed weights. The value of \( w_k \) determines the fitting radius, and it also ranks the importance the input data plays in determining the resulting fitting polynomial. The fitting is performed by setting the \( R^2 \) goodness-of-fit value to a high setting (0.998, which is a commonly reported value) and increasing the polynomial degree until convergence is reached. Depending on the curvature of the bands, higher order polynomials may be necessary, but careful attention must be paid so that the polynomial fit does not begin oscillating. To avoid this problem, we limit the polynomial degree to half the size of the data set, \( n/2 \).

The Gaussian functions used for weighting the data are shown in Figure 5.2. We call the weighting functions following Equation 5.12 first order \( \sigma \) fits and the weighting function following the form of Equation 5.13 second order \( \sigma \) fits.

5.2.1 Computational Details

Electronic band structures were computed using Density Functional Theory with PAW potentials [10, 11] and the GGA-PBE scheme [12, 13] as implemented in the Vienna Ab Initio
Figure 5.2: Weighing schemes using the Gaussian and uniform weighting distributions for the fitting algorithm.

Simulation Package (VASP)[14, 10, 15, 16]. Additionally, spin orbit coupling [17] was included in the calculation to determine the change in curvature due to the interaction between the light and heavy hole bands at the valence band edge. The \( k \)-space was sampled with a 9261 \( k \)-point cartesian grid, with equally spaced \( k \)-points in the range \([-0.05 0.05]\) along each co-ordinate of \( k \). The mesh was not reduced for symmetry as spin orbit coupling calculations do not allow this.

The radial electronic relaxation time constant is calculated from Ridley’s equation[18] for charged impurity scattering; this equation reconciles the logarithmic term between the screening (Brooks-Herring) and non-screening (Conwell-Weiskopff) scenarios when ionized impurities are the dominant factor in electronic scattering.

The algorithms developed for this fitting scheme will be available online.
References


Chapter 6

Effective Mass Calculation Results

In this chapter we apply the effective mass fitting method to the following semiconducting systems: Si, GaAs, Cu$_2$O, and the spinel structure.

6.1 Results

In the following sections we review examples of the application of the effective mass computation, and we illustrate the method for selecting parameters for the fitting algorithm. In section 6.1.1 (and supplementary section A.1) we present the cross sectional surfaces obtained for the GaAs and Si systems along different directions using the three different weighting functions: first order $\sigma$ Gaussian, square $\sigma$ Gaussian, and uniform weight distribution. We show that the uniform weight distribution is more sensitive to the selection of a radius around the extremum than the Gaussian weighting method, and that in some cases for non-parabolic bands, the fitted curve deviates at the critical $\Gamma$-point, even when the $R^2$ value of the fit is high. We also show that the square $\sigma$ Gaussian is a good way of robustly determining the quadratic fit, independent of the size of the $k$-mesh, and we show that the first order $\sigma$ Gaussian fit allows for accurate fitting for a larger radius around the extremum, while at the same time ensuring that this fit is best nearest the $\Gamma$-point. In section 6.1.2 we show how the effective mass value at the $\Gamma$-point converges with parameter adjustment for each fitting method, while in section 6.1.3 we show the importance of a non-parabolic fitting algorithm for $m^*$. In sections 6.1.4 and 6.1.5 we visualize the three dimensional effective mass space through the inverse effective mass surface and the effective mass wheels of the top three valence bands for the systems Si and GaAs. Finally, we tabulate the high
symmetry effective masses for the Si and GaAs systems in section 6.1.6 and show additional examples of the application of such calculations in sections 6.1.7 and 6.1.8.

6.1.1 Cross Sectional Surfaces

Sample cross sections of the polynomial fits of the light hole band in GaAs and the split off band in Si are shown in Figures 6.1-6.6. Samples of the cross sections of the remaining top three valence bands in both systems can be found in the supplementary materials (Figures A.1 to A.12); here, we only present a subsection of the results that illustrate errors that can result from the choice of data weights on the resulting fit. All of the fits we show have an R^2 value of 0.998 as determined from the weighted data input. Each snapshot represents a three dimensional wedge fit from k-space. Some of these wedges simplify to 1-D (near directions of high symmetry), while others simplify to 2-D. As can be seen from all of these snapshots, the resulting fits have similar curvatures and surfaces, independent of their dimensionality, although the curvature determined will be strongly dependent on ∆k at Γ. Therefore the selection of this value is critical when extrapolating data for the entire BZ. This aspect of the problem is addressed in section 6.1.4.

For the GaAs system, the split off band is roughly parabolic near Γ. The radial effective mass varies slightly depending on the radial direction from Γ, with a variation of less than 3% (see Table 6.1 for tabulated values along directions of high symmetry). Most fits of the split off band along high symmetry directions for a second order σ Gaussian fit are achieved with high accuracy for quadratic curves, although with an increase in σ some quartic fits do become necessary. For the first order σ Gaussian fits, the polynomials are usually quartic, while for the uniform weight distribution fit, the polynomials range up to 6th order. The heavy hole band shows a slightly smaller radius of parabolicity, with the narrow second order σ Gaussian resulting in mostly second order fits. However, fits with a wider σ, again, require up to 6th order polynomial fits. For both of these bands, there is no visibly noticeable distinction between the different fitting schemes, and so it is not immediately apparent why the weighted distribution method would be necessary. However, upon analysis of the light hole band fits, we begin to see errors in the uniform weighting fitting scheme.

The light hole band shows a much narrower parabolicity range, with only the narrow, square σ Gaussian distribution resulting in 2nd order fits, and in these fits we see a significant deviation from the data by the third data point closest to the extremum, which is equivalent
to the range for the highly weighted data points in this fitting scheme. For the first order $\sigma$
Gaussian and uniform weighting schemes, polynomials of up to 6th order are required. One
important distinction between the fits is that in the uniform weight fitting method, the light
hole band fit is distorted at the $\Gamma$-point. The distortion is only slight (.005 eV), but since
the value sought is the reciprocal of the curvature at this point, this slight distortion gets
magnified and can result in considerable discrepancies in the effective mass computation, as
will be shown in section 6.1.2.

The radius of convergence of the different fits is as follows: the first order $\sigma$ Gaussian weight
distribution converges for a radius of 0.05 Å$^{-1}$ when $2\sigma^2 = 0.1k_{min}$ and for a radius of 0.075
Å$^{-1}$ when $2\sigma^2 = 0.4k_{min}$, the square $\sigma$ Gaussian weight distribution converges for a radius
of 0.02 Å$^{-1}$ when $2\sigma^2 = 1.2k_{min}$ and for a radius of 0.04 Å$^{-1}$ when $\sigma = 3.5k_{min}$, while
the uniform weight distribution converges to a radius of 0.1 Å$^{-1}$, with a distortion near $\Gamma$
for the light hole fit. As expected, these values correlate closely to the weighting schemes.
Essentially, by using these alternate weighting schemes, convergence radius is sacrificed for
better fits near $\Gamma$. Convergence here is defined as the data range for which the difference
between the fitted and raw data values is no more than 5%.

The trends for the silicon calculation using the different fitting methods for the light and
heavy hole bands are similar to those for GaAs, except that sometimes higher order (by
2 degrees) polynomials are necessary in the case of the first order $\sigma$ Gaussian and uniform
weighting distributions for similar $\sigma$ settings. The split off band exhibits mostly parabolic and
quartic behavior similar to that shown by the GaAs fits; however, for wide range weighting
distribution schemes (i.e., the uniform weighting distribution method), where fits of up to
6th order were required for GaAs, in the case of Si we see solely quadratic fits, even though
this trend is inconsistent with the higher order fits at a smaller $\sigma$ range. The reason for this
unusual behavior is that, in Si the uniform weight distribution is accurate for the heavy and
light hole bands, but there is a distortion near $\Gamma$ in two of the high symmetry directions
for the split off band. We will show how this affects the magnitude of the effective mass
calculation in section 6.1.2. But again, we notice that the ability of the uniform weight
distribution to correctly fit a curve to the data near the $\Gamma$-point is severely limited by the
selection of the data input range, even though the overall fit to the data may appear to be
good based on the commonly used $R^2$ assessment for goodness-of-fit. The errors that arise
with this method can be explained by the fact that the Taylor polynomial expansion for
the band need not have a radius of convergence that approaches $\infty$; in fact, for the split off
band in Si and the light hole band in GaAs, we see these distortions because the convergence

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Figure 6.1: Examples cross sectional snapshots of fits for the light hole band in GaAs using the first order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = 0.1k_{\text{min}}$) and the second two rows are for a wide fit ($2\sigma^2 = 0.4k_{\text{min}}$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. The narrow fitting scheme yields 4th order polynomials in all high symmetry directions, while the wide fitting scheme yields a 4th order polynomial in the (110) direction, and 6th order polynomials in the (100) and (111) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure 6.2: Examples cross sectional snapshots of fits for the light hole band in GaAs using the second order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = (1.2k_{\text{min}})^2$) and the second two rows are for a wide fit ($2\sigma^2 = (3.5k_{\text{min}})^2$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. The narrow fitting scheme yields 2nd order polynomials in all high symmetry directions, while the wide fitting scheme yields 4th order polynomials in all high symmetry directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$.  

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radius is smaller than our selected input data $k_{\text{cutoff}}$ of 0.1\,Å$^{-1}$. By choosing a weighting function like the Gaussian distribution, where the importance of the data is ranked, the impact of including data outside the convergence radius on the fitting is minimized and a more automated approach to $m^*$ fitting can be attempted.

In both the Si and the GaAs systems, the light and heavy hole bands are both non-parabolic even very near the Γ-point, given our fine mesh sampling rate of 0.005 $k$ fractional units. Only the tightest $\sigma$ fitting scheme yields parabolic polynomials. If the band were to be sampled even more finely at a radius small enough near the extremum, parabolicity would eventually be achieved, as the higher order terms of the corresponding polynomial drop off, although oscillations in the ab initio converged energy levels would arise as finite computational errors would become more significant. For high throughput calculations, the fine sampling approach is inefficient, and a higher order polynomial fit on a larger radius with a lower sampling rate would yield similar results as long as the sampling rate is fine enough to capture any band warping effects. Additionally, the larger the number of $k$-points in a calculation, the less each point is weighted, so that in any subsequent transport calculations the increased sampling rate would not result in significantly altered results. From the higher order polynomial fits we can determine whether discernible parabolicity is present near Γ by looking at $m^*$ as
Figure 6.4: Examples cross sectional snapshots of fits for the split off band in Si using the first order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = 0.1k_{min}$) and the second two rows are for a wide fit ($2\sigma^2 = 0.4k_{min}$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. Both fitting schemes yield a 2nd order polynomial in the (100) direction and 4th order polynomials in the (110) and the (111) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure 6.5: Examples cross sectional snapshots of fits for the split off band in Si using the second order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = (1.2k_{\text{min}})^2$) and the second two rows are for a wide fit ($2\sigma^2 = (3.5k_{\text{min}})^2$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. The narrow fitting scheme yields 2nd order polynomials in all high symmetry directions. The wide fitting scheme yields a 2nd order polynomial in the (100) direction and 4th order polynomials in the (110) and the (111) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure 6.6: Examples cross sectional snapshots of fits for the split off band in Si using the uniform weight fit with $k_{\text{cutoff}} = 0.1\text{Å}^{-1}$. The energies are given relative to the band maximum. The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. This fitting scheme yields $2^{nd}$ order polynomials in all high symmetry directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$.

a function of $|k|$ (see section 6.1.3). The analysis of such plots can serve to show whether the sampling rate is sufficiently fine to detect the transition from parabolic to higher order behavior.

We have shown that the uniform weight distribution fit near $\Gamma$ is sensitive to the $|k|$ radius selected for the fit because of the Taylor polynomial expansion convergence radius; this causes even high $R^2$ value fits using this method to exhibit inaccuracies near $\Gamma$. The Gaussian distribution method, however, is much less sensitive to the $|k|$ radius, and is more robust at predicting a correct fit near the $\Gamma$-point, for the data provided. Ultimately, it is the sampling rate that will determine how accurate the $m^*$ determination is. However, drawbacks to increased sampling rates are oscillating behavior in the energy calculation, as well as higher computational costs. The shape of the bands nearest to the $\Gamma$-point (or the local extremum) are the most important in electronic transport property calculations since this is where most of the mobile carriers exist. It is also worth noting that the second order $\sigma$ Gaussian weight distribution results, in cases of a tight $\sigma$, represent the parabolic approximation very near the $\Gamma$ point that is often reported in the literature. This is to be expected, as the weighting falls off rapidly with distance from the local extremum. Therefore, this selection for $\sigma$ represents
Figure 6.7: Estimation of $m^*$ in the split off band of GaAs for the different fitting methods. The large symbols represent fits made on a $k$ grid with spacing 0.01 (fractional coordinates) and the small symbols represent fits made on a $k$ grid with spacing 0.005.

the commonly used parabolic band approximation of the band curvatures. The accuracy of this method is completely dependent on the sampling rate in $k$-space.

6.1.2 Convergence of Effective Mass Estimation with $\sigma$

Figures 6.7-6.12 show the convergence of the effective mass computation, as evaluated at the $\Gamma$-point, along the high symmetry lines in each of the top three valence bands for both the Si and the GaAs systems. The values are plotted as a function of $\sigma_{\text{norm}} = 2\sigma^2$, a value that determines how the data is treated in the fit; $\sigma_{\text{norm}}$ is a function of the standard deviation of each fitting method. The standard deviation for the first and second order $\sigma$ Gaussian distribution weighting methods is proportional to the first or second power of the sampling rate, respectively, and $\sigma$ for the uniform weighting function is taken as $\frac{1}{\sqrt{3}}k_{\text{cutoff}}$, the standard deviation of the normalized step function $u(k + k_{\text{cutoff}}) - u(k - k_{\text{cutoff}})$. The smaller this value, the more important the weighting of the points near the extremum, as shown in Figure 5.2. The large symbols indicate a larger $k$-space sampling rate in the Brillouin zone (0.01 fractional units), and the small symbols indicate a smaller sampling rate (0.005 fractional units). The smaller sampling rate is representative of what is reported in the literature for the determination of $m^*$, and we also show the wider sampling rate to show the effect of
Figure 6.8: Estimation of $m^*$ in the light hole band of GaAs for the different fitting methods. The large symbols represent fits made on a $k$ grid with spacing 0.01 (fractional coordinates) and the small symbols represent fits made on a $k$ grid with spacing 0.005.

Figure 6.9: Estimation of $m^*$ in the heavy hole band of GaAs for the different fitting methods. The large symbols represent fits made on a $k$ grid with spacing 0.01 (fractional coordinates) and the small symbols represent fits made on a $k$ grid with spacing 0.005.
this sampling rate on the results. For the denser sampling rate, we used both $\sigma$ widths, $2\sigma^2 = (1.2k_{\text{min}})^2$ and $(3.5k_{\text{min}})^2$ for the second order $\sigma$ Gaussian weighting distribution and $2\sigma^2 = 0.1k_{\text{min}}$ and $0.4k_{\text{min}}$ for the first order $\sigma$ Gaussian weighting distribution, while for the larger $k_{\text{cutoff}}$ values only the smaller $\sigma$ values were used, since we are only interested in the values of $m^*$ near the $\Gamma$ point. We show this data in order to illustrate the sensitivity of the calculated $m^*$ value to different factors, including $k$-space sampling rate and data weighting scheme.

As expected, overall results indicate that increasing the sampling rate strongly affects the effective mass estimation in all cases. For the light hole band there is missing data for the wider $k_{\text{cutoff}}$ settings for the uniform weighting distribution because a fit with $R^2 = 0.998$ could not be achieved for this method. Intrinsic to the fitting methods, the larger the $k_{\text{cutoff}}$ value, the better the Gaussian weighting scheme will be at determining the correct curvature near the extremum as compared to the uniform weighting scheme. Essentially, the weighting of the band data in the fitting results in a fit that is highly accurate near $\Gamma$, in the region where most carrier activity occurs, but since points in a wider radius are included in the fit rather than having an abrupt cutoff, these extra points help guide the fit to higher accuracy at the edges of the fitting region. For example, in the parabolic band approximation with uniformly weighted data points, in order to determine a parabolic fit accurately, the entire span of the data must be parabolic, and data points that contribute to non parabolicity must be dropped, so high sampling rates and small $k_{\text{cutoff}}$ values are required to yield high $R^2$. Even so, as shown in section 6.1.1, even when a small range for $k_{\text{cutoff}}$ is selected, the resulting fit will be more accurate in the mid-range of the data, rather than near the extremum. On the other hand, in the Gaussian distribution weighting scheme with a small $\sigma$, the non parabolicity does not strongly interfere with the fit of the parabolic region near $\Gamma$.

Upon numerical comparison of the fitted data with respect to the converged values, we see that $m^*$ is sometimes under or overestimated by between 10 and 43% by the uniform weight distribution method, even at the small $k_{\text{cutoff}} = 0.1\,\text{Å}^{-1}$ whereas, for example, the linear narrow $\sigma$ Gaussian distribution weighting scheme results in more robust determinations of $m^*$, with all errors consistently under 5%, except for the (111) direction in the heavy hole band of Si, where the error is 12%, and the (111) direction in the light hole band, where the error is 8%. If the $k_{\text{cutoff}}$ were to be decreased further, the uniform weight distribution fit would converge further; however, if the usual measurement of goodness-of-fit ($R^2$) was used to determine whether the original fit was good, the error at $\Gamma$ would not be apparent, and
Figure 6.10: Estimation of $m^*$ in the split off band of Si for the different fitting methods. The large symbols represent fits made on a $k$ grid with spacing 0.01 (fractional coordinates) and the small symbols represent fits made on a $k$ grid with spacing 0.005.

so one would not know that the $\Gamma$ distortion was present and that the fit had not converged in that critical parabolic region.
Figure 6.11: Estimation of $m^*$ in the light hole band of Si for the different fitting methods. The large symbols represent fits made on a $k$ grid with spacing 0.01 (fractional coordinates) and the small symbols represent fits made on a $k$ grid with spacing 0.005.
Figure 6.12: Estimation of $m^*$ in the heavy hole band of Si for the different fitting methods. The large symbols represent fits made on a $k$ grid with spacing 0.01 (fractional coordinates) and the small symbols represent fits made on a $k$ grid with spacing 0.005.

To get a sense for the effect of deviations in the effective mass magnitude on other properties, it is useful, as a simple example, to analyze the equation for electronic conductivity. From the Boltzmann Transport Equation (BTE), we have,

$$\sigma_{ij} \propto \sum_{i,j} v_i v_j \tau_e$$

(6.1)

We can calculate $p_i = m^* v_i$ directly from the wave function descriptors, so if we take $\tau_e$, as an example, to be dominantly determined by ionized impurity scattering, then the result is that $\sigma_{ij} \propto \frac{1}{m^*}$. Therefore, if $m^*$ is underestimated as $0.5m^*$, then $\sigma$ will be overestimated as $8\sigma_{ij}$, and if $m^*$ is underestimated as $0.2m^*$, then $\sigma$ will be overestimated by a factor of 125. These factors of $10^1$ to $10^2$ are significant for semiconductors, where the range of $\sigma_{ij}$ is usually $10^2$ to $10^4$ S/cm, so it would be desirable to suppress this error to under 10%.

In this section we showed that, by altering $\sigma$ rather than the raw input data to the fitting algorithm, we insure that the resulting fit is most accurate near the $\Gamma$ point where most mobile carriers are. We also note that, since the Gaussian weighting distribution methods are intrinsically dependent on the distribution of the data itself, it is easier to determine a
method that will fit the data correctly near $\Gamma$, since $\sigma$ can be selected in such a way that it weighs a desired number of data points near the extremum the most.

### 6.1.3 $k$ Dependent Inertial Effective Mass

By analysing the $k$-dependence of the effective mass in the convergence region for the non parabolic fits, we can gain understanding about the error introduced by the parabolic band approximation to calculations involving $m^*$, such as computations of the electronic properties. We can also gain insight into what the region of ‘approximate’ parabolicity is, and observe trends in possible interactions between valence bands.

Figure 6.13 shows the $k$-dependence of $m^*$ in the split off and light hole bands in GaAs using the first order Gaussian weighting function. An upwards slope in the second derivative indicates a narrower curvature than the corresponding parabolic band, while a downward slope indicates a broader curvature. Since the effective mass is the reciprocal of the second derivative, then the opposite will be true for the trend in the $m^*$ curve: an upwards slope indicates a broader curvature and a downwards slope indicates a narrower curvature than the corresponding parabolic band. As can be seen, both bands are approximately parabolic only within a radius of $0.02\text{Å}^{-1}$ of the maximum. The split-off band is narrower than parabolic outside this radius (i.e., has a quicker drop off), while the light hole band is broader in two directions and slightly narrower in the (111) direction. From Figure 6.14 we see that the heavy hole band is parabolic with different curvatures in the high symmetry directions. The broadness, or flatness, of the heavy hole band increases from the (100) to the (110) to the (111) directions. The interaction between the top three valence bands is correlated to the spacing of atoms in the different planes, where the closer the atoms are packed together, the narrower the split off band is, and the greater the separation between the light hole and heavy hole bands.

From Figures 6.15 and 6.16 we note the patterns for Si, where the split off band is, as in GaAs, narrower than parabolic in two directions, and the light hole and heavy hole bands are uniformly broader than the corresponding parabola. In Si, the split off band is not as narrow as the band in GaAs, and the heavy hole bands are not as broad as their counterparts in GaAs. The light hole band is broader than that in GaAs in all directions. The main difference between the valence character of the two systems is that the split off band energy offset, $\Delta_{so}$ is different; our calculated values are $\Delta_{so} = 0.062$ eV for Si and $\Delta_{so} = 0.35$ eV for GaAs.
Therefore, in GaAs, there will be much less interaction between the split off band and the other two bands. In this system, we notice lighter light holes and heavier heavy holes than in Si, which indicates that the dominating factor in the band character is the interaction between the heavy and light hole bands due to spin orbit interactions. In the Si system, on the other hand, the interaction between the top two valence bands due to spin orbit is less important, and the presence of the broader split off band leads to very broad light and heavy hole bands far away from Γ.

In the case of Si, there is significant effective mass increase within a very small radius of the maximum, indicating that parabolic band approximations would severely overestimate the mobility of carriers in these bands, even for light doping. Such errors for GaAs would be much less noticeable, especially in lightly doped versions of the semiconductor, since its heavy hole band is approximately parabolic for a broad range around the maximum, and changes in the effective mass for carriers in the light hole band would only be noticeable at higher doping concentrations.

The second order $\sigma$ Gaussian weight distribution fits all result in parabolic curves with similar $m^*$ values at the Γ point except in the following cases: the quadratic fit of the heavy hole band results in effective mass values that are 90-92% of the quartic fit effective masses of the first order $\sigma$ Gaussian fits; the same scenario in the Si system results in effective masses that are 88% the magnitude of the higher order polynomial fit, except in this case the value only differs in the (111) direction. Therefore, for the purpose of analyzing the heavy hole bands, it may be beneficial to use even finer $k$-space sampling rates.
Figure 6.13: \( k \)-dependence of \( m^* \) in the split off and light hole bands of GaAs in the fit convergence region for the first order Gaussian fit with \( \sigma = 0.4 k_{\text{min}} \).

Figure 6.14: \( k \)-dependence of \( m^* \) in the heavy hole band of GaAs in the fit convergence region for the first order Gaussian fit with \( \sigma = 0.4 k_{\text{min}} \).
Figure 6.15: $k$-dependence of $m^*$ in the split off and light hole bands of Si in the fit convergence region for the first order Gaussian fit with $\sigma = 0.4k_{\text{min}}$.

Figure 6.16: $k$-dependence of $m^*$ in the heavy hole bands of Si in the fit convergence region for the first order Gaussian fit with $\sigma = 0.4k_{\text{min}}$. 
6.1.4 Reciprocal Angular Effective Mass Surface

Figures 6.17-6.22 show the angular reciprocal effective mass envelope for GaAs and Si, calculated by the narrow $\sigma$ first order Gaussian distribution weighting fit schemes as well as the uniform weight fitting scheme; this is the same as the effective mass surface suggested in [1]. The plots represent cross sectional and surface scatter plots of the magnitude of the second radial derivative in each radial direction in the BZ. Additional surface results for the remaining fitting methods, as well as extrapolated curves corresponding to the surfaces presented here are presented in supplemental section A.2. This surface is a means of illustrating the rate at which the carrier group velocity changes at $\Gamma$ in different radial directions within the reciprocal space. The closer to spherical this surface is, the less that electron motion within this band is dependent on the symmetry of the lattice. The surfaces sketched correspond to the radial second derivative of the $E-k$ band fit function evaluated at the $\Gamma$ point; therefore, as shown in section 6.1.3, this surface is dependent on the radial distance $|k|$ from the $\Gamma$-point. For perfectly spherically parabolic bands, these surfaces are independent of $|k|$.

From these results, we see that the inverse effective mass surface of the split off and light hole bands have spherically elliptic surfaces, with a slight deviation from perfectly spherical behavior in the $k_z$ direction visible along the $k_x = k_y$ plane. The heavy hole band has a highly non-spherical character. As the transition from square $\sigma$ Gaussian to first order $\sigma$ Gaussian to uniform weighting occurs, there are increasingly more outliers in the general shape of the inverse effective mass surface. Upon comparison of Figures 6.17 and A.17, as well as 6.20 and A.25, the methods of fitting for which have similar distributions as shown in Figure 5.2, we see that the square $\sigma$ Gaussian distribution performs better at achieving smoother fitting in all directions than the first order $\text{sigma}$ method, so that choosing $\sigma \propto k_{\text{min}}$ is a better option.

The Si inverse effective mass surfaces show that Si has more distorted split off and light hole bands than GaAs, closer to a square character than spherical, while the heavy hole bands look similar. The stronger distortion in the split off and light hole bands can be explained, as mentioned previously, by the split off energy difference in Si, which is smaller than that in GaAs, so that there is interaction between the split off and light/heavy hole bands in Si, while in GaAs this influence is minimal.
Figure 6.17: The angular inverse effective mass surface for the GaAs bands using a first order \( \sigma \) Gaussian weight distribution with \( 2\sigma^2 = 0.1k_{\text{min}} \) and extrapolation \( k_{\text{cut}} = 0.028 \, \text{Å}^{-1} \). The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure 6.18: The angular reciprocal effective mass surface for the GaAs bands using a second order $\sigma$ Gaussian weight distribution with $2\sigma^2 = (1.2k_{\text{min}})^2$ and extrapolation $k_{\text{cut}} = 0.028$ Å$^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure 6.19: The angular reciprocal effective mass surface for the GaAs bands using a uniform weight distribution with $k_{\text{cutoff}} = 0.1\, \text{Å}^{-1}$ and extrapolation $k_{\text{cut}} = 0.028\, \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure 6.20: The angular inverse effective mass surface for the Si bands using a first order $\sigma$ Gaussian weight distribution with $2\sigma^2 = 0.1k_{\text{min}}$ and extrapolation $k_{\text{cut}} = 0.03$ Å$^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure 6.21: The angular inverse effective mass surface for the Si bands using a second order $\sigma$ Gaussian weight distribution with $2\sigma^2 = (1.2k_{\text{min}})^2$ and extrapolation $k_{\text{cut}} = 0.03$ Å$^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure 6.22: The angular reciprocal effective mass surface for the Si bands using a uniform weight distribution with $k_{\text{cutoff}} = 0.1 \text{Å}^{-1}$ and extrapolation $k_{\text{cut}} = 0.03 \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
6.1.5 Effective Mass Wheel

We introduce the effective mass wheel plot to map the effective mass space onto a 2D image. We show the truncated $k$ raw data and corresponding extrapolated data in Figures 6.23-6.28 for the narrow $\sigma$ Gaussian fits and uniform weighting distribution calculations; additional results for the remaining fitting methods are shown in the supplemental section A.3, Figures A.28-A.31. In these diagrams, each point corresponds to the $\Gamma$ effective mass in a specific radial direction in the 3D lattice space. The angle with the x-axis represents the xy-plane azimuthal angle, $\theta$, while the radial distance from the center is the projection of the spherical tilt angle unit vector onto the xy plane. The effective mass wheels shown correspond to the split off, (a), light hole, (b), and heavy hole, (c), bands respectively. As was shown from the sample cross sections, the split off and light hole bands are, in general, more spherically parabolic, whereas the heavy hole band has an irregular, flower petal shape (does this shape have a name?). There are clearly a few outliers in the first order fitting of the split off band in both systems, and a lot of discrepancies in the uniform weighting fitting method. Such errors can be eliminated by increased $k$-space sampling for the Gaussian distribution and $k$ truncation for the uniform weighting method, but the increased accuracy of band shape prediction is visible with increased $\sigma$ for the same sampling rate. By using this new, color coded visualization, we can discern patterns and ripples in the overall surface more clearly, and at the same time errors are also immediately visible so that we can tell which directions have higher warping and are thus more sensitive to sampling rate.

6.1.6 High Symmetry Direction $m^*$

Table 6.1 shows the tabulated effective masses in the high symmetry directions as determined by the method presented in this work for the valence bands that participate in carrier transport in GaAs and Si. We also tabulate data from a number of previous experimental and theoretical studies found in the literature.

Across all bands in Si, we notice a consistent lower $m^*$ estimation which can be attributed to the higher $\Delta_{so}$ in this work (0.0624 eV) than reported experimentally (0.044 eV)[2] and in the FLAPW work (0.047 eV)[3]. Therefore, in our calculations, there is less interaction between the light and heavy hole bands and the split off band, leading to uniformly steeper
Figure 6.23: GaAs effective mass wheels for a first order $\sigma$ Gaussian weight fitting with $2\sigma^2 = 0.1k_{\text{min}}$ with a cutoff radius of $k_{\text{cut}} = 0.029$.

Figure 6.24: GaAs effective mass wheels for a second order $\sigma$ Gaussian weight fitting with $2\sigma^2 = (1.2k_{\text{min}})^2$ with a cutoff radius of $k_{\text{cut}} = 0.029$. 
Figure 6.25: GaAs effective mass wheels for uniform weight fitting with $k_{cutoff} = 0.1\text{Å}^{-1}$ with an extrapolation cutoff radius of $k_{cutoff} = 0.029$.

Figure 6.26: Si effective mass wheels for a first order $\sigma$ Gaussian weight fitting with $2\sigma^2 = 0.1k_{min}$ with an extrapolation cutoff radius of $k_{cut} = 0.03$. 
Figure 6.27: Si effective mass wheels for a second order $\sigma$ Gaussian weight fitting with $2\sigma^2 = (1.2k_{min})^2$ with an extrapolation cutoff radius of $k_{cut} = 0.03$.

Figure 6.28: Si effective mass wheels for a uniform weight fitting with $k_{cutoff} = 0.1\text{Å}^{-1}$ with an extrapolation cutoff radius of $k_{cut} = 0.03$. 

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dropoffs in all bands and lower $m^*$ computed values. However, the trends are consistent with the FLAPW results.

In GaAs, where $\Delta_{so}$ was computed to within 0.001 eV of the experimental values, we can more readily compare our computed $m^*$ values to those previously reported. We see very good agreement with the lower end of experimental results, and we see that $m^*$ in the heavy hole and light hole bands in GaAs varies much less with direction than in Si.
Table 6.1: Effective masses of systems studied for high symmetry directions.

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\(^a\) Bulk average.
\(^b\) Ref. [4], non relativistic
\(^d\) Range of values as presented in review paper Ref. [6], with the outliers are presented separately.
\(^e\) Full potential linear augmented plane wave (FLAPW) method, relativistic effects, 30 \(k\)-points in IBZ.
\(^f\) Ref. [7], [8], and [9] as in [3]

6.1.7 Additional Examples

In the following subsections, we show the results obtained from effective mass analysis on cuprite, an important oxide, the study of which has led to advancements in the field of transparent conducting oxides, as well as a ferromagnetic spinel, ZnCu\(_2\)O\(_4\), one of a class of
compounds that has been recently studied for its potential as transparent conductors and catalysts.

**Cuprite (Cu$_2$O)**

The inverse effective mass surfaces for cuprite are shown in Figure 6.29 and the effective mass wheels are shown in Figure 6.30. Cuprite has a different valence character than Si and GaAs. Perhaps most importantly, the top valence band splits off from the next two valence bands, so that the heavy-light hole degenerate pair of bands is not at the top of the valence and is not the primary characterizing factor for this material. From the effective mass wheels we see the complementary nature of the heavy-light hole pair. This pattern is also discernible in the inverse effective mass surface plots. None of the top three valence bands has a spherical effective mass surface.
Figure 6.29: The angular reciprocal effective mass surface for the cuprite bands using phi=1 and a Gaussian weight distribution. The graph represents the extrapolated data for the entire first Brillouin zone. The fitting method used was the first order \( \sigma \) Gaussian with \( 2\sigma^2 = 0.1k_{\text{min}} \) and \( k \) space sampling of \( k = 0.01 \) units in fractional coordinates.
Figure 6.30: Cuprite effective mass wheels for the light hole band (a), the heavy hole band (b) and the top valence split off band (c). The fitting method used was the first order $\sigma$ Gaussian with $2\sigma^2 = 0.1k_{min}$ and $k$ space sampling of $k = 0.01$ units in fractional coordinates.

We also present the computed hole effective masses in Cu$_2$O in Table 6.2, which are, to our knowledge, the first such reported values in the literature. Cuprite shows high assymetry in all of its top three valence bands, but shows relatively low hole effective masses for a wide band gap oxide. Because the top valence band is split from the next two valence bands, this band has higher curvature and thus, is associated with lower effective masses than is in general seen in semiconducting oxides.

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Table 6.2: Effective masses of Cu$_2$O for high symmetry directions.

Spinel (ZnCu$_2$O$_4$)

In Figures 6.31-6.33 and Table 6.3 we show the calculated effective mass attributes of a ferromagnetic spinel, ZnCu$_2$O$_4$. This spinel has a band gap of 2.67 eV and the top 6 valence
spinors are split into triplet degenerate states with a splitting distance of $\Delta_{so} = 0.398$ eV. Therefore the top three valence bands are most important for carrier transport in this system. All effective mass surfaces are highly non-spherical, and the character of all three bands resembles the character of the heavy hole band in the GaAs and the Si systems, which may provide an explanation for why transport in these oxides is poor compared to those of narrow gap semiconductors. Since the gap between the two triplet spinor states is large, we don’t expect that there is much interaction between these bands.

From the tabulated $m^*$ values along the high symmetry directions, we see that the top triplet of spinors consists of two heavy hole bands and one light hole band. The lowest effective masses are observed in the (100)-direction.

Table 6.3: Effective masses for high symmetry directions of top three valence bands in the spinel system studied.

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6.1.8 Application to Electron Transport

In Figures 6.34-6.37 we extend the effective mass analysis to a population analysis of effective masses and $\tau_e$ values for a couple of simulated carrier concentrations in both GaAs and Si. From these results we notice that (a) at low temperatures the split off band does not play an important role in electronic properties of the doped compounds, especially in GaAs, (b) a large portion of carriers have high effective masses in both compounds, and thus dominate the electronic properties of the material, (c) radially non-parabolic deviations in the effective mass are more emphasized for higher carrier concentrations, resulting in a smearing of the relaxation time populations as a function of electron energy, and (d) the smearing effect results in overall higher relaxation time constants than the parabolic band approximation at lower temperatures for highly doped systems.
Figure 6.31: The angular reciprocal effective mass surface for the spinel split off bands (the lower triplet) using a first order $\sigma$ Gaussian weighting scheme with $2\sigma^2 = 0.1k_{min}$ and $k$ space sampling of $k = 0.01$ units in fractional coordinates. The graph represents the extrapolated data for the entire first Brillouin zone.
Figure 6.32: The angular reciprocal effective mass surface for the spinel top valence bands (the upper triplet) using a first order $\sigma$ Gaussian weighting scheme with $2\sigma^2 = 0.1k_{\text{min}}$ and $k$ space sampling of $k = 0.01$ units in fractional coordinates. The graph represents the extrapolated data for the entire first Brillouin zone.
Figure 6.33: Spinel effective mass wheels for the bottom (a-c) and top (d-e) triplets. The angular reciprocal effective mass surface for the spinel split off bands (the lower triplet) using a first order $\sigma$ Gaussian weighting scheme with $2\sigma^2 = 0.1k_{min}$ and $k$ space sampling of $k = 0.01$ units in fractional coordinates.
Figure 6.34: Effective mass distribution population for GaAs as a function of electron kinetic energy for temperatures in the range 100K to 400K. The left panel represents a simulated carrier concentration of $10^{16} / cm^3$, and the panel on the right represents a carrier concentration of $10^{19} / cm^3$. 
Figure 6.35: $\tau_e$ distribution population for GaAs as a function of electron kinetic energy for temperatures in the range 100K to 400K. For this calculation, it was assumed that the ionized impurity scattering dominates. The left panel represents a simulated carrier concentration of $10^{16}/cm^3$, and the panel on the right represents a carrier concentration of $10^{19}/cm^3$. 
Figure 6.36: Effective mass distribution population for Si as a function of electron kinetic energy for temperatures in the range 100K to 400K. The left panel represents a simulated carrier concentration of $10^{17}/cm^3$, and the panel on the right represents a carrier concentration of $10^{21}/cm^3$. 

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Figure 6.37: $\tau_e$ distribution population for Si as a function of electron kinetic energy for temperatures in the range 100K to 400K. For this calculation, it was assumed that the ionized impurity scattering dominates. The left panel represents a simulated carrier concentration of $10^{17}/cm^3$, and the panel on the right represents a carrier concentration of $10^{21}/cm^3$. 
6.2 Conclusion

We have developed an automated fitting method for the effective mass in the entire Brillouin zone by using high order polynomial fitting in radial wedges around the local extremum. We show that the weighting of band data during the fitting algorithm is important if the regions of the band edge that contribute the most to carrier transport properties is to be fitted as accurately as possible from the available data. We also show that the parabolicity region of the heavy hole band exists, but is much narrower than that of the light and split off bands. We have used the results of these calculations to develop an effective mass wheel approach to evaluating the effective mass character of different bands in common p-type semiconductors, and have shown that apparently spherically symmetric bands in these types of semiconductors do not always follow parabolic curves in all radial directions. The effective mass wheel is a powerful means of visualizing valence and conduction bands to gain insight into their effect on the motion of carriers in a semiconductor. This tool for fitting effective masses can be used to not only characterize mobilities in semiconductors, but it can also be used to sketch electronic relaxation times and can help determine the magnitude of phonon scattering effects in semiconductors when total scattering rates have been measured experimentally.
References


Chapter 7

Conclusions

This dissertation presented the development and application of a means of calculating the elementary electron properties, $v_g$ and $m^*$, from first principles in an automated manner that is compatible with BTE electronic property calculations. These algorithms are the first step in the development of progressively more sophisticated methodologies that can screen and predict the electronic properties of large sets of unexplored compounds. Such methods are necessary for advanced screening of materials to find potential candidates for different applications, and can help alleviate the experimental burden by eliminating from the candidate list materials that do not have predicted promising properties.

We implemented the momentum matrix method within the PAW approach to DFT for calculating $v_g$ and used the constant electronic time constant approximation to study the electrical transport properties of the Ag, Au, and La fractionally filled bulk skutterudites: CoSb$_3$, CoAs$_3$, and CoP$_3$. The Seebeck coefficient ($S$), electrical conductivity ($\sigma$), and power factor ($S^2\sigma$) were calculated as a function of temperature and filling fraction using the momentum matrix method along the entire first Brillouin zone. We showed that calculated trends in the electrical transport properties agreed with previously published experimental measurements for p-type unfilled and La filled CoSb$_3$. The calculated $S$ and $\sigma$ values for the Ag and Au filled compounds indicated that the most promising electronic properties are exhibited by p-type Au$_{0.125}$(CoSb$_3$)$_4$, Au$_{0.25}$(CoSb$_3$)$_4$, and Au(CoSb$_3$)$_4$. Au was therefore recommended as a promising filler for improved thermoelectric properties in cobalt antimonides. Ag was also a good filler for cobalt phosphides; the creation of a negative indirect band gap was observed in Ag(CoP$_3$)$_4$, which indicates semimetallic behavior, so this compound may possibly exhibit lower thermal conductivity than metallic CoP$_3$. Additionally, within the electronic conductivity trends, we detected a resonance quality in the lattice
where the coordination of electrons resulted in greatly enhanced electrical conductivities in the fully filled skutterudites; this enhancement is most notable at high temperatures.

Next, we studied highly correlated systems using the momentum matrix method in conjunction with hybrid DFT. We reported the electronic and optical properties of two theoretically predicted stable spinel compounds of the form $\text{ZnB}_2\text{O}_4$, where $B = \text{Ni}$ or $\text{Cu}$; neither compound had been previously synthesized, so we compared them to the previously studied p-type $\text{ZnCo}_2\text{O}_4$ spinel. These new materials exhibited spin polarization that is useful for spintronics applications, and broad conductivity maxima near the valence band edge that indicate good p-type behavior. We showed that $3d$ electrons on the octahedrally coordinated $\text{Zn}$ atom fall deep within the valence band and do not contribute significantly to the electronic structure near the band edge of the material, while the O $2p$ and tetrahedrally coordinated $B$ $3d$ electrons hybridize broadly in the shallow valence states, resulting in increasing curvature (i.e., decreased electron effective mass) of valence bands near the band edge. In particular, $\text{ZnCu}_2\text{O}_4$ exhibits high electrical conductivities in the p-doping region near the valence band edge that, at $\sigma = 2 \times 10^4$ S/cm, were twice the maximum found for $\text{ZnCo}_2\text{O}_4$, a previously synthesized compound in this class of materials. This material also exhibited ferromagnetism in all of its most stable structures, which makes it a good candidate for further study as a dilute magnetic semiconductor.

Lastly, we presented a methodical procedure for determining the 3-D effective mass surface for the application of transport property calculations from first principles, using radial wedge divisions in the Brillouin zone to allow for proper sampling, and a Gaussian distribution weighting scheme to insure correct determination of the effective mass near the local extremum where most carriers exist. We applied this method to the commonly investigated narrow bandgap semiconducting systems of Si and GaAs, as well as to the wide band gap cuprite and spinel systems to illustrate how the effective mass surface in these materials is determined by their structure and the degeneracies near the extremum.

In future work, we desire to extend the effective mass calculation to apply universally to non ideal (i.e., non parabolic band) transport. In order to do this, we need to go back to the original derivation of the effective mass which states that

$$v_g = \frac{dE}{dp} = \frac{1}{\hbar} \frac{\partial E}{\partial k}. \quad (7.1)$$
It is standard practice to use the right hand side of equation 7.1 as the expression for $v_g$. The right hand side has also been derived in terms of Block functions[1], but the assumption in that derivation was that $p = m^* v_g$. This is not true for the non-parabolic band case, where $E_k \neq \frac{\hbar^2 k^2}{2m^*}$, but from the deBroglie relation we know that $v_g = \frac{dE}{dp}[2]$. Therefore, the right hand side of Equation 7.1 is not valid for non-parabolic bands since a non-parabolic band does not obey the relationship $p = \hbar k$. Indeed, if we pursue the next steps of the derivation we obtain, using the chain rule,

$$a = \frac{d}{dt} \frac{dE}{dp} = \frac{d^2 E}{dp^2} \frac{dk}{dt}. \quad (7.2)$$

and subsequently solving for the force,

$$dE = F dx = F v_g dt \quad (7.3)$$

$$F = \frac{1}{v_g} \frac{dE}{dt} = \frac{1}{v_g} \frac{dE}{dp} \frac{dk}{dt}. \quad (7.4)$$

We immediately recognize the form $F = m^* a$, and thus we obtain

$$m^* = \frac{1}{\left(\frac{d^2 E}{dp^2}\right)} \quad (7.5)$$

which has a similar form to equation 2.5, except that we have not expanded $p$ in terms of $k$. We propose that by fitting $p$ to $k$ and plugging back in to equation 7.5 we will be able to obtain generic fits for the effective mass even in non-parabolic band cases. This is a slightly more involved process, as $E$ is now a functional of $p$. Additionally, this procedure is the ideal extension of the methods that have been implemented in this dissertation as we derive the momentum directly from the wave function descriptors (equation 2.7), and since this momentum is derived directly from the Hamiltonian, it should have the effective mass information built in.
References


Appendix A

Supplementary Figures

A.1 Additional Cross Sectional Fit Curves
Figure A.1: Examples cross sectional snapshots of fits for the split-off band in GaAs using the first order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = 0.1k_{min}$) and the second two rows are for a wide fit ($2\sigma^2 = 0.4k_{min}$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. Both fitting schemes yield a 2\textsuperscript{nd} order polynomial in the (100) direction, and a 4\textsuperscript{th} order polynomial in the (110) and (111) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure A.2: Examples cross sectional snapshots of fits for the split-off band in GaAs using the second order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = (1.2k_{\text{min}})^2$) and the second two rows are for a wide fit ($2\sigma^2 = (3.5k_{\text{min}})^2$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. Both fitting schemes yield a $2^{nd}$ order polynomial in all directions, except the wide setting, which gives a $4^{th}$ order polynomial along (110). The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 


Figure A.3: Examples cross sectional snapshots of fits for the split-off band in GaAs using the uniform weight fit with \( k_{\text{cutoff}} = 0.1\,\text{Å}^{-1} \). The first three fits (first row) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. This fitting method yields a 6\(^{th}\) order polynomial in the (100) direction and 4\(^{th}\) order polynomials in the other two directions. The 2-D fits are wedges that simplify with a constant \( \theta \) and a variable \( \phi \).
Figure A.4: Examples cross sectional snapshots of fits for the heavy hole band in GaAs using the first order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = 0.1k_{\text{min}}$) and the second two rows are for a wide fit ($2\sigma^2 = 0.4k_{\text{min}}$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. The narrow fitting scheme yields 2nd order polynomials in all high symmetry directions, while the wide fitting scheme yields a 6th order polynomial in the (110) direction, and 4th order polynomials in the (100) and (111) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure A.5: Examples cross sectional snapshots of fits for the heavy hole band in GaAs using the second order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = (1.2k_{min})^2$) and the second two rows are for a wide fit ($2\sigma^2 = (3.5k_{min})^2$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. The narrow fitting scheme yields 2$^{nd}$ order polynomial in all high symmetry directions, while the wide fitting scheme yields a 4$^{th}$ order polynomial in the (110) direction, and 2$^{nd}$ order polynomials in the (100) and (111) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure A.6: Examples cross sectional snapshots of fits for the heavy hole band in GaAs using the uniform weight fit with $k_{\text{cutoff}} = 0.1\text{Å}^{-1}$. The first three fits (first row) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. This fitting method yields 4th order polynomials in the (100) and (110) directions and a 2nd order polynomial in the (111) direction. The 2-D fits are wedges that simplify with a constant $\theta$ and a variable $\phi$. 
Figure A.7: Examples cross sectional snapshots of fits for the light hole band in Si using the first order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = 0.1k_{\text{min}}$) and the second two rows are for a wide fit ($2\sigma^2 = 0.4k_{\text{min}}$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. The narrow fitting scheme yields $4^{th}$ order polynomials in all high symmetry directions, while the wide fitting scheme yields an $8^{th}$ order polynomial in the (111) direction, a $6^{th}$ order polynomial in the (110) direction, and a $4^{th}$ order polynomial in the (100) direction. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure A.8: Examples cross sectional snapshots of fits for the light hole band in Si using the second order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = (1.2k_{min})^2$) and the second two rows are for a wide fit ($2\sigma^2 = (3.5k_{min})^2$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. The narrow fitting scheme yields 2nd order polynomials in all high symmetry directions, while the wide fitting scheme yields a 6th order polynomial in the (110) direction and 4th order polynomials in the (100) and (111) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure A.9: Examples cross sectional snapshots of fits for the light hole band in Si using the uniform weight fit with $k_{\text{cutoff}} = 0.1 \text{Å}^{-1}$. The energies are given relative to the band maximum. The first three fits (first row) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. This fitting scheme yields a 4$^{th}$ order polynomial in the (100) direction, a 6$^{th}$ order polynomial in the (110) direction, and an 8$^{th}$ order polynomial in the (111) direction. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure A.10: Examples cross sectional snapshots of fits for the heavy hole band in Si using the first order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = 0.1k_{\min}$) and the second two rows are for a wide fit ($2\sigma^2 = 0.4k_{\min}$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. The narrow fitting scheme yields a $2^{nd}$ order polynomial in the (111) direction and $4^{th}$ order polynomials in the (100) and (110) directions, while the wide fitting scheme yields a $6^{th}$ order polynomial in the (110) direction, and $4^{th}$ order polynomials in the (100) and (111) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 

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Figure A.11: Examples cross sectional snapshots of fits for the heavy hole band in Si using the second order $\sigma$ Gaussian fit. The energies are given relative to the band maximum. The first two rows represent cross sections for a narrow fit ($2\sigma^2 = (1.2k_{min})^2$) and the second two rows are for a wide fit ($2\sigma^2 = (3.5k_{min})^2$). The first three fits (first and third rows) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. The narrow fitting scheme yields 2$^{nd}$ order polynomials in all high symmetry directions, while the wide fitting scheme yields a 2$^{nd}$ order polynomial in the (111) direction and 4$^{th}$ order polynomials in the (100) and (110) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 
Figure A.12: Examples cross sectional snapshots of fits for the heavy hole band in Si using the uniform weight fit with $k_{\text{cutoff}} = 0.1\text{Å}^{-1}$. The energies are given relative to the band maximum. The first three fits (first row) represent the high symmetry, (100), (110), and (111) directions, for which the 3D wedge simplifies to 1D due to sampling. This fitting scheme yields a 4th order polynomial in the (100) direction, a 6th order polynomial in the (110) direction and 4th order polynomials in the (100) and (111) directions. The 2-D fits are wedges with a constant $\theta$ and a variable $\phi$. 

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A.2 Extrapolated Inverse Effective Mass Surfaces

The graphs in this section are the extrapolated inverse effective mass surfaces for GaAs and Si under different fitting conditions, as indicated. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.13: The extrapolated angular inverse effective mass surface for the GaAs bands using a first order $\sigma$ Gaussian weight distribution with $2\sigma^2 = 0.1k_{min}$ and extrapolation $k_{cut} = 0.028 \, \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.14: The angular inverse effective mass surface for the GaAs bands using a first order $\sigma$ Gaussian weight distribution with $2\sigma^2 = 0.4k_{\text{min}}$ and extrapolation $k_{\text{cut}} = 0.028 \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.15: The extrapolated angular inverse effective mass surface for the GaAs bands using a first order $\sigma$ Gaussian weight distribution with $2\sigma^2 = 0.4k_{\text{min}}$ and extrapolation $k_{\text{cut}} = 0.028 \, \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.16: The extrapolated angular reciprocal effective mass surface for the GaAs bands using a second order $\sigma$ Gaussian weight distribution with $2\sigma^2 = (1.2k_{\text{min}})^2$ and extrapolation $k_{\text{cut}} = 0.028$ Å$^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.17: The angular reciprocal effective mass surface for the GaAs bands using a second order $\sigma$ Gaussian weight distribution with $2\sigma^2 = (3.5k_{\text{min}})^2$ and extrapolation $k_{\text{cut}} = 0.028 \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.18: The extrapolated angular reciprocal effective mass surface for the GaAs bands using a second order $\sigma$ Gaussian weight distribution with $2\sigma^2 = (3.5k_{\text{min}})^2$ and extrapolation $k_{\text{cut}} = 0.028 \text{ Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.19: The extrapolated angular reciprocal effective mass surface for the GaAs bands using a uniform weight distribution with $k_{\text{cutoff}} = 0.1\,\text{Å}^{-1}$ and extrapolation $k_{\text{cut}} = 0.028\,\text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
A.3 Effective Mass Wheel Supplementary Figures
Figure A.20: The angular inverse effective mass surface for the Si bands using a first order \( \sigma \) Gaussian weight distribution with \( 2\sigma^2 = 0.4k_{\text{min}} \) and extrapolation \( k_{\text{cut}} = 0.03 \) Å\(^{-1}\). The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.21: The extrapolated angular inverse effective mass surface for the Si bands using a first order \( \sigma \) Gaussian weight distribution with \( 2\sigma^2 = 0.1k_{\text{min}} \) and extrapolation \( k_{\text{cut}} = 0.03 \ \text{Å}^{-1} \). The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.22: The extrapolated angular inverse effective mass surface for the Si bands using a first order $\sigma$ Gaussian weight distribution with $2\sigma^2 = 0.1k_{\text{min}}$ and extrapolation $k_{\text{cut}} = 0.06 \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.23: The extrapolated angular inverse effective mass surface for the Si bands using a first order $\sigma$ Gaussian weight distribution with $2\sigma^2 = 0.4k_{\text{min}}$ and extrapolation $k_{\text{cut}} = 0.03$ Å$^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.24: The extrapolated angular inverse effective mass surface for the Si bands using a second order $\sigma$ Gaussian weight distribution with $2\sigma^2 = (1.2k_{\text{min}})^2$ and extrapolation $k_{\text{cut}} = 0.03 \, \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.25: The angular inverse effective mass surface for the Si bands using a second order $\sigma$ Gaussian weight distribution with $2\sigma^2 = (3.5k_{\text{min}})^2$ and extrapolation $k_{\text{cut}} = 0.03$ Å$^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.26: The extrapolated angular inverse effective mass surface for the Si bands using a second order $\sigma$ Gaussian weight distribution with $2\sigma^2 = (3.5k_{\text{min}})^2$ and extrapolation $k_{\text{cut}} = 0.03 \ \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.27: The extrapolated angular inverse effective mass surface for the Si bands using a uniform weight distribution with $k_{cutoff} = 0.1 \text{Å}^{-1}$ and extrapolation $k_{cut} = 0.03 \text{Å}^{-1}$. The graphs represent the split off band (1), the light hole band (2), and the heavy hole band (3). For each band, 2 planar cross sections are shown in (a) and (b), while graphs (c) and (d) show the top down and full three dimensional view of the surface.
Figure A.28: Si effective mass wheels for a first order $\sigma$ Gaussian weighting fit with $2\sigma^2 = 0.4k_{\text{min}}$ and an extrapolation cutoff of $k_{\text{cut}} = 0.028\text{Å}^{-1}$.

Figure A.29: Si effective mass wheels for a second order $\sigma$ Gaussian weighting fit with $2\sigma^2 = (3.5k_{\text{min}})^2$ and an extrapolation cutoff of $k_{\text{cut}} = 0.028\text{Å}^{-1}$.
Figure A.30: Si effective mass wheels for a first order $\sigma$ Gaussian weighting fit with $2\sigma^2 = 0.4k_{min}$ and an extrapolation cutoff of $k_{cut} = 0.03\text{Å}^{-1}$.

Figure A.31: Si effective mass wheels for a second order $\sigma$ Gaussian weighting fit with $2\sigma^2 = (3.5k_{min})^2$ and an extrapolation cutoff of $k_{cut} = 0.03\text{Å}^{-1}$.
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