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Theory of Carrier Transport From First Principles: Applications in Photovoltaic and Thermoelectric Materials

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Theory of Carrier Transport From First Principles: Applications in Photovoltaic and Thermoelectric Materials

by

Alireza Faghaninia

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

May 2016
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Alireza Faghaninia

Washington University in Saint Louis
May 2016
Dedicated to my parents and my wife, Agnes.
ABSTRACT OF THE DISSERTATION

Theory of Carrier Transport From First Principles: Applications in Photovoltaic and Thermoelectric Materials

by

Alireza Faghaninia

Doctor of Philosophy in Energy, Environmental, and Chemical Engineering

Washington University in St. Louis, May 2016

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New sources of energy that are environmentally friendly, cost-effective, and renewable are essential if we are to combat the effects of global climate change. Two of these sources are solar photovoltaic (PV) cells to convert sunlight into electricity and thermoelectric (TE) devices to convert heat to electricity. To be practical on a large scale, the properties (e.g. electrical conductivity, band gap, Seebeck coefficient, etc) of the underlying materials must be improved significantly through judicious control of structure and composition. Significant understanding of materials properties is required to design and engineer new high-performing materials. First principles calculations using density functional theory (DFT) help us to predict materials behavior, with reasonable accuracy, before they are even made.

We first calculate the energy and density of states of electrons, the frequency of lattice vibrations (i.e. phonons), dielectric constants and deformation potential. We then use this as an input to the model that we have developed: \textit{ab initio} model for calculating the mobility.
and Seebeck coefficient using Boltzmann transport equation (BTE), aMoBT. We solve the BTE via Rode’s iterative method considering both elastic and inelastic mechanisms such as ionized impurity and polar optical phonon scattering mechanisms respectively to calculate the electrical mobility and conductivity and Seebeck coefficient of the semiconductor with minimum to no reliance on any experimental data. We have tested and validated aMoBT by predicting the electronic properties of GaAs, InN, Cu- and Al-doped ZnS all of which agree very well with experimental measurements. Without fitting to experimental data, aMoBT enables us to understand how the structure and composition of a given material exhibits certain properties, and facilitates screening of new materials without the need for costly and time-consuming experimental synthesis and characterization.

In addition to aMoBT, we have developed and adapted methods for \textit{ab initio} thermodynamic calculations to understand the formation of neutral and charged point defects in semiconductors and their effect on the conduction mechanism; for example, we identified the negatively charged Zn vacancies in thermoelectric zinc antimonide ($\beta - Zn_4Sb_3$) as the reason for its native p-type behavior and the difficulty to n-dope it. Furthermore, we found that Cu and Al are feasible candidates to dope ZnS p- and n-type respectively to make promising transparent conducting materials (TCM) which then can be used in solar cells, LCD, touch screens, transparent devices, etc. These type of calculations are essential for predicting the behavior of real materials in presence of all the impurities and defects. Finally, combining these methods implemented as automated computer codes enables us to perform high-throughput screening of materials properties for design and discovery of new materials for specific applications. We screened 75 binary and ternary oxides to find, via aMoBT, the most conductive n-type and p-type oxides with reasonably large band gap as high performing TCM. We can use the same principles used in this work to predict semiconductors behavior for a broad range of applications.
Chapter 1

Introduction

New environmentally-friendly and cost-effective sources of renewable energy are essential to minimize our dependence on fossil fuels and combat the effects of climate change. One of the most important aspects in the shift towards efficient and renewable sources of energy is material development. Silicon has dominated the solar cell industry for a long time, and it is still the main technology in the photovoltaic (PV) industry, due to its cost efficiency and technology maturity. Another source of renewable energy, or waste heat recovery, is theremoelectrics (TE), which again rely on high performing semiconductors to generate electricity. Both the PV and TE industries are constantly on the lookout for newer and better performing semiconductors. One of the main factors in determining the ”performance” of these semiconductors is the electrical conductivity, which is calculated via Equation 1.1:

\[ \sigma = n e \mu_e + p e \mu_h \]  

(1.1)

where \( e \) is the charge of an electron, \( n \) and \( p \) are electron and hole (i.e., lack of electron) concentrations, and \( \mu_e \) and \( \mu_h \) are electron and hole mobility. Semiconductors are either n-type or p-type. In the n-type (p-type) semiconductors, the concentration of electrons (holes) is orders of magnitude larger than the concentration of holes (electrons) and therefore
Equation 1.1 reduces to $\sigma = ne\mu$, where $n$ and $\mu$ are the concentration and the mobility of carriers. Since $e$ is a constant, the electrical conductivity of a semiconductor depends on $\mu$ and $n$. Having very high values of $\mu$ and $n$ is not necessarily good, as it depends on the application. For example, in thermoelectric materials, if $n$ is too high, the Seebeck coefficient is inevitably low, which is detrimental to the TE performance; therefore, one needs to focus on increasing the mobility, $\mu$, while keeping $n$ moderate in this specific application. However, it is not easy to simultaneously control these two parameters. In Chapter 2, we explain how we employ density functional theory (DFT), together with Boltzmann transport equation (BTE), to develop an ab initio model for calculating the mobility and Seebeck coefficient in the BTE framework. This tool helps us to understand the scattering mechanisms that limit the mobility of currently available semiconductors. It also enables us to predict the transport properties of newly designed semiconductors, with minimum dependence on experimental data, to evaluate their performance for applications such as PV and TE.

Furthermore, controlling the carrier concentration, $n$, is not trivial. Carrier concentration is mainly affected by the defects that are present in semiconductors. In n-type (electron-rich, high electron concentration) semiconductors, the Fermi level, which is the potential of electrons, is high, and in p-type (electron-deficient, high hole concentration) materials, the Fermi level is low. At equilibrium, the Fermi level is dictated by the defects. In Chapter 3, we use DFT to either understand the formation of different defects and their charge states and/or propose introduction of new defects to control the carrier concentration in semiconductors such as $\beta-Zn_4Sb_3$, ZnS, ZnO, and SnS. Since DFT is a ground state theory at 0 K temperature, we also use density functional perturbation theory (DFPT) to calculate the frequencies of phonons (i.e. lattice vibrations) to obtain the vibrational entropy, so that we can examine the formation of defects at high temperatures. Once we have a reasonable understanding of the mobility and carrier concentration in semiconductors, we can also
calculate the Seebeck coefficient, which is very important for thermoelectric materials. The
details are presented in Chapter 2.

Figure 1.1 shows a schematic of the outline of this dissertation, with a brief description of
each chapter and the materials that are discussed within. In Chapters 2 and 3, we explain
how aMoBT and *ab initio* thermodynamics calculations help us better understand the be-
havior of semiconductors. To examine this, as described in Chapter 4, we have integrated
these two methods to screen many different semiconductors and select those exhibiting the
most promise as transparent conducting materials with excellent relevant properties: physi-
cal stability, large band gap (transparency) and high electrical conductivity. These include
Cu-doped ZnS and Al-doped ZnS (AZS), from our extensive defect study of ZnS, and ox-
ides such as K₂Sn₂O₅, NaNbO₂, and ZrPbO₃ as p-type transparent conductors from our
high throughput screening of oxides. We identify several other promising candidates, which
require further investigation. Finally, in Chapter 5, we propose future directions, which
include the development of a 2D aMoBT, and automating aMoBT and defect calculations
efficiently so that screening of numerous new materials is possible with minimal dependence
on experimental data. Part of this automation is already underway, as described in Chapter
4.

1.1 Applications of *Ab initio* Modeling

In the following, we briefly discuss the TE and PV materials and their applications.
Motivation, Chapter 1
The goal: accurate first principles calculation of the properties of real PV & TE semiconductors

Combining aMoBT and Defects to Search for TCMs
Cu- & Al-doped ZnS, Cu-doped ZnO
Screening of potential TCOs: K$_2$Sn$_3$O$_5$, NaNbO$_2$, ZrPbO$_2$, etc (all in Chapter 4)

Figure 1.1: Schematic of the outline of this dissertation.
1.1.1 Thermoelectric Materials

Thermoelectric materials are n-type and p-type semiconductors used in a thermoelectric device known as a "solid-state heat engine"[20] to convert heat, or, more accurately, temperature difference, to electricity. This can be one of the promising solutions for the energy crisis. The resemblance of thermoelectric systems to heat engines has been clearly demonstrated before.[25] The advantages of this new generation of heat engines are: 1) being simple to use, 2) lack of moving parts, 3) no greenhouse gas emissions, and 4) capability of converting waste heat \(^1\) or concentrated solar thermal energy directly to electricity.

In the early 1800’s, Thomas Johann Seebeck observed that when two different metals are held together and the junction is exposed to a temperature difference, a voltage difference proportional to the temperature difference develops.[1]; this phenomenon is called the Seebeck effect. The potential difference between the hot and cold sides of the materials, per degree temperature difference, is called the Seebeck coefficient, which is an intrinsic property of the materials. Now if a voltage difference is applied on the same junction, a temperature difference develops; this is called the Peltier effect and can be used in cooling applications.

As can be seen in Figure 1.2, a combination of n-type and p-type semiconductors is the best junction for a thermoelectric device. The temperature gradient, \(\nabla T\), is the driving force of electrons from the hot side to the cold side in power generation mode, causing an electrical current to form via diffusion — hence the potential gradient, \(\nabla V\). It can be seen that the lower the thermal conductivity, \(k\), of the TE material, the easier it is to maintain the temperature difference. Also, the higher the Seebeck coefficient and electrical conductivity are to generate more current, the more efficient the thermoelectric device becomes. In order

\(^1\)A detailed study of waste heat applications of thermoelectricity is available in Chapter 50 of [26]
to quantify the performance, a dimensionless figure of merit is defined as:

$$ZT = \frac{\sigma S^2 T}{k}$$  \hspace{1cm} (1.2)

where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the temperature, and $k$ is the thermal conductivity of the material. Also, engineering $ZT$, $(ZT)_{eng}$, has been recently introduced by Kim et al. [27], which correlates better with the thermodynamic efficiency of the device since it takes into account the variation of TE properties over a temperature range. $(ZT)_{eng}$ can be calculated via Equation 1.3, where PF stands for power factor and $\Delta T$ is the difference between the hot temperature, $T_H$ and the cold temperature, $T_C$. It should be noted, however, that due to simplicity we only consider traditional $ZT$ throughout this dissertation.

$$(ZT)_{eng} = Z_{eng} \Delta T = \frac{\left(\int_{T_C}^{T_H} S(T)dT\right)^2 \int_{T_C}^{T_H} \sigma(T)dT}{\int_{T_C}^{T_H} k(T)dT} \Delta T = \frac{(PF)_{eng}}{\int_{T_C}^{T_H} k(T)dT} \Delta T$$  \hspace{1cm} (1.3)

When only the electronic properties of the material are studied, a parameter called the power factor is used to represent the electronic performance of the material. Power factor is the $\sigma S^2$ part of the numerator in the definition of the figure of merit.

The thermodynamic efficiency of these solid-state heat engines is related to the figure of merit via Equation (1.4)[1]:

$$\eta = \frac{W}{Q_H} = \frac{T_H - T_C}{T_H} \left[\frac{(1 + ZT_M)^{1/2} - 1}{(1 + ZT_M)^{1/2} + (T_C/T_H)}\right]$$  \hspace{1cm} (1.4)

where $T_H$ and $T_C$ are the hot and cold temperatures, respectively, and $T_M$ is the arithmetic average of these two temperatures. It can be seen that the larger the figure of merit becomes,
the closer the thermoelectric device’s thermodynamic efficiency is to the maximum/Carnot efficiency.

Waste heat coming from different sources, such as automobile exhaust, boilers and steam generators in different industries, power plants (all fossil fuel types, nuclear and even solar power plants), natural gas pumping stations, etc., are usually in the medium temperature range defined as 450-850 K [26] for thermoelectric materials. Significant research efforts have been devoted to to increase the efficiency of thermoelectric materials by even a few percent.

After reviewing the literature and most of the thermoelectric research that have been performed for optimizing the figure of merit of different materials, details of which are presented in Appendix B, we selected pure and doped zinc antimonides, specifically Zn$_4$Sb$_3$ for this study. $\beta$–Zn$_4$Sb$_3$ is one of the best-performing thermoelectric materials in the medium temperature range, whereas the $\alpha$ phase is stable at low temperatures[28].
metastable material, $\beta$-Zn$_4$Sb$_3$, has a complex crystal structure (including disorder, defects, and vacancies[29]), which is the main reason for its very low thermal conductivity, and therefore, high thermoelectric figure of merit[29, 30]. Furthermore, the electrical conductivity and Seebeck coefficient of this material are reasonably large — all of which result in a large ZT of 1.3 at 670 K [31]. For more information on thermoelectric materials, see Appendix B.

1.1.2 Photovoltaic Materials

Since 1873, when Willoughby Smith discovered the photoconductivity of selenium, and 1921, when Albert Einstein won the Nobel prize for his theories (1904) explaining the photoelectric effect [32], significant progress has been made in the efficient use of solar energy to produce electricity, particularly in the photovoltaic cells. In 1954, Daryl Chapin, Calvin Fuller, and Gerald Pearson developed the silicon photovoltaic (PV) cell at Bell Labs, with 4% efficiency, and PV technology was thus born in the United States [32]. Nowadays, record efficiencies are frequently reported by various research groups. The official chart that keeps track of these efficiencies is presented in Figure 1.3 which includes the record efficiencies for various families of solar cells: 1) crystalline silicon cells, 2) single-junction gallium arsenide cells, 3) multijunction cells, 4) thin-film technologies, and 5) emerging photovoltaics. The main area of PV on which we focus in this work is transparent conducting materials, which have applications in almost every PV technology, particularly thin film and emerging photovoltaics. These materials should have a high enough band gap to be transparent (i.e., not to absorb/block the visible light at the top of the solar cell); they should also be highly conductive to minimize the resistivity loss during electron transport in the PV cell.
Figure 1.3: The record efficiency of various families of photovoltaic solar cells reported and confirmed by independent, recognized test labs (e.g., NREL, AIST, Fraunhofer) from 1976 to the present. This plot is courtesy of the National Renewable Energy Laboratory, Golden, CO.
Scientists have made so much progress on the efficiency of the solar cell that their focus has now switched to the cost and reliability of each photovoltaic technology. For example, the DOE SunShot Initiative has the goal of making large-scale solar energy systems cost- competitive with other energy sources by 2020. “As of November 2015, four years into the decade-long SunShot Initiative, the solar industry is about 70% of the way to achieving SunShots cost target of $0.06 per kilowatt-hour for utility-scale PV (based on 2010 baseline figures)”.

In this work, we will be using the model we have developed, aMoBT, to calculate the electronic properties of various semiconductors as transparent conducting candidates. We also perform \textit{ab initio} thermodynamic calculations to identify the dominant conduction mechanism (n-type vs p-type) in these compounds. Furthermore, in a SERIIUS collaboration with Alex Polizzotti and Tonio Buonassisi at MIT, we study defect formation in SnS for use as a possible absorber layer in a PV cell, and identify the most relevant defects that may be detrimental to its lifetime, and hence the efficiency, of solar cells composed of these materials.

\subsection{1.2 Introduction to Density Functional Theory}

In this section, we briefly summarize the basics of density functional theory (DFT). It is meant to be particularly helpful for those with little to no background in quantum physics and DFT. Kohn and Sham formulated this theory, as presented in the Kohn-Sham Equation 1.5:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + V_H(\vec{r}) + V_{XC}(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r})$$

\footnote{http://energy.gov/eere/sunshot/photovoltaics}
where the terms are, respectively, kinetic energy, electron-ion potential, Hartree potential, and exchange correlation potential. The Hartree potential is basically the electron-electron potential, $V_{ee}$, expressed in terms of electron density as shown in Equation 1.6:

$$V_H(\vec{r}) = e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r'$$  \hspace{1cm} (1.6)

The first three terms in Equation 1.5 are physical terms that are generally familiar. However, the fourth term arises from the decoupling of the orbitals equation. Therefore, the exchange-correlation potential is everything that we do not know about the potential in DFT. More details on KS-DFT and other theories are available in Appendix A. The GGA-PBE [33, 34] functional has been used in all of our calculations, as it works well for semiconductors.

The density of electrons is a function of the orbitals, as seen in Equation 1.7, which are the solution to KS-equation themselves. Therefore, in the Kohn-Sham equation (Equation 1.5), the density is a function of the orbital solution itself. As a result, this equation should be solved in an iterative way (i.e., self-consistently). Starting from an electron density, Equation 1.5 can be solved to obtain the orbitals, and a new density can be calculated via Equation 1.7 so that the same procedure can be performed on this new density. This can be repeated until the electron density converges. The details on how to choose the initial density and how to update the density to converge rapidly are skipped here, but can be found in the literature[35]. Once the density is calculated (i.e., converged), the charge distribution, and

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3 Based on the Born-Oppenheimer approximation, we assume that the ions are fixed
4 The word "functional" is used since density itself is a function. The exchange-correlation potential is the function of another function (the density) or simply a functional.
5 The star denotes complex conjugate
6 We call the electron density converged when the difference in the total energy of two consecutive iterations are less than a pre-defined number (e.g. $1.0 \times 10^{-5} eV$)
therefore, all the terms in Equation 1.5, are known; the density will be fixed and the non-self-consistent calculation can be performed in order to calculate the orbitals and energies at particular $k$-points in the Brillouin zone. Only at this step can we calculate the magnitude of the energy states at each point in the unit cell, and therefore, the band structure.

$$n_{KS}(\vec{r}) = n(\vec{r}) = 2 \sum_i \psi_i^*(\vec{r})\psi_i(\vec{r}) \quad (1.7)$$

In periodic crystalline solids, by only calculating the energies at a periodic unit cell and applying a periodic boundary condition, we can describe the bulk solid far from the edges. This unit cell (or Wigner-Seitz cell or simulation box) is the smallest repeating unit of the crystal lattice. Everything that has been described in this chapter can be presented in reciprocal space. The unit cell itself can be transformed into the Brillouin zone which is the smallest repeating unit of the reciprocal lattice. The DFT calculations in VASP are actually performed in reciprocal space. Since the are performed done numerically, Equation 1.5 is solved in VASP only on a grid, called the $k$-point mesh, across the Brillouin zone. The Brillouin zone is the same concept as the Wigner-Seitz cell, from which it can be obtained with certain transformations. The name $k$-point stems from the fact that the position vector, $\vec{r}$, has a counterpart in the reciprocal lattice called the wave vector, $\vec{k}$, which is directly related to electron momentum. By increasing the number of $k$-points, the calculation becomes more accurate but more computationally demanding. Accordingly, the number of $k$-points should be increased until the calculated property in which we are interested, or the total energy, becomes insensitive to this number.

In this section, we briefly introduced DFT and how it is implemented in VASP. This is the first-principles part of the model — describing the electrons and ions with no specific
labels. We can consider this part as a computer code, which takes as inputs the structure of the unit cell and the number of \(k\)-points, and outputs energy states, \(\varepsilon(\vec{k})\), for electrons at each \(k\)-point, for further input to the Boltzmann transport equation and the theory and methodology that follow.

### 1.3 Introduction to the Boltzmann Transport Equation

In order to describe electron transport, we need to know the changes in the electron distribution due to various perturbations. At equilibrium, the electrons (Fermions) adopt the Fermi-Dirac distribution (Equation 1.8), \(f_0\):

\[
f_0(\epsilon, T) = \frac{1}{1 + e^{(\epsilon-\epsilon_F)/k_B T}}
\]

(1.8)

In the absence of any external force, the electron distribution maintains the Fermi-Dirac form; however, the distribution changes when external forces, such as electric fields or temperature gradients, are present. Furthermore, the distribution changes by inelastic scattering phenomena, such as electron-optical phonon scattering, which is described in Section A.2.4.

The Boltzmann transport equation has been developed to describe the distribution function in the presence of external forces and inelastic scattering processes. The distribution is crucial for calculating macroscopic properties of materials.

The distribution is not affected by elastic scattering processes in which the energy of the pre-scattering state and post-scattering state are equal. This has been shown by Rode [5].
The details and steps on how the BTE is derived can be found in [36]. In the steady state, in the presence of a low electric field, the BTE can be written as Equation 1.9:

\[ v(\vec{k}).\nabla_r f(\vec{k}, T) + \frac{e\vec{E}}{\hbar}\nabla_k f(\vec{k}, T) = \int \left\{ s(\vec{k}', \vec{k}) f(\vec{k}', T)[1 - f(\vec{k}, T)] \\
- s(\vec{k}, \vec{k}') f(\vec{k}, T)[1 - f(\vec{k}', T)] \right\} d\vec{k}' \]  

where \( f(\vec{k}, T) \) is the distribution at the wave vector, \( \vec{k} \), and the temperature \( T \). \( \frac{\partial f(\vec{k}, T)}{\partial t} \) is the temporal rate of change of \( f \) due to all scattering processes. \( \frac{e\vec{E}}{\hbar}\nabla_k f(\vec{k}, T) \) is due to the external electric field, and \( v(\vec{k}).\nabla_r f(\vec{k}, T) \) is the diffusion term from the carrier density gradient. \( v(\vec{k}) \) is the carrier’s group velocity and is calculated by Equation (1.10).

\[ v(\vec{k}) = \nabla_k \epsilon(\vec{k}) / \hbar \]  

\( s(\vec{k}', \vec{k}) \) is the differential scattering rate from the state \( \vec{k}' \) to the state characterized by \( \vec{k} \); the rates for different scattering mechanisms have been calculated and are available in the literature [37, 5]. Equations are available for elastic scattering rates, including neutral, ionized impurity, piezoelectric acoustic, and deformation potential scattering mechanisms. These mechanisms are briefly introduced in Section A.2.3. In order to take inelastic scattering mechanisms into account, the changes in the electron distribution must be calculated. This can be done via the method described in Section A.2.4. Polar optical phonon scattering is an example of inelastic scattering mechanism described in Section A.2.4.

We can implicitly account for only elastic scattering mechanisms by using the relaxation time approximation (RTA) to BTE. This has been used in the widely-used BoltzTraP[38] code. However, we show in Chapter 2 that this is an oversimplification. We briefly explain BTE-RTA and how it results in closed-form expressions for conductivity and Seebeck coefficient in
Section A.2.2. The drawbacks of the constant relaxation time approximation are discussed in Chapter 2.
Chapter 2

aMoBT: \textit{ab initio} model for transport properties

Accurate models of carrier transport are essential for describing the electronic properties of semiconductor materials, which are particularly important for clean energy applications such as photovoltaics and thermoelectrics. There has been an increased focus on using compound semiconductors, including those that are degenerately and heavily doped, for these applications. To better understand existing materials and discover new ones, a fully predictive model that correlates electronic structure to properties is essential. Unfortunately, to the best of our knowledge, no model, based on \textit{ab initio} calculations, currently exists to fully capture the elastic and inelastic scattering effects of charge carriers; as a result, errors

\footnote{Parts of this chapter has been reprinted with permission from the following references (copyright permissions available at the beginning of the dissertation). The co-author Dr. Joel Ager has provided his semi-empirical model\cite{8} in Mathematica for starting point learning and comparison. Also, he co-advised this work together with the primary supervisor, Professor Cynthia Lo.}


- \textbf{Alireza Faghaninia}, Joel W. Ager, and Cynthia S. Lo, Ab initio Electronic Transport Model for Photovoltaics. In \textit{Photovoltaic Specialist Conference (PVSC)}, 2015 IEEE 42nd, pages 1-4, June 2015 \cite{39}
arise when utilizing the current models. While an ab initio model will certainly improve our understanding of the carrier transport mechanism(s) in existing semiconductors, it can also aid in the search for high-performing materials by improving the accuracy of high-throughput computations [40, 41].

There currently exist two main categories of models, based on the Boltzmann transport equation (BTE), for calculating the conductivity and Seebeck coefficient of semiconductors that are governed by band conduction. The first category of BTE-based models are commonly known as single parabolic band models, even though the treatment of the conduction band may not be explicitly parabolic. These models can be described as "semi-empirical", since experimentally measured parameters, such as the electron or hole effective mass, band gap, dielectric constant and polar optical (PO) phonon frequency, are used in closed-form expressions for the various scattering rates. Note that the overall mobility due to elastic scattering is calculated by averaging, according to Matthiessen’s rule, the mobilities due to each scattering contribution. The main adjustable parameter in these models is the effective mass, which can be varied to fit the calculated transport properties to the experimental measurements. While such models often impressively capture the changes in properties over various ranges of temperature and carrier concentration, they are restricted to the materials for which experimental data are available; therefore, the predictability of such models are very limited.

There are numerous examples of models in this category [5, 7, 42, 43, 44], such as that by Ehrenreich [43], who modeled the GaAs band structure and PO-phonon scattering by reviewing the experimental data [43], and that by Sankey et al. [42], who considered the effects of resonance, ionized impurity, and polar optical phonon scattering in GaAs. In these models, all of the scattering mechanisms are commonly treated using the relaxation time
approximation (RTA); here, the relaxation time is written as a power law function of energy – thus, the details of elastic and inelastic scattering (e.g., PO phonon) captured by the \textit{ab initio} band structure are disregarded. Scattering rates, particularly inelastic ones, have already been shown to not follow such power law distributions [5, 8], so the basic assumptions fail. Even in cases where the BTE is explicitly solved for PO phonon and the perturbation to the electronic distribution is obtained without the RTA assumption, the results are still heavily dependent on available experimental data. As an example, Miller et al. [8] used the latter approach to calculate the mobility and Seebeck coefficient of InN samples, which had been grown by molecular beam epitaxy (MBE) and plasma assisted MBE so that all exhibited heteroepitaxial growth with linear charged dislocations; thus, these dislocations were found to be the limiting scattering mechanism.

The second category of BTE-based models relies on the \textit{ab initio} band structure of the material, rather than specific experimentally measured parameters, but generally utilizes the relaxation time approximation to the BTE (BTE-RTA) as a simplification. Restrepo et al. [45] calculated the mobility of n-doped silicon at different electron concentrations in BTE-RTA and \textit{ab initio} framework where electron-phonon interactions are treated as elastic with the electron distribution unchanged from the equilibrium Fermi-Dirac. On the other hand, the constant relaxation time approximation (BTE-cRTA) simplifies the equation even more, which enables closed form expressions for both conductivity divided by relaxation time and Seebeck coefficient. The advantage of these models is the ability to calculate properties of new materials, for which experimental data is unavailable. This type of model works well for some materials for which the relaxation time is fairly constant, as evidenced by the work of Madsen and Singh [38]. However, inelastic scattering mechanisms change the electron energy and directly affect the distribution. Lumping all the elastic and inelastic scattering mechanisms into a single constant and assuming an equilibrium Fermi-Dirac distribution
in BTE-cRTA framework greatly damages the predictive ability of such models; as an example, transport properties in some cases are very far from experimental measurements. Furthermore, the relaxation time constant is usually determined by fitting the calculated conductivity to experimental data. It should be noted that the calculation of this constant is not necessary when calculating the Seebeck coefficient. This is due to the simplifying assumptions that the relaxation time is both a constant and direction independent [38] which does not always hold. Therefore, BTE-cRTA suffers not only from inaccuracy in predicting the changes of properties with temperature or carrier concentration in many materials, but also from lack of pure predictability since it still relies on experimental data for the computation of the relaxation time.

Instead, we propose [23] that accurate calculations of electronic transport properties, within the Boltzmann transport framework, are possible by combining relevant treatment of the elastic and inelastic scattering mechanisms with \textit{ab initio} calculations of the electronic and phonon band structures. Ultimately, an \textit{ab initio} theory for carrier transport will need to qualitatively and quantitatively predict trends in material properties, such as conductivity and Seebeck coefficient, as a function of temperature or carrier concentration. Validation of the theory against experimentally measured properties will thus give insight into which scattering effects are dominant.

In this chapter, we present a band transport model for calculating low-field electrical drift mobility and Seebeck coefficient with both single-band and coupled-band BTE formulation for both n-type and p-type semiconductors which we refer to as aMoBT: \textit{ab initio} Model for calculating mobility and Seebeck coefficient using Boltzmann Transport (aMoBT) equation. We then validate aMoBT by calculating the properties of both n-type and p-type GaAs, InN, Cu-doped and Al-doped ZnS with different carrier concentrations over various temperatures,
and comparing them to experimental values as well as those calculated using the other transport models described above. We choose these materials because the ab initio band structure of GaAs is similar to those used in the earlier semi-empirical models at it can be reasonably well described with a single band model, whereas the ab initio band structure of InN and the limiting scattering mechanisms are quite different; furthermore, we examine the feasibility of doped ZnS as a transparent conducting material. Thus, these materials allow us to bracket the range of expected behavior of our proposed model. Furthermore, p-GaAs and Cu-doped ZnS provide additional validation for the coupled band formulation for these two degenerate p-type semiconductors.

2.1 aMoBT: Single Band Formulation

In this section we describe the single band formulation of aMoBT. This means that we assume that the transport is mainly governed by a single conduction or valence band for either n-type or p-type semiconductor respectively. For the coupled band formulation see Section 2.2.

2.1.1 Solution to the Boltzmann Transport Equation

In order to calculate the mobility and Seebeck coefficient, we solve the Boltzmann transport equation (BTE) using Rode’s iterative method [5, 8, 46, 47, 37, 48, 49, 50, 51] (Appendix A.2) to obtain the electron distribution in response to a small driving force (e.g. a small electric field or a small temperature gradient). It is important to note that we do not use the relaxation time approximation (RTA) in solving the BTE, so neither a variable nor a constant
relaxation time appears in this expression. Due to the assumption of a small driving force, we aim to calculate only the linear response to the perturbation; thus, the general form of the electron distribution remains the at equilibrium Fermi-Dirac distribution. We can then write:

\[ f(k) = f_0[\varepsilon(k)] + xg(k) \]  

(2.1)

where \( f \) is the actual distribution of the electrons, including both elastic and inelastic scattering mechanisms, \( f_0 \) is the equilibrium Fermi-Dirac distribution, \( x \) is the cosine of the angle between the small driving force and \( k \), \( g(k) \) is the perturbation to the distribution caused by the small driving force and finally \( k = |k| \). For the sake of simplicity, we express the conduction band as the average energy of the electrons as a function of distance, \( k \), from the conduction band minimum (CBM) or the valence band maximum (VBM) which are often at the center of the Brillouin Zone (i.e. Γ point); furthermore, we assume that the small driving force is aligned with \( k \) (i.e., \( x=1 \)). Although this is similar in spirit to the isotropic band assumption, we take the anisotropy into account by averaging the energy values of the \textit{ab initio} calculated band structure, \( \varepsilon(k) \), as a function of \( k \) rather than explicitly including \( k \) in every direction. Alternatively, if we wish to consider the directional transport properties, we can include the calculated band structure only in that specific direction. Here, we will focus on calculating and reporting the overall average mobility and Seebeck coefficient.

Our goal is to calculate the perturbation to the distribution \([5], g(k)\). In the reformulated Boltzmann transport equation (Equation 2.2), there are scattering-in, \( S_i(g) \), and scattering-out, \( S_o \), terms for inelastic scattering mechanisms. However, these terms also depend, in turn, on the electronic distribution as well as elastic scattering rates, \( \nu_{el} \). Therefore, the
BTE must be solved self-consistently to obtain $g(k)$:

$$g(k) = \frac{S_i [g(k)] - v(k) \left( \frac{\partial f}{\partial z} \right) - eE \left( \frac{\partial f}{\partial k} \right)}{S_o(k) + \nu_{el}(k)}$$

(2.2)

where $E$ is the low electric field and $v(k)$ is the electron group velocity. The derivation of the BTE in the form shown in Equation 2.2 can be found in the literature[5]. The inelastic scattering mechanism that tends to dominate at room temperature is polar optical (PO) phonon scattering, for which we have provided the description of the $S_o$ and $S_i (g)$ terms in Equations A.63 and A.64. The influence of inelastic scattering mechanisms on $g$, and therefore the overall mobility, are captured through the terms $S_i (g)$ and $S_o$ in Equation 2.2, while elastic scattering mechanisms affect the overall mobility by the term $\nu_{el}$. This term is the sum of all elastic scattering rates inside the material, it can be evaluated according to Matthiessen’s rule:

$$\nu_{el}(k) = \nu_{ii}(k) + \nu_{pe}(k) + \nu_{de}(k) + \nu_{dis}(k)$$

(2.3)

where the subscripts $el$, $ii$, $pe$, $de$, and $dis$ stand for elastic, ionized impurity, piezoelectric, deformation potential and dislocation scattering rates, respectively. Therefore, the effect of relevant elastic and inelastic scattering mechanisms are taken into account by explicitly solving the BTE (Equation 2.2) to obtain $g(k)$.

The most relevant elastic scattering mechanism for compound semiconductors is expected to be ionized impurity scattering at low temperatures. Ionized impurity scattering occurs when a charged center is introduced inside the bulk material. As a result of Coulombic interactions between the electron and ion, electrons scatter to different states (i.e., become distracted). The ionized impurity scattering rate, $\nu_{ii}$ (i.e., a component of the overall $\nu$),
may be expressed using Brooks-Herring theory [52]:

\[ \nu_{ii} = \frac{e^4 N}{8\pi \epsilon_0^2 \hbar^2 k^2 v} \left[ D \ln \left( 1 + \frac{4k^2}{\beta^2} \right) - B \right] \] (2.4)

where the charge screening potential, \( \phi \), is obtained by solving Poisson’s equation:

\[ \phi = \frac{q}{4\pi \epsilon_0 r} \exp (-\beta r) \] (2.5)

and inverse screening length, \( \beta \), is given by:

\[ \beta^2 = \frac{e^2}{\epsilon_0 k_B T} \int D_S (\varepsilon) f (1 - f) d\varepsilon \] (2.6)

where \( f \) is the electron distribution and \( \epsilon_0 \) is the low-frequency dielectric constant. Details on the \( D \) and \( B \) parameters are given in the literature [5].

When calculating various properties, several terms in Equation 2.2 will be set to zero. For a Seebeck coefficient, \( S \), calculation, the applied electric driving force, \(- (eE/\hbar) (\partial f/\partial k)\), is set to zero. Only the thermal driving force, \( v (\partial f/\partial \varepsilon) \), in Equation 2.2 is taken into consideration when calculating the perturbation to the electron distribution [5]. Seebeck coefficient can be calculated via Equations 2.7-2.10 where \( S \) is Seebeck coefficient, \( J \) is current density, and \( \sigma = ne\mu \) is the electrical conductivity \( n \) being the density of electrons.

\[ J = \sigma [E - (\nabla \epsilon_F/e) - S \nabla T] \] (2.7)
When $J = 0$, as in open circuit measurement of $S$ and assuming that the electric field and the temperature gradient are in the $z$ direction:

\[ S = \frac{E}{\bar{T}} \partial T / \partial z \]  

(2.8)

\[ S = -\frac{\partial E / \partial z}{e} + \frac{J}{\sigma} \partial T / \partial z \]  

(2.9)

\[ S = \frac{k}{e} \left[ \frac{\int k^2 f(1 - f) \epsilon F/dk}{\int k^2 f(1 - f) dk} - \epsilon F/kT \right] - \frac{J}{\sigma} \partial T / \partial z \]  

(2.10)

Assuming a uniform electron concentration over the space at which a small temperature difference exists, the Seebeck coefficient is [5]:

\[ S = \frac{k_B}{e} \left[ \frac{\epsilon F}{k_B T} - \frac{\int k^2 f (1 - f) \left( \frac{\epsilon}{k_B T} \right) dk}{\int k^2 f (1 - f) dk} \right] - \frac{J}{\sigma} \partial T / \partial z \]  

(2.11)

We will compare results from Equation 2.10 with the ones calculated before via Equation A.37 derived from BTE-RTA. Also, the main improvement to the theory for inelastic scattering is to calculate parameters required for obtaining $S_o$ and $S_i$ using DFT rather than relying on experimental data. This improves the predictability. For example for polar optical scattering mechanism, scattering rates are strongly dependent on polar optical phonon frequencies (Equations A.72 and A.73). Since we have previously calculated phonon dispersion including optical phonon frequencies (phonon dispersion or phonon band structure)
at each k-point in the lattice, we can use the same DFT approach to calculate and to include these frequencies in Equation A.74. Another example are parameters \( a, c, \) and \( d \) in Equations A.75-A.78 which are related to the experimentally measured effective mass, \( m^* \); even though, as shown in Equation 2.22, we can calculate effective mass via DFT, we do not include this parameter in the formulation as we calculate the group velocities directly from the DFT band structure. Calculating all these parameters from first principle rather than taking the experimental values, increase the predictability of the model and also enables prediction for new materials for which experimental data is unavailable.

For a mobility calculation, the thermal driving force in Equation 2.2 is set to zero, so that only the contribution of the electric driving force is included. The mobility is:

\[
\mu = \frac{1}{3} \int \frac{v(k) \left( \frac{k}{\pi} \right)^2 \left( \frac{g}{E} \right)}{\int \left( \frac{k}{\pi} \right)^2 f dk} \, dk
\]  

(2.12)

Note that in Equation 2.12, the free electron density of states, \( \left( \frac{k}{\pi} \right)^2 \), has been used, which would limit its applicability in compound semiconductors. Thus, the replacement of this term by its \textit{ab initio}-calculated counterpart would greatly improve the accuracy of the resulting mobility. Furthermore, the scalar group velocity, \( v(k) \), is used since the energy is averaged as a function of distance from the \( \Gamma \) point. In general, we use the band structure, density of state, electron group velocity, conduction band wavefunction admixture and PO phonon frequency in calculating the mobility and Seebeck coefficient. Therefore, all of the required inputs to Equation 2.12 are calculated \textit{ab initio}, which greatly enhances the predictability of the model. In other words, the main difference between our proposed carrier transport model and previous semi-empirical models [5, 53, 7, 42, 43, 8, 46, 47, 37, 48, 54, 55] is the use of \textit{ab initio} parameters instead of experimentally measured electron effective mass, band
gap, etc., which eliminates the need for theories such as $\mathbf{k} \cdot \mathbf{p}$ to describe the nonparabolicity or anisotropy of the conduction band. Instead, for calculating the overlap integral, we express the conduction band wavefunction as a linear combination of s-type and p-type basis functions, with coefficients of $a$ and $c$, respectively [5]. These coefficients can be directly calculated \textit{ab initio} without the need to assume an s-like conduction band wavefunction (i.e., no assumption of a parabolic band).

The rates of the elastic scattering mechanisms, $\nu_{el}$, are calculated from the electron group velocities, $v$, and density of states, $D_S$; thus, the mobility may be calculated directly from the electronic band structure. The original form of these equations from $\mathbf{k} \cdot \mathbf{p}$ theory, and the modified equations that we propose, are listed in Table 2.1. Note that in every equation, $\frac{\hbar k}{md(k)}$, which, in semi-empirical models, is the group velocity fitted to experiment by the band gap and effective mass of the semiconductor (included in $d(k)$, see Table 2.1), has been replaced by its \textit{ab initio} counterpart, or $v(k)$, which is calculated directly from the band structure.

As an example, the DFT-calculated density of states (DOS) can be plugged into Equation 2.6 to obtain the inverse charge screening length, $\beta$, in ionized impurity scattering. Furthermore, the numerator and denominator of the integrand in Equation 2.12 both contain the density of states of a free electron gas, $\left(\frac{\hbar}{2}\right)^2$. Since this can also be calculated \textit{ab initio} for the specific system of interest, $D_S$ can instead be substituted in the equation for calculating the mobility and reformulated in terms of the energies, $\varepsilon$:

$$\mu = \frac{1}{3E} \frac{\int v(\varepsilon) D_S(\varepsilon) g(\varepsilon) d\varepsilon}{\int D_S(\varepsilon) f(\varepsilon) d\varepsilon}$$

(2.13)
Table 2.1: The original equations [5, 8], based on $\mathbf{k} \cdot \mathbf{p}$ theory for elastic scattering rates and overall drift mobility, and proposed modifications, based on \textit{ab initio} parameters, introduced in this work.

<table>
<thead>
<tr>
<th>$\mathbf{k} \cdot \mathbf{p}$ theory with empirical parameters</th>
<th>\textit{ab initio}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \nu_{ii} (k) = \frac{e^4 N md(k)}{8 \pi \epsilon_0 \hbar^2 k^2} \left[ D(k) \ln \left( 1 + \frac{4 k^2}{\beta^2} \right) - B(k) \right]$</td>
<td>$\nu_{ii} (k) = \frac{e^4 N}{8 \pi \epsilon_0 \hbar^2 k^2 v(k)} \left[ D(k) \ln \left( 1 + \frac{4 k^2}{\beta^2} \right) - B(k) \right]$</td>
</tr>
<tr>
<td>$\beta^2 = \frac{e^2}{\epsilon_0 k_B T} \int \left( \frac{k}{\pi} \right)^2 f (1 - f) , dk$</td>
<td>$\beta^2 = \frac{e^2}{\epsilon_0 k_B T} \int D_S (\varepsilon) , f (1 - f) , d\varepsilon$</td>
</tr>
<tr>
<td>$\nu_{pe} (k) = \frac{e^2 k_B T \beta^2 m d(k)}{6 \pi \hbar^2 e_0 k} \left[ 3 - 6 c^2 (k) + 4 c^4 (k) \right]$</td>
<td>$\nu_{pe} (k) = \frac{e^2 \hbar^2 \beta^2}{6 \pi \hbar^2 e_0 v(k)} (3 - 6 c^2 (k) + 4 c^4 (k))$</td>
</tr>
<tr>
<td>$2 \ c^2 (k) = 1 - \frac{1 + \alpha}{2 \alpha}, \ \alpha^2 (k) = 1 + \frac{2 \hbar^2 k^2}{m \epsilon_g} \left( \frac{m}{m^*} - 1 \right)$</td>
<td>$c (k)$: obtained directly from wavefunctions</td>
</tr>
<tr>
<td>$\nu_{de} (k) = \frac{e^2 k_B T \beta^2 m d(k)}{3 \pi \hbar^2 e_0 \epsilon_g} \left[ 3 - 8 c^2 (k) + 6 c^4 (k) \right]$</td>
<td>$\nu_{de} (k) = \frac{e^2 \hbar^2 \beta^2}{3 \pi \hbar^2 e_0 e_0 v(k)} \left[ 3 - 8 c^2 (k) + 6 c^4 (k) \right]$</td>
</tr>
<tr>
<td>$\nu_{dis} (k) = \frac{N_{dis} e^4 m d(k)}{h^2 r^2 \epsilon_0 \epsilon_g} \left( \frac{1 + \frac{4 k^2}{\beta^2}}{1 + \frac{4 k^2}{\beta^2}} \right)^{3/2} \beta^4$, \ $\frac{1}{d(k)} = 1 + \frac{m/m^* - 1}{\alpha}$</td>
<td>$\nu_{dis} (k) = \frac{N_{dis} e^4 k}{h^2 r^2 \epsilon_0 \epsilon_g v(k)} \left( \frac{1 + \frac{4 k^2}{\beta^2}}{1 + \frac{4 k^2}{\beta^2}} \right)^{3/2} \beta^4$</td>
</tr>
<tr>
<td>$\mu_{overall} = \frac{\hbar}{3 m} \int k^3 (g(k)/E \beta (k)) , dk \int k^2 f , dk$</td>
<td>$\mu_{overall} = \frac{1}{3 E} \int \frac{v(\varepsilon)}{D_S (\varepsilon)} g(\varepsilon) , d\varepsilon$</td>
</tr>
<tr>
<td>$g (k) = f (k) - f_0 (k)$</td>
<td>$g (\varepsilon) = f (\varepsilon) - f_0 (\varepsilon)$</td>
</tr>
</tbody>
</table>
where, again, \( v(k) \) is the electron group velocity and \( g \) is the perturbation to the electron distribution, which is calculated iteratively using Equation 2.2, and can be expressed both as a function of \( k \) or \( \varepsilon(k) \) (i.e., the band structure).

Once the mobilities of the electrons and holes are known, the electrical conductivity can be readily calculated:

\[
\sigma = ne\mu_e + pe\mu_h \tag{2.14}
\]

where \( n \) and \( p \) are the concentration of electrons and holes, respectively, \( e \) is the absolute value of the charge of an electron and \( \mu_e \) and \( \mu_h \) are the mobility of electrons and holes respectively.

It should be noted that there are fundamental differences between the model that we have presented here and those relying on the relaxation time approximation (RTA), and particularly, BTE-cRTA. Rather than simplification of the collision term in the BTE (Equation A.26) through the RTA (Equation A.27), we fully involve this term by considering both elastic and inelastic scattering mechanisms. It is noteworthy that the BTE-cRTA formulation only implicitly takes into account elastic and inelastic scattering mechanisms, by fitting the overall relaxation time to experimental data with no explicit consideration of changes in electron distribution from each type of scattering mechanism. Furthermore, unlike the semi-empirical models that were described above, we use \textit{ab initio} parameters; thus, higher predictability and little to no dependence on experimental data is achieved.
2.1.2 *Ab initio* Parameters

The main input that is needed for the transport model is the crystal structure of the semiconductor material, from which *ab initio* parameters, such as the (optimized) lattice constant, PO phonon frequency, dielectric and piezoelectric constants, deformation potential and effective mass, can be computed.

We also need to know the Fermi level to compute scattering rates in Table 2.1. In order to obtain the Fermi level, we calculate the carrier concentration and match it to the given concentration (input), $n$, according to Equation 2.15:

$$n = \frac{1}{V} \int_{\varepsilon_c}^{+\infty} D_S(\varepsilon) f(\varepsilon) \, d\varepsilon$$  \hspace{1cm} (2.15)

The concentration of ionized impurities, $N_{ii}$ (see Table 2.1), is the sum of the concentration of all ionized centers regardless of the sign of their charge, since they are scatterer centers in both cases [52]:

$$N_{ii} = N_A + N_D + \frac{N_{\text{dis}}}{c_l}$$  \hspace{1cm} (2.16)

where $N_D$ and $N_A$ are concentration of donors and acceptors, respectively. $N_{ii}$ can then be calculated at a given electron concentration, $n$, by iteratively solving the charge balance equation [8]:

$$n + N_A = N_D + \frac{N_{\text{dis}}}{c_l}$$  \hspace{1cm} (2.17)

where the density of dislocations, $N_{\text{dis}}$, is only relevant for InN and is considered to be zero for GaAs. In both GaAs and InN, temperatures lower than 20 K need not be considered due to the deionization of shallow donors at lower temperatures, as observed experimentally [60]. In the case of InN, electronic scattering from existing linear charged dislocations thus
becomes important. The density of the dislocations, \( N_{\text{dis}} \), can be determined from TEM images, in the units of \((\text{cm}^{-2})\). We can thus obtain the overall density in bulk, by assuming that these linear dislocations are uniformly developed along the \( c \)-axis. This is reflected in dividing the dislocation density by the lattice constant, \( c_l \), in Equation 2.17. By doing that, we are assuming that there is one unit of positive charge (donor) per unit cell. For InN samples, according to Miller et al. [8], one can assume full ionization of the donors, and therefore, a compensation level of one (i.e., \( \frac{N_D + N_A}{n} = 1 \) or \( N_D >> N_A \)). Also, the assumption of donor or acceptor charged dislocations yields similar results [8]; therefore, we assume donor dislocations dominate here. It should be noted that we compare the calculated \( N_{\text{dis}} \) with the corresponding experimental data if available; otherwise, the limit for electronic properties at different values of \( N_{\text{dis}} \) can be calculated without the need for experimental data.

On the other hand, in a pure, epitaxially-grown, high-mobility GaAs sample with an electron concentration of \( n = 3.0 \times 10^{13} \), no dislocations exist (i.e. \( N_{\text{dis}} = 0 \)). The concentrations of donors and acceptors have been separately reported [60, 5], so this provides validation of the accuracy of aMoBT, without needing to solve for \( N_{ii} \). However, in the general case where the electron concentration is unknown, we can plot the mobility and Seebeck coefficient at different compensation ratios to define the limit of the transport properties, as shown in Figure 2.8. Therefore, it is important to note that only when comparing with experimental mobilities/Seebeck coefficients do we use experimentally measured electron concentrations; otherwise, we may calculate \textit{ab initio} mobility or Seebeck coefficient, for example, at various electron concentrations, without any reliance on experimental data (e.g., as shown in Figure 2.8).
We use Brooks-Herring theory for singly-charged ionized impurity scattering [52], as shown in Table 2.1. This is supported by the fact that in GaAs, oxygen impurities, O$_{As}^{+1}$, have been confirmed to be dominant and singly charged [61], while in InN, nitrogen (donor) vacancies, V$_{N}^{+1}$, are dominant and singly charged [62]. It should be noted that the Brooks-Herring formulation is more accurate at low carrier concentrations, since at high concentrations, despite the inherent assumption of the theory, not all electrons are screened by the charge of an ionized center. More information on the Brooks-Herring ionized impurity model is available in Appendix A.

In order to calculate the static and high-frequency dielectric constants, we use density functional perturbation theory (DFPT), as implemented in VASP, to determine Born effective charges, dielectric and piezoelectric tensors, including local field effects in DFT, as well as the force-constant matrices and internal strain tensors[63, 64]. Where available, we use experimental data for low- and high-frequency dielectric constants. However, when this data is not available or we want to do high throughput calculations, we use DFPT to calculate the static dielectric constant, $\epsilon_0$ and Lyddane-Sachs–Teller relation (Equation 2.18) to calculate the high frequency dielectric constant, $\epsilon_\infty$.

$$\frac{\epsilon_\infty}{\epsilon_0} = \left(\frac{\omega_{TO}}{\omega_{LO}}\right)^2$$

(2.18)

where $\omega_{TO}$ and $\omega_{LO}$ (same as $\omega_{po}$) are respectively the transverse and longitudinal optical phonon frequencies. We calculate these frequencies automatically by finding the peaks in phonon density of states. The program then automatically calculate the phonon DOS, then take the last peak as LO-phonon peak, $\omega_{LO}$, and then look at the next largest peak at a
frequency larger than half of the maximum calculated frequency. This is shown in an example DOS plot of B$_6$O in Figure 2.1.

We can also calculate the phonon dispersion using the Phonopy code [2] which solves for dynamical matrix from the force constants calculated using density functional perturbation theory (DFPT), as implemented in VASP. The phonon band structures for GaAs and InN are shown in Figure 2.2.

To calculate \textit{ab initio} the deformation potential, $E_D$, we isotropically strain the material and calculate the energy of the conduction (valence) band of unit cells at different volumes. Then, we approximate the deformation potential using the following equation:

$$ E_D = -V \left( \frac{\partial E_{CBM/VBM}}{\partial V} \right) \bigg|_{T \text{ at } V = V_0} $$  \hspace{1cm} (2.19)
where $V$ is the volume, $E_{CBM}$ is the energy of the CBM and $V_0$ is the volume of the relaxed structure (i.e., zero pressure)[65, 66]. It should be noted that since the absolute value of $E_{CBM}$ is a function of the volume itself, we use the difference between the energy of the first conduction band and the first valence (core) band. Furthermore, the elastic and piezoelectric constants have been already calculated \textit{ab initio} for GaAs and InN, and are available in the literature. For GaAs, we use the values calculated by Beya-Wakata et al.[67], and for InN we use the values calculated by Sarasamak et al.[68], to obtain the piezoelectric coefficient and elastic constant used in the equations for piezoelectric scattering in Table 2.1.

As a comparison, the electrical conductivity and Seebeck coefficient are also computed using the widely-used BTE-cRTA formulation. We choose the BoltzTraP package [38], which uses Fourier interpolation of the calculated bands, and differentiate the band energies to find the group velocities of the electrons. Other than the need to fit the relaxation time to experimental measurements of the conductivity, the BoltzTraP/BTE-cRTA implementation represents an otherwise parameter-free model that can be adapted to different semiconductor materials.
In order to calculate the group velocities, \( v(k) \), we fit polynomials to the calculated conduction band around the CBM, with \( R^2 > 0.99 \). It is important for the fitted polynomial to be most accurate near the CBM, since the group velocity at those points has an impact on the calculated mobility. In order to achieve this goal, we split the fitting into 3 or 4 segments, depending on the number of available \( k \)-points. However, there will be a discontinuity associated with the regions where the segments meet. In order to minimize this discontinuity, and therefore maximize the smoothness of the results, we minimize the loss function presented in Equation 2.20:

\[
L = \sum_{i=1}^{n-1} \frac{|\varepsilon_{i,l} - \varepsilon_{i,r}|}{\bar{\varepsilon}_i} \exp\left(-\frac{\varepsilon_{i,l}}{\varepsilon_{\text{max}}}\right) \tag{2.20}
\]

where \( n \) is the total number of segments (3 or 4), subscripts \( l \) and \( r \) signifies the left and right, respectively, of where segment \( i \) and \( i + 1 \) meet, subscript \( \text{max} \) signifies the maximum calculated energy (normalization factor), and, finally, \( \bar{\varepsilon}_i \) is the average of the energy of the left and right sides where the segments \( i \) and \( i + 1 \) meet. The exponential function enforces smoother curvatures at lower energies. Similar fittings are done to the \textit{ab initio} calculated density of states. By an efficient grid-search algorithm, we find the energy values at which the segmentation minimizes the loss function, \( L \). After polynomials are carefully fitted to the \textit{ab initio} calculated conduction band, the group velocity, \( v(k) \), is calculated using Equation 2.21, where \( \varepsilon(k) \) is the \textit{ab initio} band structure.

\[
v(k) = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k} \tag{2.21}
\]

Also, the effective mass is calculated using Equation 2.22:
It should be noted that we do not use the value of effective mass in the proposed carrier transport model. Rather, we calculate it solely to compare with experiment and evaluate the effect of the shape of the conduction band (i.e., group velocities) calculated by various methods, such as GGA, GGA+U, and GW. Fitting polynomials to the numerically calculated conduction band and density of states results in smooth plots of mobility and Seebeck coefficient, as presented here, while preserving the values that are calculated \textit{ab initio} with \( R^2 > 0.99 \) in all segments fitted. We fit these polynomials at different segments of the band structure and carefully choose only the ones that result in the maximum \( R^2 \) and minimum discontinuity where the polynomials meet. This results in very smooth calculated group velocities, and, subsequently, other transport properties.

\[ m^* = \left( \frac{1}{\hbar^2 \frac{\partial^2 \varepsilon}{\partial k^2}} \right)^{-1} \bigg|_{at \ k=0} \]  

(2.22)

\textbf{2.2 aMoBT: Coupled Band Formulation}

In Section 2.1, we described the methodology for calculating the mobility and Seebeck coefficient of a semiconductor using Rode’s iterative method for solving BTE. However, we used a single-band formulation, meaning that we inherently assumed that the transport is governed only by a single band only at and around the CBM (VBM) for an n-type (p-type) semiconductor. However, this is not the case for all semiconductors; many p-type semiconductors are degenerate at the VBM meaning that at least two bands have the same energy level at VBM or CBM hence ”coupled-band”. The two bands are commonly referred to as
the "heavy hole" and the "light hole" since they have high and low effective masses respectively. This introduces an extra inter-band scattering that should be taken into account. Here we consider three main scattering mechanisms: ionized impurity, polar optical phonon and deformation acoustic phonon scattering mechanisms all in a coupled band formulation. We also present formula for non-polar phonon scattering mechanisms yet we include this less often since it is not a limiting scattering mechanism and it requires knowledge of more parameters/properties.

The scattering rate expressions presented here is mainly based on the work done by kranzer (1974) [69] and later trimmed by Ramu (2011) [49, 70]. The self consistent solution to BTE is similar to the single-band formulation based on Rode’s iterative scheme [5]. However, the BTE is solved for each; then the overall mobility considering also the inter-band scatterings is calculated. The coupled BTE that needs to be simultaneously solved to obtain \( g_i \) \( (i = 1, 2) \) for each band is presented in Equation 2.23:

\[
g_i(k_i) \left[ \nu_{ii}^{\text{inelas}}(k_i) + \nu_{ii}^{\text{elas}}(k_i) + \nu_{ji}(k_i) \right] = - \left[ v_i(k_i) \left( \frac{\partial f_i}{\partial z} \right) + \frac{qE}{\hbar} \left( \frac{\partial f_i}{\partial k_i} \right) \right] \\
+ \int_{k_i'}^\infty \Gamma_{ii}^{\text{inelas}}(k_i', k_i) dk_i' + \int_{k_j'}^\infty \Gamma_{ji}^{\text{inelas}}(k_j', k_i) dk_j' 
\]

where \( \nu_{ii} \) and \( \nu_{ij} \) are scattering-out and \( \frac{1}{\Gamma_{ii}} \) and \( \frac{1}{\Gamma_{ij}} \) roughly function as scattering-in terms. Looking at Equation 2.23 one can see that here again the perturbation term, \( g_i(k_i) \), as well as the electron distribution which in turn is a function of \( g_i \) appear on both sides of the equation hence the equation is solved iteratively.

The momentum scattering rates, \( \nu(k) \), are no longer scalar at each \( k \) but a \( 2 \times 2 \) matrix. \( \nu_{ii} \) and \( \nu_{jj} \) are decoupled scattering rates at each of the two bands and \( \nu_{ij} \) and \( \nu_{ji} \) are
the inter-band scattering rates. We present here how to calculate these rates. Once the 
rates are known, we can solve the Equation 2.23 to obtain \( g \) and integrate over \( k \) or \( \varepsilon \) like 
before (Section 2.1) to calculate the mobility. In the following, we present the equations 
used in aMoBT for ionized impurity (II), polar (PO) and nonpolar (NPO) optical phonon 
and acoustic phonon deformation potential (DE) scattering mechanisms. The principle for 
deriving these expressions is to start from the overlap term, \( G_{m,n}(k_m, k_n) \), particular to a 
scattering mechanism and then trace the states that scatter into and out of the state, \( k_i \). 
Thus, the scattering rate, \( S(k_m, k_n) \), can be built and then integrated over the brillouin zone 
which for convenience, is done in the spherical coordinates. The step-by-step derivations of 
the expressions are not the main focus of this work. The details can be found elsewhere 
[49, 70].

2.2.1 Ionized Impurity Scattering: Coupled-Band

Similar to what we did for single-band formulation (Section 2.1), to incorporate the explicitly 
calculated group velocities, \( v(k) \), rather than using a fitting parameter such as the effective 
mass, \( m^* \), or \( d(k) \), we replace \( \frac{\hbar k}{m^* d} \) with \( v(k) \) whenever possible. Therefore, with slight 
modification we obtain Equation 2.24 for ionized impurity scattering rate:

\[
\nu_{II,ii}(k_i) = \frac{N_{II} q^4}{8\pi v_i(k_i) \epsilon_0^2 \hbar^2 k_i^3} \left| (3A - 1)^2 \log \left| \frac{A+1}{A-1} \right| - 2 \left( 9A - 6 + \frac{4}{A+1} \right) \right| 
\]  

(2.24)

where \( N_{II} \) is again the concentration of ionized centers, \( q \) is the charge of an electron, \( v(k) \) 
is the group velocity and \( A \) is the screening length constant calculated via Equation 2.25:

\[
A = \frac{1}{2} \left( 2 + \frac{\beta_i^2}{k_i^2} \right) 
\]

(2.25)
where $\beta_i$ is the inverse screening length of the $i^{th}$ band. Similarly, the inter-band ionized impurity scattering can be calculated via Equation 2.26:

$$
\nu_{II,ij} = \frac{3q^4N_{II}}{8\pi \sqrt{v_i(k)v_j(k)}e_0^2\hbar^2k^2} \left| 2F_{ij}\log \left| \frac{F_{ij} + 1}{F_{ij} - 1} \right| - 4 \right|
$$

where $F_{ij}(k)$ can be obtained via Equation 2.27:

$$
F_{ij}(k) = \frac{1}{2} \left( \sqrt{\frac{v_i(k)}{v_j(k)}} + \sqrt{\frac{v_j(k)}{v_i(k)}} \right) + \left( \frac{\lambda_i^2}{2k^2} \right) \sqrt{\frac{v_j(k)}{v_i(k)}}
$$

Similarly, the $\nu_{ji}$ terms of the scattering matrix can be calculated simply by switching $i$ and $j$ in scattering expressions presented here. Furthermore, the scattering-in term for ionized impurity scattering can be obtained via Equation 2.28

$$
\int_{k'_j = 0}^{\infty} \Gamma_{ji}^{II}(k'_j, k_i) \frac{g_j(k'_j)}{d(\vec{k}_i) v_i(\vec{k}_i)} d\vec{k}'_i = \frac{3q^4N_{II}}{8\pi \sqrt{v_i(\vec{k}_i)v_j(\vec{k}_j)}e_0^2\hbar^2k^2} \left| (3F_{ij}^2 - 1) \log \left| \frac{F_{ij} + 1}{F_{ij} - 1} \right| - 6F_{ij} \right| g_j(k_{ij})
$$

where the $g_j(k_{ij})$ is the perturbation caused by the second band. Looking back at coupled-band BTE (Equation 2.23), one can see how it must be solved self consistently for $g_i$ and $g_j$.

### 2.2.2 Polar Optical Phonon Scattering: Coupled-Band

Similar to what we did for single-band formulation (Section 2.1), to incorporate the explicitly calculated group velocities, $v(k)$, rather than using a fitting parameter such as $d(k)$, we
replace $\frac{\hbar k}{md}$ with $v(k)$ whenever possible. Therefore, with slight modification we obtain Equations 2.29-2.32 for ionized impurity scattering rate:

$$\nu_{PO,ii} = \left( \frac{q^2 \omega_{PO}}{16\pi \hbar v(k_i)} \right) \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \left[ B^+ \left( N_{OP} \left[ 1 - f_i(k_i^+) \right] + (N_{OP} + 1) f_i(k_i^+) \right) \right]$$

$$+ B^- \left( (N_{OP} + 1) \left[ 1 - f_i(k_i^-) \right] + N_{OP} f_i(k_i^-) \right) \right)$$

$$\int_{k_i'=0}^{\infty} \frac{g_i(k_i')}{\Gamma_{PO,ii}(k_i', k_i)} = \left( \frac{q^2 \omega_{PO}}{16\pi \hbar v(k_i)} \right) \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \left( g_i(k_i^+) C^+ \left( (N_{OP} + 1) (1 - f_i(k_i)) + N_{OP} f_i(k_i) \right) \right)$$

$$+ g_i(k_i^-) C^- \left[ N_{OP} (1 - f_i(k_i)) + (N_{OP} + 1) f_i(k_i) \right] \right)$$

$$\int_{k_j'=0}^{\infty} \frac{g_j(k_j')}{\Gamma_{PO,ji}(k_j', k_i)} = \left( \frac{3q^2 \omega_{PO}}{16\pi \hbar v_j(k_i)} \right) \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \left( g_j(k_j^+) E^+ \left( (N_{OP} + 1) (1 - f_i(k_i)) + N_{OP} f_i(k_i) \right) \right)$$

$$+ g_j(k_j^-) E^- \left[ N_{OP} (1 - f_i(k_i)) + (N_{OP} + 1) f_i(k_i) \right] \right)$$

where $\omega_{OP}$ is the frequency of the optical phonon and $N_{OP}$ is the phonon occupation number which can be obtained from Bose-Einstein distribution, $N_{OP} = \frac{1}{\exp \left( \frac{\hbar \omega_{OP}}{kT} \right) - 1}$. and:
\[ B^\pm = \left( \frac{1 + 3c_i^{\pm 2}}{2} \right) \log \left| \frac{1 + c_i^\pm}{1 - c_i^\pm} \right| - 3c_i^\pm \] \quad c_i^\pm = \frac{k_i^2 + k_i^{\pm 2}}{2k_i k_i^\pm} \quad (2.33) \]

\[ C^\pm = \left( \frac{c_i^\pm + 3c_i^{\pm 2}}{2} \right) \log \left| \frac{1 + c_i^\pm}{1 - c_i^\pm} \right| - \left[ 2 + 3c_i^{\pm 2} \right] \] \quad c_i^\pm = \frac{k_i^2 + k_i^{\pm 2}}{2k_i k_i^\pm} \quad (2.34) \]

\[ D^\pm = \left( \frac{1 - c_{ij}^{\pm 2}}{2} \right) \log \left| \frac{1 + c_{ij}^\pm}{1 - c_{ij}^\pm} + c_{ij}^\pm \right| \] \quad c_{ij}^\pm = \frac{k_i^2 + k_{ij}^{\pm 2}}{2k_i k_{ij}^\pm} \quad (2.35) \]

\[ E^\pm = \left( \frac{c_{ij}^\pm - c_{ij}^{\pm 3}}{2} \right) \log \left| \frac{1 + c_{ij}^\pm}{1 - c_{ij}^\pm} + \frac{3c_{ij}^{\pm 2} - 2}{3} \right| \] \quad c_{ij}^\pm = \frac{k_i^2 + k_{ij}^{\pm 2}}{2k_i k_{ij}^\pm} \quad (2.36) \]

where \( k_i^\pm \) is the solution to the equation \( \varepsilon_i(k_i^\pm) = \varepsilon_i(k_i) \pm \hbar \omega_{OP} \) and \( k_{ij}^\pm \) is the solution to the equation \( \varepsilon_j(k_{ij}^\pm) = \varepsilon_i(k_i) \pm \hbar \omega_{OP} \) representing phonon absorption and emission respectively in a particular momentum state, \( k_i \).
2.2.3 Non-Polar Optical Phonon Scattering: Coupled-Band

Unlike the single-band formulation, here we also take into account the non-polar optical phonon (NPO) scattering. However, due to more number of parameters required for this mechanism, we only include it when parameters are known. It has been shown that, generally, this mechanism does not have a limiting effect on the conductivity. The scattering rates can be calculated via Equations 2.37 and 2.38:

\[ \nu_{NPO,ii}(k_i) = \frac{E_{NPO}^{2} \omega_{OP} k_i}{2 \pi \hbar \bar{c} v_i(k_i)} (k_i^+ [N_{OP} (1 - f_i(k_i^-)) + (N_{OP} + 1) f_i(k_i^-)] + k_i^- [(N_{OP} + 1) (1 - f_i(k_i^+)) + N_{OP} f_i(k_i^+)]) \] (2.37)

\[ \nu_{NPO,ij}(k_i) = \frac{E_{NPO}^{2} \omega_{OP} k_i}{2 \pi \hbar \bar{c} v_j(k_i)} (k_{ij}^+ [N_{OP} (1 - f_j(k_{ij}^+)) + (N_{OP} + 1) f_j(k_{ij}^+)] + k_{ij}^- [(N_{OP} + 1) (1 - f_j(k_{ij}^-)) + N_{OP} f_j(k_{ij}^-)]) \] (2.38)

where \( E_{NPO} \) and \( \bar{c} \) are the parameters mentioned above. For more details, see [70, 69]. Furthermore, since the transition probability rate is independent of the angle between the initial and final states:

\[ \frac{1}{\Gamma_{NPO,ii}(k_i, k_i)} = \frac{1}{\Gamma_{NPO,ji}(k_j, k_i)} = 0 \]

2.2.4 Deformation Acoustic Phonon Scattering: Coupled-band

The deformation potential scattering is the same as presented in Section 2.1 calculated for each band. For the inter-band, \( ij^{th} \) terms, we use[49] Equation 2.39:
\[ \nu_{DE,ij}(k_i) = \frac{k_B T E_D^2 k_{ij}^2}{2\pi h^2 C_l v_2(k_i)} \]  

(2.39)

where \( C_l \) is the longitudinal elastic constant and \( k_{ij} \) is the solution to the equation \( \varepsilon_j(k_{ij}) = \varepsilon_i(k_i) \). Here, similar to single-band formulation, we treat the acoustic phonon deformation potential scattering as elastic. Also, the common approximation of momentum randomizing due to Lawaetz is made\[49] hence \( \Gamma_{DE,ji}(k_{ij},k_i) = 0 \).

2.3 Results and Discussions

In this section, we will validate aMoBT by comparing the calculated properties vs. experimental data for n-type and p-type GaAs, InN, Cu-doped ZnS and Al-doped ZnS. Also, we will describe how we calculate the necessary parameters \textit{ab initio} to minimize our reliance on experimental data in the following and Chapter 4.

2.3.1 N-type GaAs and InN

Here we present our calculations for GaAs and InN. Since extensive amount of experimental data is available for these material, we calculate the mobility, conductivity and Seebeck coefficient for both n-type GaAs and InN to evaluate the accuracy and predictability of aMoBT.
Figure 2.3: Band structure of cubic GaAs and wurtzite InN, normalized so that the Fermi level is set to zero at the conduction band minimum.

2.3.2 *Ab initio* Calculated Parameter Inputs to the Transport Model

The computed band structures of GaAs and InN are shown in Figure 2.3. We have calculated a GW0 band structure, which starts from the wavefunctions previously computed using the GGA-PBE functional, as shown in Figure 2.3a.

The band structures used in previous semi-empirical models [8, 5] express the energy of the conduction band as a function of the distance from the Γ point. Instead, we calculate the *ab initio* band structure in a three-dimensional grid around the CBM, and then average the energy values of the \( k \)-points that share the same distance from the Γ point (Figure 2.4). For both GaAs and InN, the *ab initio* and \( k \cdot p \) band structures agree well at small \( k \)-points; however, they diverge at larger \( k \)-points. This directly impacts the group velocity of the electrons and, ultimately, the transport properties – particularly at higher temperatures where higher energy electrons have nonzero occupation.
Table 2.2: Inputs to the transport model, as calculated \textit{ab initio} compared to experimentally measured values. The bolded numbers are used in our transport property calculations; note that not all appear in the final expressions listed in Table 2.1. The parameters are: $c_l$ (lattice constant), $\omega_{po}$ (PO phonon frequency), $\epsilon_0$ (low-frequency dielectric constant), $\epsilon_\infty$ (high-frequency dielectric constant), $E_D$ (deformation potential), $m^*$ (effective mass), $\varepsilon_g$ (band gap). The GaAs effective masses are calculated as 0.053 (GGA+U, this work), 0.066 (GGA+U, with published $U$ [24]), and 0.063 (GW0).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GaAs $ab\ initio$</th>
<th>Exp.</th>
<th>GaAs $ab\ initio$</th>
<th>Exp.</th>
<th>InN $ab\ initio$</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_l$ (nm)</td>
<td>0.562</td>
<td>0.575 [5]</td>
<td>0.565</td>
<td>0.569 [5]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_{po}$ (THz)</td>
<td>8.16</td>
<td>8.73 [5]</td>
<td>17.83 [5]</td>
<td>17.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>12.18</td>
<td>12.91 [5]</td>
<td>11.42</td>
<td>10.3 [8]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m^*$</td>
<td>0.053-0.066</td>
<td>0.0636-0.082 [71, 72]</td>
<td>0.062, 0.071 (GW)</td>
<td>0.05-0.08 [73, 74]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_g$ (eV)</td>
<td>0.96, 1.19 (GW)</td>
<td>1.424 [43]</td>
<td>0.50</td>
<td>0.675-0.7 [75, 76]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We have also calculated a GGA+U [77] band structure, with $U$ values taken from the published literature [3, 4], as shown in Figure 2.3. For InN, GGA+U correctly yields an s-like conduction band and a band gap of 0.5 eV, which is comparable to the self-interaction corrected band gap of 0.58 eV reported by Furthmüller et al. [78] and the experimental values of 0.675-0.7 eV [75, 79, 76] (Table 2.2). We include DFT+U calculations only to show the feasibility of these less-expensive methods, in the case of more complex semiconductor materials for which a $GW$ calculations is too expensive. Also, DFT usually suffers from vastly underestimating the effective mass[40, 41], and the introduction of the fitting parameter $U$ may reduce the predictability of the \textit{ab initio} model as a whole. Therefore, we stress that all reported transport properties are calculated here using the parameter-free $GW$ band structures, unless otherwise stated.

Although we do not directly use the value of the electron effective mass in the transport property expressions, we see that the calculated effective mass of 0.062 for InN is consistent
with the previously calculated effective mass (0.066) using an empirical pseudopotential [80],
and well within the range (0.05-0.08) measured experimentally [75, 79, 81, 73, 82, 74].

We also show the calculated phonon band structure and density of states of these two com-
ounds in Figure 2.2. For GaAs, the calculated PO-phonon frequency of 8.16 THz is shown
in Figure 2.2a. For InN, the calculated optical phonon frequency of 17.83 THz is close to the
17.65 THz value reported by Bungaro et al. [83, 79]. We have listed all the parameters that
are used in our transport model in Table 2.2. We have calculated all of these parameters, as
bolded in Table 2.2, \textit{ab initio} to demonstrate the feasibility of a fully predictive model for
transport properties. The only exceptions are the elastic and piezoelectric constants, which
are necessary to calculate the piezoelectric coefficient, $P$, in Table 2.1. As described earlier,
we have instead used the previously calculated values from published DFT studies for these
constants[67, 68]. Thus, all the parameters in Table 2.2 are calculated \textit{ab initio}.

The momentum relaxation time, $\tau(\varepsilon) = 1/\nu_{el}$, is calculated at 300 K for both GaAs and InN,
as presented in Figure 2.5. It should be noted that $\tau(\varepsilon)$ is calculated by the group velocity
determined \textit{ab initio}. As shown in Figure 2.5, the calculated $\tau(\varepsilon)$ is well described by the
power law expression, $\tau(\varepsilon) = \tau_0\left(\frac{\varepsilon}{k_B T}\right)^r$, which is basically $\tau(\varepsilon) = \tau_0\varepsilon^r$; for both GaAs
and InN, $r$ is calculated to be -0.56 for the deformation potential scattering mechanism
and 0.47 for the piezoelectric scattering mechanism. These values are in agreement with
the equivalent textbook predictions ($r$ being -0.5 and 0.5, respectively) [36, 8]. However, the
prediction of $\tau(\varepsilon)$ by a power law still depends on experimentally measured parameters, such
as the deformation potential, elastic constants, and the effective mass, whereas we calculate
$\tau(\varepsilon)$ \textit{ab initio}. Furthermore, we found that the momentum relaxation time scales with
$r = 1.4$ for both ionized impurity and dislocation scattering in GaAs. This value is close to
the previous prediction of 1.5 for non-degenerate semiconductors, as found in the literature
Figure 2.4: The conduction bands expressed in terms of the average energy as a function of distance from the CBM (i.e., center of Brillouin zone, or Γ point), as calculated from semi-empirical expressions (in $k \cdot p$ formulation) versus ab initio. The difference at higher $k$ values has a significant impact on transport properties, especially at high temperatures. The values of U for the $d$ orbitals of Gallium and Arsenic, respectively, are in parentheses, while those for InN are taken from the published literature [3, 4].
Figure 2.5: Momentum relaxation time, \( \tau(\varepsilon) \), calculated \textit{ab initio} for different scattering mechanisms.

[8, 36]. However, in the case of InN, as a degenerate semiconductor, this prediction does not hold; the momentum relaxation time cannot be described with a power law, and, instead, should be explicitly calculated \textit{ab initio} from the electronic band structure. Furthermore, as shown in Figure 2.5, the dislocation and ionized impurity scattering can be described by a power law only at higher energies, with \( r \) values of 1.4 and 1.05, respectively. This shows the importance of \textit{ab initio} consideration of the scattering mechanisms for each specific semiconductor material, rather than a general power law treatment.

### 2.3.3 Model Validation on GaAs

In order to evaluate the accuracy of aMoBT, we first calculate the mobility of three experimentally synthesized and characterized GaAs samples, as described by Stillman et al. [60]. We also perform this analysis over a wide temperature range for high purity GaAs samples with very low electron concentrations, as labeled as ”pure” in Table 2.3.
As shown in Figure 2.6a, the most accurate GW band structure results in the best agreement with experimental data. The DFT+U band structure, however, does provide us with limits of the mobility over different temperatures. When calculating the mobility and Seebeck coefficient, we calculate the Fermi level by first calculating the electron concentration through Equation 2.15, and then matching it to a given concentration. The calculated properties are very sensitive to the calculated Fermi level. Therefore, for comparison, we have included the results using both the ab initio DOS used in Equation 2.15, and the free electron DOS.

As shown in Figure 2.6a, the ab initio model for DOS performs better for lower electron concentrations and lower temperatures, while the free electron DOS is more suitable for higher temperatures, and, particularly, at higher electron concentrations. We acknowledge that because of the log scale in Figure 2.6a, seeing the quantitative agreement is difficult. Therefore, we report the calculated relative error compared to the experiment for the best cases for each sample – from the ab initio DOS for sample a and from the free electron DOS for samples c and e. The minimum, maximum and the relative error in calculating the mobility of sample a are 2.25% (at 195 K), 29.42% (at 29 K), and 13.33%, respectively. These numbers are 1.02% (at 167K), 15.01% (at 49K), and 7.97% for sample c and 0.22% (at 195K), 7.90% (at 40K), and 4.04% for sample e. Overall, the agreement is poorer at higher electron concentrations and lower temperatures; this is attributed to the inaccuracy of the Brooks-Herring ionized impurity scattering model at high electron concentrations, as briefly...
(a) Comparison of model trends with varying temperature and electron concentration to experimental data. The values of U used for the d-orbitals of Gallium and Arsenic, respectively, are in parentheses.

(b) Limitation of "pure" GaAs mobility from each scattering mechanism.

Figure 2.6: The calculated and experimental [5, 6] mobility data for GaAs at various electron concentrations and temperatures. More details on the experimental data, including donor and acceptor concentrations, are available in Table 2.3.

described in Section A. Furthermore, the model has also been validated with the data on crystalline samples with very high purity. The calculated electron mobilities, assuming the limit that only one scattering mechanism exists at a time, along with the overall mobility, are shown in Figure 2.6b. The reasonable agreement between the calculated and experimental mobilities provides independent validation of the transport model. The minimum, maximum and average relative error of calculated mobility are 0.46% (at 394K), 23.55% (at 175K) and 9.53% respectively for temperatures above 20 K. The mobility is mainly limited by ionized impurity scattering at low temperatures, piezoelectric scattering at intermediate temperatures, and polar optical phonon scattering at higher temperatures (> 60 K); all of these are consistent with the previous results shown by semi-empirical models [5, 43, 7] yet no experimental parameter has been used here in predicting the correct changes with the temperature and the carrier concentration.
Figure 2.7: Electrical conductivity of GaAs calculated using aMoBT (solid line) and the BTE-cRTA framework, and compared to experimental [5] data. The Fermi level is calculated by matching the calculated carrier concentration to $n = 3 \times 10^{13}$. This has been done either at the mentioned temperature and kept constant over the whole temperature range, or in the case of ”matched Fermi”, at each temperature, the Fermi level is adjusted to the given $n$. The relaxation time, $\tau$, is determined by fitting the calculated conductivity to the corresponding experimental value at 300 K. The calculated value for $\tau$ is $5 \times 10^{-13}$s.

Once we have the calculated mobility, at a given electron concentration, we can calculate the electrical conductivity of GaAs by Equation 2.14. For now, we assume that the carrier concentration remains constant with temperature over the range of interest. We then compare to the experimental conductivity and those values calculated using the BTE-cRTA framework, under the scenarios listed in Figure 2.7. As shown, not only does BTE-cRTA fail to correctly predict the trend for conductivity with temperature, but also quantitatively differs from the experimental values.

Finally, we calculate the Seebeck coefficients of the GaAs samples (assumed to be at 300 K), and compare them to the values reported previously by Rode and Knight [7] (Figure 2.8). Since the data are for various samples with different electron concentration and compensation ratios, we choose various values of $N_{ii}/n = (N_D + N_A)/n$. As shown, a range of Seebeck coefficients are calculated at each electron concentration, which includes the experimentally
measured points. It should be noted that not knowing beforehand the compensation and concentration of donors and acceptors, as well as their charge states, limits the overall predictability of aMoBT. However, even given these limitations, the close fit between \textit{ab initio} and experimental properties provides independent validation of the viability of aMoBT. For further evaluation, we have calculated the Seebeck coefficient, assuming Pisarenko behavior and compared it to aMoBT in Figure 2.8. We use Equation 2.40 with two fitting parameters: effective mass, $m^*$ and $r$. It should be noted that in the case where the best agreement with experiment, through Pisarenko behavior, is only achievable by choosing either $m^* = 0.11$ or $r = 0.35$, both of these values are far from experimental measurements and thus lack physical meaning. Furthermore, in Figure 2.8 BTE-cRTA correctly predicts the change of Seebeck coefficient with carrier concentration fully \textit{ab initio} without the need to calculate the relaxation time constant. However, the predicted values are far from the experimental results and those calculated by aMoBT. This is attributed to the treatment of $\tau(\epsilon)$ as a single constant, $\tau$, which affect both conductivity and Seebeck coefficient when integrated over energy.

\[
S \simeq \frac{k_B}{e} \left[ \frac{5}{2} + r + \ln \frac{2(2\pi m^* k_B T)^{3/2}}{h^3 n} \right] \tag{2.40}
\]

### 2.3.4 Model Validation on InN

In order to further evaluate the accuracy of aMoBT and its applicability to more complicated semiconductors, we also calculate the mobility and Seebeck coefficient (Figure 2.9) of three experimentally synthesized and characterized InN samples by Miller et al. [8]. These
Figure 2.8: Calculated (by aMoBT) and experimental [7] GaAs Seebeck coefficient, at different ratios of the ionized impurity concentration, $N_{ii}$, to the electron concentration, $n$. For the Pisarenko plot, using Equation 2.40, we have used values of $r = -\frac{1}{2}$ for acoustic phonons, and $m^* = 0.063$. The Fermi levels for BTE-cRTA calculations were obtained by integrating the density of state to obtain the corresponding carrier concentrations; thus the same band structure and Fermi levels have been used to obtain the black and green lines.

Table 2.4: Measured [8] and calculated InN dislocation density, corresponding to the mobility and Seebeck coefficient reported in Figures 2.9a and 2.9b.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Semi-empirical[8]</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$\approx 1 \times 10^{11}$</td>
<td>$1.5 \times 10^{11}$</td>
<td>$8.20 \times 10^{10}$</td>
</tr>
<tr>
<td>B</td>
<td>$2 - 5 \times 10^{10}$</td>
<td>$1.5 \times 10^{10}$</td>
<td>$1.18 \times 10^{10}$</td>
</tr>
<tr>
<td>C</td>
<td>$\approx 1 \times 10^9 - 5 \times 10^{10}$</td>
<td>$4.1 \times 10^9$</td>
<td>$3.47 \times 10^9$</td>
</tr>
</tbody>
</table>

calculations are more challenging due to the reported presence of linear charged dislocations in the crystal structure [8, 84, 85, 86], due to the processing conditions employed. For each sample at a given carrier concentration, as shown in Table 2.4, we change the concentration of dislocations, $N_{dis}$, until the calculated mobility values match the experimental measurements. The fitted $N_{dis}$ (Table 2.4) is within the range of measured concentrations from transmission electron microscopy analysis (TEM) [8], which confirms that the limiting mechanism is indeed scattering from dislocation lines.
Figure 2.9: Calculated (by aMoBT) and experimental transport properties of the three InN samples listed in Table 2.4. The dashed line is calculated by the semi-empirical model used by Miller et al. [8], while the solid line is calculated by the proposed \textit{ab initio} transport model (aMoBT).

As shown in Figure 2.9a and 2.9b, while there is an excellent agreement between the calculated and experimental mobility, the calculated Seebeck coefficients for samples B and C exhibit more pronounced changes with temperature than the experimental Seebeck coefficients. The mobility of the samples is found to be limited by charged dislocations, particularly at low temperatures. The next limiting mechanism is polar optical phonon scattering, which is more important at higher temperatures while ionized impurity scattering is more important at lower temperatures. This can be seen in Figure 2.10, which shows the mobility of sample B if it were limited by each type of scattering mechanism, as well as the overall mobility. These findings are in agreement with the semi-empirical transport model [8], except that all parameters are obtained from \textit{ab initio} calculations that require knowledge only of the crystal structure of the material. Comparing the transport properties calculated from using model with those calculated using semi-empirical models (including experimentally measured band gap and effective mass (See Table 2.2 under ”Exp.”) in Figure 2.9 shows that although
Figure 2.10: Calculated and experimental [8] values for InN mobility at $n = 9 \times 10^{17} \text{ cm}^{-3}$ (sample B in Table 2.4). Each line represents the mobility if limited only by the corresponding mechanism.

quantitative agreement with experiment is slightly better with the semi-empirical model, Seebeck coefficient calculations on samples B and C, and the mobility of the sample at high temperature, show much better accuracy with the ab initio model presented here.

Finally, we should once again acknowledge the assumptions and limitations of the current model when applied to the other types of semiconductors. Most importantly, the formulation presented in this work is for low-field transport (particularly drift mobility and Seebeck coefficient), in which the changes to the electron distribution are merely a linear perturbation to the equilibrium Fermi-Dirac distribution; thus, the applicability of the current model for high-field transport or heavily doped and polar semiconductors where the linear BTE formulation fails [87], is very limited. Furthermore, we have averaged the energy around CBM and expressed the energy values in the band structure as a function of the absolute value of $k$, or simply, the distance from Γ point in the reciprocal space. Therefore, the reported mobility values are averaged and the effect of band structure anisotropy is not fully captured. It is
possible, however, to include the band structure of the material only in the specific orientation of interest to account for anisotropy. Currently, the model is limited to a single conduction band. Although the single band \textit{ab initio} model can be used for prediction of many direct band gap semiconductors, it will only result in an overestimation of transport properties of semiconductors with more complex band structure. This is due to the fact that currently, interband scatterings between several bands that are participating in transport are neglected. In future, we will solve coupled-BTE and take into account two and more participating bands which enables calculation of both electron and hole mobilities in more materials. Finally, although the usage of the Hubbard $U$ parameter in the band structure calculation might limit the predictability of the model in calculating overall transport properties, this can be properly addressed by using more accurate methods of band structure calculations as reported here. We include DFT+U calculations here only to show the feasibility of working with the model when $GW$ or other less commonly used methods are not technically or otherwise feasible.

### 2.3.5 Sensitivity Analysis

We have done sensitivity analysis for the calculated mobility of GaAs pure sample at different dielectric constants. As shown in Figure 2.11, the result is sensitive to dielectric constants at low and high temperatures but much less sensitive at temperatures in 100-200K range. Inaccurate calculation of dielectric constant in this case can result in up to -41% (at 40 K) calculated value of mobility compared with measured values in case of -20% from the base value for dielectric constant and it can go up to +43% (at 5K) for +20% from the base value. The base values are the ones reported in Table 2.2 calculated from \textit{ab initio} assuming the
Figure 2.11: Sensitivity analysis of the mobility of GaAs pure sample (see Table 2.3). We changed here only the static, $\varepsilon_s$, and high frequency, $\varepsilon_\infty$, dielectric constant from -20% to +20% of the base case values reported in Table 2.2. The results are sensitive to dielectric constant at low and high temperatures.

relaxed structure. This shows the importance of accurate calculation of these constants at least with 5-10% accuracy.

We also applied ±3% strain to the lattice constant of the relaxed GaAs and recalculated the band structure, DOS and optical phonon frequencies to see how sensitive is the calculated mobility with respect to the crystal structure. We assume that everything else is kept constant according to the base case (see Table 2.2). According to Figure 2.12, the calculated mobility is extremely sensitive to the crystal structure. This is mainly due to the impact that the structure has on the band shape (i.e. group velocity of the electrons) since the mobility at any temperature is affected. For example, the GW band structure of -3% strained GaAs gives the effective mass of 0.026 while that of +3% strained GaAs gives the effect of 0.10 . Both of these values are well outside of the range of the reported experiemntal values 0.064-0.082 (see Table 2.2). Also, these strained structures are extremely unlikely to be relaxed with any functional since their built in pressure with GGA-PBE functionals are already 10.66
Figure 2.12: Sensitivity analysis of the mobility of GaAs pure sample (see Table 2.3) calculated by aMoBT. We changed here the crystal structure and subsequently the newly calculated optical phonon frequencies. The calculated mobility is sensitive to the strain at all temperatures.

\[\text{kB} \text{ and } -74.77 \text{ kB while the relaxed structure that we have calculated and reported in Table 2.2 has a built in pressure of only } -0.3 \text{ kB. Nevertheless, Figure 2.12 shows the importance of accurate calculation of the crystal structure and subsequently the band structure (i.e. group velocities).}\]

### 2.3.6 P-type GaAs

Once again, since extensive experimental data are available for GaAs that date back to 1960’s and 70’s, we have calculated the mobility of p-type GaAs at different temperatures and conditions using coupled-band formulation (see Section 2.2) of aMoBT. These results are demonstrated in Figure 2.13. The discrepancy at intermediate temperatures (\(\approx 30 - 100K\)) visible in Figure 2.13a is due to the lack of piezoelectric scattering in coupled-band formulation in the current version of aMoBT. Piezoelectric scattering partially limits the mobility for n-GaAs in the same temperature range (see Figure 2.6b). The overall agreement...
Figure 2.13: The mobility of p-type GaAs calculated via aMoBT (coupled-band) and validated with independent experimental measurements[9, 10, 11, 12, 13, 14, 15].

with experimental data is very good which shows the ability of aMoBT in predicting the mobility of also such p-type semiconductors with degenerate valence band enabled by the coupled-band formulation.

### 2.3.7 Cu-doped ZnS

For Cu-doped ZnS we chose k-points close to the valence band maximum (VBM), which for these systems was always the Γ-point. An adaptive k-points mesh is used which is denser close to the VBM (same used for p-GaAs). It should be noted that we only used the PBE (DFT) functional for electronic calculations, due to computational limitations for larger supercells. We used aMoBT for calculating the mobility and conductivity. The mobility and conductivity are calculated under the assumptions that the systems are crystalline and that either all Cu atoms are ionized with +1 or +2 charge states. It should be noted that in Figure 2.14, we demonstrate that in aMoBT, external defects can be modeled assuming different
charge states. If experimentally known, accurate values of charge states related to different concentrations of different defects can make the model more accurate; on the other hand, if this is not known, which is more likely, possible charge states with different concentration can be tested and fitted to the experimental conductivity data for better understanding of external defects and their charge states. In Figure 2.14, other copper concentrations are not calculated since they are not experimentally synthesized and their carrier concentration is unknown hence cannot be properly simulated and compared with the available data.

According to Figure 2.14a, the mobility of Cu$_x$Zn$_{1-x}$S is expected to increase even at Cu-concentrations higher than 30%. However, the measured mobility is decreasing at a higher copper concentration. This trend is also visible for conductivity in Figure 2.14b. This may be attributed to the fact that not all the copper is incorporated in the lattice in the experimental samples.
2.4 Summary and Conclusions

In this chapter we explained in detail how we can calculate the electronic properties of semiconductors from first principles, with little to no reliance on experimental data. Predicting the properties of semiconductors helps us design new and better semiconductors that have not been synthesized previously, or to understand the limiting mechanisms in the current materials. These properties include electrical mobility and conductivity, as well as Seebeck coefficient.

aMoBT (ab initio model for calculating the mobility and Seebeck coefficient in Boltzmann transport framework) is the model we have developed, which works in both single-band and coupled-band formulations for semiconductors with nondegenerate and degenerate bands, respectively. We first calculate the band structure, density of states, phonons dispersion and density of states, longitudinal and optical phonon frequencies, dielectric constants, conduction and valence band deformation potential all using density functional theory with no reliance on experimental data. We next use this information to calculate the rate of all or some the following scattering mechanisms: ionized impurity, acoustic phonon deformation potential, piezoelectric and dislocation scattering. We then solve the Boltzmann transport equation (BTE) using Rode’s iterative method taking into account the inelastic polar optical phonon scattering to calculate the perturbation to the electron distribution in the presence of a low electric (thermal) driving force to calculate the mobility (Seebeck coefficient).

We have validated aMoBT by comparing the calculated properties against experimental measurements data available in the literature. We did this for GaAs (n-type and p-type), n-type InN and p-type Cu-doped ZnS, and in all cases the agreement with experimental data is very good. We performed sensitivity analysis by altering the crystal structure and
the values of the dielectric constants to show the importance of accurate calculations of these
properties for obtaining accurate properties. aMoBT is currently available for public use on
nanoHUB.
Chapter 3

*ab initio* Thermodynamics of Defects in Semiconductors

Understanding the formation of various point defects in promising thermoelectric and photovoltaic materials is crucial for theoretical determination of the origins of their behavior and possible ways of improving their performance. In this chapter, we describe our methodology for calculating the energy of formation of various intrinsic and extrinsic (dopants) point defects in semiconductors under different synthesis conditions (i.e. cation-rich and anion-rich). We then demonstrate the application of such calculations in the following examples: thermoelectric $\beta$-Zn$_4$Sb$_3$, SnS, doped ZnS and ZnO.

8 Parts of this chapter has been reprinted with permission from the following references (copyright permissions available at the beginning of the dissertation). The co-author Mr. Kunal R. Bhatt has done some of the defect formation energy calculations for the cubic structure of ZnS.

- **Alireza Faghaninia**, Kunal R. Bhatt, and Cynthia S. Lo. Alloying ZnS in the Wurtzite Phase to Create High-Performing Transparent Conducting Materials, Submitted, 2016 [17]
Zinc antimonide, $\beta$-Zn$_4$Sb$_3$, with its exceptionally low bulk thermal conductivity, is one of the most promising earth-abundant thermoelectric materials for utilizing waste heat from industrial power plants and concentrating solar thermal energy over the 450-700 K temperature range [90, 31, 91, 92, 26]; however, both $\beta$-Zn$_4$Sb$_3$ and its crystalline counterpart, ZnSb, are naturally p-type semiconductors. Defect calculations enable us to determine the origin of its p-type behavior and considerations of potential n-type dopability.

Furthermore, understanding of defects in solar cell materials such as tin(II) sulfide, SnS, helps to find ways of purifying this material via control of the relevant and most important defects identified by defect formation energy calculations. We report the results of our extensive defect energy calculations for this material which have been performed accurately via the hybrid HSE functional in Section 3.2.2. Finally, with the same hybrid functional, we have studied the defects in ZnS and ZnO to understand the doping mechanisms in these compounds and how they can be used as transparent conducting materials.

*Ab initio* thermodynamic calculations of defects in semiconductors have proven to be very effective and powerful technique for understanding of the types and charges of the defects forming in semiconductors as well as stability of different phases of the material[93, 94]. Tracking these defects experimentally is an extremely challenging task that requires advance equipment such as synchrotron-based analytical x-ray microprobe techniques[95], deep level transient spectroscopy, etc and lengthy analysis and interpretation done by experts which can be very expensive. In real world applications, semiconductors (at least in bulk form) behavior are mainly governed by and can be manipulated via defects hence, the insight that this methodology offers is the main link between idealized calculations and experimental observations.
3.1 Methods

Here we describe the methods we have used to calculate the enthalpy of formation of defects in semiconductors. Furthermore, by calculating the lattice vibrations (i.e. phonons) and taking vibrational entropy into account, we calculate the Gibbs free energy of compounds at different temperatures. *Ab initio* thermodynamic calculation that is used in this work help us understand the formation of defect and their charge states in semiconductors as well as stability of various phases of a material. We also describe the settings and inputs that we have used for DFT calculations of thermoelectric zinc antimonide, $\beta$-Zn$_4$Sb$_3$, SnS, doped ZnS and ZnO.

3.1.1 Formation Energy of Neutral or Charged Defects at 0 K

We use Equation 3.1 to calculate the formation enthalpy of various defects:

$$\Delta H_f(D, q) = E_{tot}(D, q) - E_{tot}(I, 0) - \sum_i \Delta n_i (E_i + \Delta \mu_i) + qE_F$$  \hspace{1cm} (3.1)

where $E_{tot}(D, q)$ and $E_{tot}(I, 0)$ are the total energies of the defective (e.g. Zn$_{38}$Sb$_{30}$ for simulating zinc vacancy) and ideal supercells (e.g. Zn$_{39}$Sb$_{30}$), respectively that are taken directly from DFT calculations, $\Delta n_i$ is the change in the number of element $i$, $E_i$ is the energy of bulk element $i$, $q$ is the charge state of the defect, $E_F$ is the absolute value of the Fermi level, which can be expressed as the sum of valence band maximum and relative Fermi level, and $\Delta \mu_i$ is determined by the growth conditions. Under Zn-rich, Sb-poor conditions, we calculated $\Delta \mu_{Zn} = 0.0$ eV and $\Delta \mu_{Sb} = \Delta H_f (Zn_{39}Sb_{30}) = 0.008$eV while under Zn-poor, Sb-rich conditions, $\Delta \mu_{Zn} = 0.006$eV and $\Delta \mu_{Sb} = 0.0$ eV. For the Te dopant, as an example,
we assume that it is as rich as possible; therefore, the secondary phase ZnTe does not form. This means that under Zn-rich conditions, $\Delta \mu_{Te} < \Delta H_f (ZnTe) = -0.94 \text{ eV}$, and under Sb-rich conditions, $\Delta \mu_{Te} = 0 \text{ eV}$. For other dopant elements, we similarly calculated their chemical potentials at the two limiting conditions: Zn-rich/Sb-poor and Zn-poor/Sb-rich. In Section 3.2 we explain how we similarly calculate the chemical potential of other cations and anions in SnS, ZnS and ZnO considering relevant possible intermediate phases.

In the event of any charged defect, to avoid the electrostatic self-interaction error due to the periodic boundary condition, we use the energy correction of Makov and Payne [96]:

$$\Delta H_f(D_{\infty}, q) = \Delta H_f(D, q) + \frac{q^2 \alpha}{2L\epsilon} + \frac{2\pi qQ}{3L^3 \epsilon} + O(L^{-5})$$

(3.2)

where $\Delta H_f(D_{\infty})$ represents the formation enthalpy of the defect in an infinitely large supercell where no electrostatic self-interaction error is present; this correction is necessary since, by computational limitations, we are limited to finite-sized supercells. Also, $\alpha$ is the Madelung constant, $\epsilon$ is the static dielectric constant, which we have calculated to be 35 for Zn$_{39}$Sb$_{30}$, $L$ is the distance between defect centers, and $Q$ is the quadrupole moment.

We use density functional perturbation theory, as implemented in VASP, to calculate the static dielectric constant; the ionic contributions to the dielectric tensor are also included. Unfortunately, only the first order ($L^{-1}$) correction is implemented in VASP for non-cubic cells, as is the case for distorted rhombohedral Zn$_{39}$Sb$_{30}$. Therefore, we only apply the first order correction, but we compensate for this limitation by also calculating the formation energy in a double size supercell (i.e. 138 atoms in an ideal supercell). Empirically in case of negatively charged defects, it has been shown that more reliable values may be calculated if the energies are linearly extrapolated in a plot of the formation energy vs. $L^{-3}$. We stress that this method, as described in VASP website under the section titled "Monopole, Dipole
Figure 3.1: Extrapolation of formation energy of negatively charged defects as $L \to \infty$. All values are obtained at 300 K at the valence band maximum.

and Quadrupole corrections”, works empirically only for negatively charged defects in the unit cells. The results are summarized in Figure 3.1.

### 3.1.2 *Ab initio* Thermodynamics at High Temperatures

We use density functional perturbation theory (DFPT) to calculate the force constants and dynamical matrix in semiconductors. This information is then processed by Phonopy [2] to calculate the phonons frequencies. The phonon dispersion and density of states and thermal properties can be calculated including the heat capacity, entropy and Gibbs free energy which is basically the DFT energy at 0K plus the vibrational contribution to the entropy. Therefore, this parameter is really vibrational Gibbs free energy that lacks magnetic contributions or
configuration entropy, etc but for simplicity we refer to it as Gibbs free energy. This energy consist of different terms which can be seen in Equation 3.3, reproduced here from the work of Jackson and Walsh [97, 94] who first used this methodology to determine the stability of copper zinc tin sulfide (CZTS) solar cells.

\[
\mu_i(T, p_i) = E^{\text{DFT}} + E^{ZP} + [H^0_i - H^0_i] + \int_{T^0}^T C_v dT + PV - TS(T, p_i^0)
\]  

(3.3)

\(E^{\text{DFT}}\) is the ground state energy, which is determined from GGA-PBE calculations. \(E^{ZP}\) is the zero point vibrational energy. \([H^0_i - H^0_i]\) is the difference in enthalpy between an immediate state and a reference state. \(\int_{T^0}^T C_v dT\) is the contribution from specific heat, \(PV\) is the pressure contribution and \(TS(T, p_i^0)\) is the entropy contribution. All the terms outside of the \(E^{\text{DFT}}\) are computed from the phonon frequencies obtained from density functional perturbation theory, as facilitated by Phonopy 1.8 [2]. In all calculations, the pressure is set to 1 atm.

Considering only modes of the vibration frequencies as the microstates of the system (i.e. the crystalline material) we can simply sum over all states at each \(q\)-points (\(q\) is the wave vector in reciprocal space) at each band index, \(\nu\). The energy of each state, \(\varepsilon = \hbar \omega_{q,\nu} \left( \frac{1}{2} + n \right)\), the energy of a harmonic oscillator, with the frequency \(\omega\); \(n\) is the phonon number which is calculated via Bose-Einstein equation, \(n = \frac{1}{\exp(\hbar \omega_{q,\nu} / k_B T) - 1}\). We can then calculate the total energy through the Equation 3.4:

\[
E = \sum_{q,\nu} \hbar \omega_{q,\nu} \left[ \frac{1}{2} + \frac{1}{\exp(\hbar \omega_{q,\nu} / k_B T) - 1} \right]
\]

(3.4)
Here we assume that the internal energy comes from vibrations of the atoms (heat) with no electric component for a semiconductor (insulator) in absence of magnetic energy. We can then simply calculate the heat capacity via Equation 3.5:

\[
C_V = \left( \frac{\partial E}{\partial T} \right)_V = \sum_{q,\nu} k_B \left( \frac{\hbar \omega_{q,\nu}}{k_B T} \right)^2 \frac{\exp (\hbar \omega_{q,\nu} / k_B T)}{[\exp (\hbar \omega_{q,\nu} / k_B T) - 1]^2} \tag{3.5}
\]

Also by knowing the energy of the microstates, via principles of statistical mechanics, after calculating the partition function, \( Z \), we can calculate the free energy and entropy as well. The total partition function is a multiplication of partition function of each phonon mode (i.e. subsystem) denoted by \( \zeta_{q,\nu} \). Therefore:

\[
Z = \exp \left( \frac{\Phi}{k_B T} \right) \prod_{q,\nu} \zeta_{q,\nu} \\
= \exp \left( \frac{\Phi}{k_B T} \right) \prod_{q,\nu} \sum_n \exp \left( -E_{q,\nu} / k_B T \right) \\
= \exp \left( \frac{\Phi}{k_B T} \right) \prod_{q,\nu} \exp \left( -\hbar \omega_{q,\nu} / 2k_B T \right) \sum_n \left( \exp \left( -\hbar \omega_{q,\nu} / k_B T \right) \right)^n \\
= \exp \left( \frac{\Phi}{k_B T} \right) \prod_{q,\nu} \frac{\exp \left( -\hbar \omega_{q,\nu} / 2k_B T \right)}{1 - \exp \left( \hbar \omega_{q,\nu} / k_B T \right)} 
\tag{3.6}
\]

where \( \Phi \) is an arbitrary energy reference (i.e. potential energy, constant). Also, \( \frac{1}{2} \sum_{q,\nu} \hbar \omega_{q,\nu} \) is referred to as zero-point energy, \( E^{ZP} \), which is the summation of the ground state energy of phonon modes. In Equation 3.6, the following equality has been used: \( \sum_{n=0}^\infty x^n = \frac{1}{1-x} \) for \( 0 \leq x < 1 \). Once the partition function is known, the Helmholtz free energy can be readily calculated via Equation 3.7:
\[ F = -k_B T \ln Z \]
\[ = \Phi + \frac{1}{2} \sum_{q,\nu} \hbar \omega_{q,\nu} + k_B T \sum_{q,\nu} \ln [1 - e^{\frac{-\hbar \omega_{q,\nu}}{k_B T}}] \]  

and finally when calculating the entropy via Equation 3.8 the constant term goes to zero:

\[ S = -\frac{\partial F}{\partial T} \]
\[ = \frac{1}{2T} \sum_{q,\nu} \hbar \omega_{q,\nu} \coth (\frac{\hbar \omega_{q,\nu}}{2k_B T}) - k_B T \sum_{q,\nu} \ln [2 \sinh (\frac{\hbar \omega_{q,\nu}}{2k_B T})] \]

All of these equations are also available in Phonopy documentation[98].

3.1.3 Overview of Motivations and Methods Used For Zinc Antimonide Calculations

The crystal structure of "amorphous" zinc antimonide is quite complex, with numerous defects and vacancies, especially zinc interstitials [29], that create short-range and long-range disorder; this accounts for its extremely low thermal conductivity and high dimensionless thermoelectric figure of merit, \( ZT \) (up to 1.3 at 670 K) [29, 30, 31]. \( \beta \)-Zn\(_4\)Sb\(_3\) is the metastable phase with a defected structure, which has been stabilized via its configuration and vibration entropy [99, 100]. The structure and stability of \( \beta \)-Zn\(_4\)Sb\(_3\) has been extensively synthesized, using various techniques, and characterized at different temperatures [101, 102, 103, 104, 100, 105, 106, 107, 108, 109, 110]. It also vastly outperforms ZnSb in thermoelectric efficiency.
Prototypes of $\beta$-Zn$_4$Sb$_3$-based thermoelectric devices have been shown to be stable up to 400 °C[106] as the p-type leg of the thermoelectric device. Additionally, numerous attempts have been made to n-dope $\beta$-Zn$_4$Sb$_3$ and/or ZnSb. Specifically, n-type behavior due to tellurium dopants may have been expected, due to the one additional valence electron in tellurium, compared to antimony. Abou-Zeid and Schneider [111] reported n-type conductivity in Te:ZnSb, but did not comment on the stability of this material. Additionally, Ueda et al.[112] reported n-type conductivity for some dopant concentrations of Te:ZnSb and p-type conductivity at other dopant concentrations. Also, Zhao et al. suggested in a first principles study that the substitution of tellurium for antimony does result in n-type conductivity for some compositions of Te:ZnSb [113], but results in p-type conductivity for the others. Other researchers tried to substitute Zn with Al, In or Ga, but these doped semiconductors were either p-type, or exhibited only temporary n-type conductivity or a decrease in the hole concentration before switching back to p-type conductivity [114, 115]. Similar studies have also been performed on $\beta$-Zn$_4$Sb$_3$. Li et al.[116] synthesized and measured Zn$_4$Sb$_{3-x}$Te$_x$ with varying Te dopant concentrations, and reported p-type conductivity for $x = 0.02, 0.04, 0.06, 0.08$ in the 300-700 K temperature range. Additionally, samples of Al-doped[117, 115], Ga-doped[114, 115] and In-doped[118, 115] $\beta$-Zn$_4$Sb$_3$ have been synthesized and characterized to be p-type (or, at most, fleetingly n-type). Therefore, it remains unclear why Te, Al, Ga and In result only in p-type conductivity in $\beta$-Zn$_4$Sb$_3$, and whether stable n-type $\beta$-Zn$_4$Sb$_3$ can even be synthesized.

To understand the origin of the p-type behavior in this material and the reason for the difficulty in inducing n-type behavior, we sought to study defect formation in the material – by thoroughly calculating the formation energy of intrinsic defects as well as external dopants. The effect of intrinsic point defects on the thermoelectric properties of the ZnSb phase is well established. According to Bjerg et al. [119], negatively charged Zn vacancies
are the dominant defects inside the ZnSb lattice. The p-type behavior of ZnSb is also attributed to these defects. This makes it difficult to n-dope the material, since formation of the defect becomes even more favorable as the Fermi level increases. Although Bjerg et al. suggested that the defect structure of the $\beta$-Zn$_4$Sb$_3$ should be similar, it has not previously been confirmed. Here we similarly performed a thorough study of intrinsic point defects in $\beta$-Zn$_4$Sb$_3$; to verify our results, we calculated the Seebeck coefficient, $S$, and compared it with available experimental data over the temperature range 300-700 K.

We then calculated the formation energy of Te:Zn$_4$Sb$_3$ with a range of Te charge states: -3, -2, -1, 0, and +1. We did this to computationally understand why Te-doping may have been reported to result in p-type $\beta$-Zn$_4$Sb$_3$[116]. Finally, we investigated other defects through substitution of Zn by Li, Na, B, Al, Ga, In, and Tl; we calculated the formation energy for different charge states to determine whether the stability of this material can be increased by introducing external defects/dopants. Our hypothesis is that since some of these elements (B, Al, In, Ga, and Tl) have one excess valence electron compared to Zn, they stand the best chance of inducing n-type behavior. If, instead, only p-type behavior is observed upon cation doping, we nevertheless are interested in knowing whether the dopants improve the stability of the host material and/or increase the thermoelectric figure of merit.

The crystal structure of $\beta$-Zn$_4$Sb$_3$ is consistent with the disordered rhombohedral $R\bar{3}c$ spacegroup[120], and contains partially-occupied sites, which are not possible to explicitly model in static calculations. Instead, we formed a large supercell and selectively removed and added Zn atoms, according to published procedures [121], to form Zn$_{39}$Sb$_{30}$ (Figure 3.2). In particular, the main Zn1 site (36f) is only partially occupied, with the Zn-A site having 0.846 occupancy and each of the Zn-B, Zn-C, and Zn-D sites having 0.0513 occupancy; this results in an overall stoichiometry of Zn$_{39}$Sb$_{30}$, which is equivalent to the theoretically charge
balanced composition [99]. From this point forward, we refer to $\beta$-Zn$_4$Sb$_3$ as Zn$_{39}$Sb$_{30}$. We acknowledge that this structure we have chosen to simulate is one of several possible configurations of the Zn$_{39}$Sb$_{30}$ structure – including 138-atom supercells. We have constructed two test configurations in which three Zn atoms in the main sites (Zn-A) have been removed and six interstitial Zn atoms have been added randomly. It should be noted that in the structure that we have chosen as a representation of amorphous zinc antimonide, we have added the 6 interstitial atoms of Zn-B, Zn-C and Zn-D sites based on the maximum distance from each other and the minimum distance from the three Zn atoms that had been removed from the Zn-A site to ensure the minimum total energy and therefore maximum stability. Indeed the energy of the two test structures are 0.19 and 1.08 eV higher than the selected structure. Furthermore, we have calculated the formation energy of the defects $V_{\text{Zn}}$ and Li$_{\text{Zn}}$ using the test structures; the order of these energies are the same in all three cases meaning that Li$_{\text{Zn}}$ is more favorable thus our conclusions do not change. Therefore, due to computational limitations and the selected structure having the lowest energy, we have chosen to investigate only this unit cell configuration and treat it as representative of amorphous zinc antimonide.

Next, the unit cell is optimized using Kohn-Sham density functional theory (KS-DFT) [122, 35], as implemented in the Vienna Ab Initio Simulation Package (VASP) [56, 57, 58, 59]. The generalized gradient approximation of Perdew, Burke, and Ernzerhof [33, 34] is used to express the exchange-correlation potential, and Projector Augmented Wave (PAW) potentials [123, 124] are used to represent the valence wavefunctions. No symmetry is observed in the optimized Zn$_{39}$Sb$_{30}$ unit cell (i.e., it is amorphous), starting from the $R\bar{3}c$ symmetry group reported with partial occupancies [120]. All forces are converged to 0.02 eV/Å, and the total energy is converged to $10^{-5}$ eV. Upon geometry optimization, the changes to the lattice dimensions of the unit cell are: $\Delta|a|=0.64\%$, $\Delta|b|=-0.35\%$, and $\Delta|c|=-0.21\%$. 

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Figure 3.2: Optimized structure of Zn$_{39}$Sb$_{30}$, as created by simulating the partial occupancy of Zn sites to achieve the theoretically charge-balanced $\beta$-Zn$_4$Sb$_3$ (see the text). The blue spheres represent Zn atoms and the orange represent Sb atoms.

The relaxed structure is distorted rhombohedral with lattice parameters of: $|a| = 12.473$ Å, $|b| = 12.395$ Å, $|c| = 12.548$ Å, and $\alpha = 90.35^\circ$, $\beta = 89.52^\circ$, $\gamma = 120.38^\circ$.

We then compute the electronic band structure of Zn$_{39}$Sb$_{30}$. The energy cutoff for the plane wave basis set is set to 400 eV, since no major changes are observed upon increasing it to 500 eV such that energy difference is less than 0.01 eV. The lower energy cutoff facilitates calculations on the larger supercell without significant loss of accuracy. The band structure is computed in line mode along seven high-symmetry $k$-points in the IBZ, with 20 $k$-points between each pair of high-symmetry points. A self-consistent calculation is performed using a $k$-point mesh of $4 \times 4 \times 4$, which we deem sufficiently large since the use of a larger $6 \times 6 \times 6$ $k$-point mesh changes the total energy of the unit cell by only 0.001 eV. Density of states (DOS) calculations are performed using the same $k$-point mesh. These mesh sizes represent
the smallest number of $k$-points that still provide converged property results; furthermore, the unit cell size is sufficiently large that fewer $k$-points are necessary to achieve convergence.

3.2 Results and Discussions

We have done extensive defect formation energy calculation for various compounds both for thermoelectric and solar cell applications. The details of these calculations were described in Section 3.1. In the following, we present the results of our \textit{ab initio} thermodynamics calculation for defects in zinc antimonide, SnS, ZnS and ZnO as well as the phase stability of doped ZnS. We will also discuss the insight that these methods provide.

3.2.1 Defects in Thermoelectric Zinc Antimonide, $\beta$–Zn$_4$Sb$_3$

Before doing the calculations on the complex structure of Zn$_{39}$Sb$_{30}$, to validate our methodology, we first confirmed the results previously obtained by Bjerg et al. \cite{119}, by calculating the formation energy of intrinsic defects of ZnSb, using both 32- and 64-atom supercells. Our results are not shown here but the trend in the energies is in agreement. As suggested by Bjerg et al., since a negatively charged Zn vacancy is the dominant defect in the material, whose formation become even more favorable at higher Fermi levels, it is thus impossible to n-dope the material in a way that n-type behavior remains stable. We also investigated the formation energy of an extrinsic defect – Te substituted for one Sb atom in a 32- or 64-atom supercell – and calculated, however, a lower formation energy for this defect than the negatively charged Zn vacancy. This suggests that doping of the material is thermodynamically favorable but only for the acceptor Te atoms. This increases the concentration of holes in
charge balance equation (Equation 3.9) and results in p-type conductivity as synthesized, measured and reported by Justi et al. [114] and Ueda et al. [112] over a range of tellurium dopant compositions. We thus believe that previous theoretical findings of n-type Te:ZnSb [113] did not take into account a negatively charged Te dopant, which is more energetically favorable than a neutral Te dopant; hence, it is very unlikely that tellurium doping will result in n-type conductivity in ZnSb.

We next performed a similar analysis on Zn$_{39}$Sb$_{30}$. Since the Kohn-Sham DFT formulation contains a discontinuity in the exchange potential, this results in a systematic underestimation of the electronic band gap. The magnitude of the underestimation is proportional to this discontinuity, and disappears only in a band structure calculation of a metal [125, 126]. As an example, we calculate a band gap of $E_g = 0.04$ eV for the simple phase, ZbSb, using DFT, while the band gap calculated using the GW method and the HSE hybrid functional is $E_g = 0.39$ eV and $E_g = 0.58$ eV, respectively; these are much closer to the experimental value of $E_g = 0.61$ eV [127]. Unfortunately, since the Zn$_{39}$Sb$_{30}$ unit cell contains 69 atoms, compared to 16 in ZnSb, we are limited in our ability to perform full HSE band structure calculations on doped Zn$_{39}$Sb$_{30}$. Instead, we used DFT to calculate the band structure of Zn$_{39}$Sb$_{30}$, as shown in Figure 3.3, and find that DFT underestimates the band gap to be 0.23 eV. Furthermore, we performed non-self-consistent HSE calculation only at the following $k$-points: $\Gamma$, $B$ and $G$ (see Figure 3.3) to calculate an HSE indirect band gap of 0.60 eV; this is not surprising given the similarity of electronic structure of the two phases of zinc antimonide [120, 128]. Thus, we use $E_g = 0.60$ eV for our subsequent formation energy calculations. This does introduce some error, especially near the conduction band edge. Since this material is inherently p-type and the Fermi level is close to VBM, the error is expected to be minimized in our calculation.
Figure 3.3: Band structure of Zn$_{39}$Sb$_{30}$, as calculated using the GGA-PBE functional. The band gap is calculated to be 0.23 eV, as compared to 0.60 eV calculated with a hybrid functional (HSE). In this figure, the Fermi level is set to zero at the midgap, but generally is obtained iteratively from the charge balance (Equation 3.9).
We performed the defect formation energy analyses for a zinc vacancy, $V_{Zn}$, and an antimony vacancy, $V_{Sb}$, in $\text{Zn}_{39}\text{Sb}_{30}$ for charge states -3, -2, -1, 0, and +1, and for Fermi levels along the band gap. Figure 3.5 shows the formation enthalpy of various neutral and charged defects, with the Fermi level sitting inside the band gap and also outside of it. It can be seen that the negatively charged Zn vacancy is again the dominant intrinsic defect in $\text{Zn}_{39}\text{Sb}_{30}$, so that it is favored to form in higher Fermi levels. This explains the inherent p-type behavior of this material, since the accepted electrons create holes. It also suggests that n-doping of the material is rather difficult. Once the formation energy of intrinsic defects in various charge states is determined, at equilibrium, the concentration of each defect, $c_d \approx c_0 e^{-\Delta H_f / k_B T}$, can be calculated. $\Delta H_f$ is calculated using Equation 3.1 and is dependent on the Fermi level for charged defects. The Fermi level is calculated by iteratively solving the charge balance equation:

$$n_h - n_e = - \sum_d q_d c_d$$

(3.9)

where $c_d$ is the actual concentration of the defect $d$ inside the material, $c_0$ is the concentration of the defect in the calculated cell, and $q_d$ is the charge of the defect $d$. The right hand side of Equation 3.9 is summed over the most stable charge states of each defect at any Fermi level. The left hand side of Equation 3.9 contains the concentration of holes, $n_h$, and the concentration of electrons, $n_e$. This equation shows why the formation of negatively charged zinc vacancies will result in a higher concentration of holes, and therefore lead to inherent p-type behavior. The hole and electron concentrations are calculated by integrating over the DFT-calculated density of states (Equations 3.10 and 3.11, respectively):

$$n_h = \frac{1}{V} \sum_{\epsilon} g(\epsilon) \left[ 1 - f(\epsilon) \right] \Delta \epsilon$$

(3.10)
\[ n_e = \frac{1}{V} \sum_{\epsilon = \epsilon_c}^{+\infty} g(\epsilon) f(\epsilon) \Delta \epsilon \]  

(3.11)

where \( V \) is the cell volume, \( \epsilon_v \) and \( \epsilon_c \) are the energies of the VBM and CBM, respectively, \( g \) is the DFT-calculated density of states, and \( f(\epsilon) \) is the Fermi-Dirac distribution function. These concentrations strongly depend on the Fermi level as well; therefore, the charge balance equation must be calculated iteratively at different temperatures to obtain the Fermi level.

After calculating the formation energy of various charged defects, we iteratively solved the charge balance equation and obtained the Fermi level at a given temperature. The two sides of Equation 3.9 are plotted in Figure 3.4.

At room temperature, we calculate the Fermi level to be 0.0721 eV below the valence band edge (See the Appendix). We also calculate an overall carrier/hole concentration of \( n_h - n_e = 1.11 \times 10^{20} \text{cm}^{-3} \) based on the calculated Fermi level from the charge balance equation. The experimentally measured carrier concentration for undoped Zn$_{39}$Sb$_{30}$ has been reported to be \( 9.0 \times 10^{19} \text{cm}^{-3} \) \cite{31}, so the calculated and experimental values are in good agreement. The small difference between these values can be attributed to the errors in the DFT-calculated values for the formation energy of charged defects and the density of states of the defect-containing material, which also may slightly differ from that of the original undoped material.

Unfortunately, due to computational limitations on the size of the unit cell (i.e., 69 atoms for the unit cell and 138 atoms for the supercell), it is nearly infeasible to perform either hybrid functional (HSE) or Hubbard \( U \)-corrected calculations to potentially improve the accuracy of these values; furthermore, we found that the Hubbard \( U \) correction does not significantly change the computed density of states for this system.

We then calculated the carrier concentration at other “hypothetical” Fermi levels and plotted the Seebeck coefficient as a function of carrier concentrations (Figure 3.6). The so-called
Figure 3.4: Left hand side and right hand side of Equation 3.9 at 300 K. The $x$-axis represents the Fermi level relative to the valence band maximum (denoted as 0 in the $x$-axis).
Figure 3.5: Formation energy (ordinate) of various defects in Zn$_{39}$Sb$_{30}$. The chemical potential of the electrons (abscissa) ranges from -0.1 eV below the valence band maximum (VBM) up to 0.1 above the HSE-calculated band gap of 0.6 eV. At each Fermi level, the charge state with the lowest energy is plotted. For the case of lithium, however, Li$^{+1}$ Zn is also plotted alongside Li Zn, since it is notably more energetically favorable than other donor defects considered here. The slope of each line represents the charge state (See V$_{\text{Sb}}$, Te$_{\text{Sb}}$ and Tl Zn for example). See Table 3.1 for the exact values of energies presented in this figure.
"hypothetical" Fermi levels are labeled as such because of the high concentration of negatively charged zinc vacancies, which keeps the hole concentrations very high and the Fermi level low. As seen in Figure 3.6, the Seebeck coefficient of undoped p-type Zn$_{39}$Sb$_{30}$ can be further increased by reducing the carrier concentration. Kim et al. [129] had previously predicted this trend and also suggested using higher Zn concentrations for marked improvements in the thermoelectric figure of merit. However, as we have shown, the very high carrier concentration in Zn$_{39}$Sb$_{30}$ is attributed to the formation of acceptor zinc vacancies, which are dominant even under Zn-rich conditions and thus difficult to overcome through defect engineering. Among all the dopant candidates considered here, we believe that doping with lithium may have the potential to lower the carrier concentration and improve the thermoelectric performance of p-type Zn$_{39}$Sb$_{30}$. As an example, the Seebeck coefficient of 2% Li-doped zinc antimonide can be increased by up to 20%, as shown in Figure 3.6; the implications of this choice will be discussed later. We also plotted Seebeck coefficient vs. temperature and compared it with the experimental[31] results shown in Figure 3.7. Our calculated Seebeck coefficients have excellent agreement with the best fit possible with the BoltzTraP code [38] along a given temperature range; we note, however, that we did not do any additional fitting when calculating Fermi levels at different temperatures, so they were obtained solely from the solution of the charge balance equation (Equation 3.9).

In Figure 3.7, the deviation between the best fit values output by BoltzTraP and experimental values for the Seebeck coefficient may be attributed to BoltzTraP’s use of the constant relaxation time approximation to Boltzmann transport equation (BTE-cRTA), where the relaxation time is assumed to be a constant that is independent of the temperature, electron energy, or different electronic scattering mechanisms – including inelastic mechanisms that change the electronic distribution and affect the transport properties of the material at different temperatures. Therefore, BoltzTraP will only provide an approximation to the
Figure 3.6: Calculated Seebeck coefficient as a function of carrier concentration for Zn$_{39}$Sb$_{30}$ at 300 K. The Fermi level (carrier concentration) denoted by the dashed line on the right is calculated with the assumption that the intrinsic defects are dominated by acceptor zinc vacancies. Lowering the carrier concentration will increase the Seebeck coefficient. However, the very high carrier concentration in Zn$_{39}$Sb$_{30}$ is attributed to the formation of acceptor zinc vacancies, which are dominant even under Zn-rich conditions and are difficult to overcome by most intrinsic or extrinsic defects except lithium. The improved Seebeck coefficient for 2% dopant concentration of Li is shown.
Figure 3.7: Calculated Seebeck coefficient as a function of temperature. The best fit possible with BoltzTraP is obtained by varying the Fermi level and selecting the values that minimize the least squared error to the experimental data; this is compared to the calculated values for the Fermi levels at different temperatures using only the charge balance (Equation 3.9), without further fitting.
thermoelectric properties of complex Zn$_{39}$Sb$_{30}$. It should be emphasized that we are not aiming here for strict accuracy in the calculation of transport properties, but rather, we now have independent validation of our calculated Fermi level and energy of formation for an intrinsic charged defect in Zn$_{39}$Sb$_{30}$ since the calculated Seebeck coefficient has an excellent match with the best prediction of this property that can be calculated using BoltzTraP. It should be noted that the best fit possible with BoltzTraP (solid line in Figure 3.7) is obtained by varying the Fermi level and selecting the values that minimize the least squared error to the experimental data while the Fermi level that we have used to calculate the Seebeck coefficient (dashed line in Figure 3.7) has been calculated through Equation 3.9 using the calculated formation energies for intrinsic defects and no fittings were involved in these calculations.

We calculated the formation energy of various defects and dopants in Zn$_{39}$Sb$_{30}$, as shown in Figure 3.5. Only the formation energy of the most stable charge state is presented for each defect/dopant type, as a function of Fermi level. Various charge states of -3, -2, -1, 0, and +1 were considered for both intrinsic defects as well as the tellurium dopant. It should be noted that the charge was simulated by adding or removing electrons to/from the cell as a whole. Therefore, we use the notation, (Zn$_{39}$Sb$_{29}$Te)$_{-q}$, to emphasize that the charge state, $q$, of a tellurium-doped cell, in this example, is applied to the cell as a whole rather than to the tellurium atom itself. When we manually change the number of electrons in the cell, the VASP algorithm introduces a neutralizing background charge to avoid an overall charged system. This is a standard practice in formation energy calculation of defects [119, 91, 130, 131, 132]. It should be noted that not all of the charge, $q$, is localized to the corresponding defect. Therefore, we performed Bader charge analyses on the defect-containing supercells to verify that the charge of the defect changes as we change the number of electrons; thus, the supercell can be an accurate representation of a material with a donor
or acceptor defect. Starting from the ideal cell of Zn$_{39}$Sb$_{30}$, we calculated an average charge of +0.250 for Zn and -0.325 for Sb. These values are close to, but consistently different from, the values calculated previously for the crystalline phase, ZnSb [133, 134]; this may be solely attributed to the difference in stoichiometry between the two phases. We calculated a Bader charge of -0.442 for (Zn$_{39}$Sb$_{29}$Te)$_{-3}^-$ and -0.396 for neutral Zn$_{39}$Sb$_{29}$Te. Therefore, tellurium is indeed an acceptor when doped into Zn$_{39}$Sb$_{30}$. The remainder of the charge is thus delocalized and accepted mostly by the neighboring antimony atoms.

We see that the formation energy of (Zn$_{39}$Sb$_{29}$Te)$_{-q}$ is most favorable for $q = -2$ or $-3$, compared to $q = -1, 0,$ or $1$. This suggests that any attempt to dope Zn$_{39}$Sb$_{30}$ with Te will result only in the formation of acceptor states, which leads to p-type conductivity. It is clear from Equation 3.9 that as the concentration of negatively charged defects increases, the concentration of holes must also increase. Indeed, p-type conductivity has been reported for experimentally-synthesized Te:Zn$_{39}$Sb$_{30}$ [116].

The formation energy plots in Figure 3.5, only present the most favorable charge state of each defect. Formation energy of all charge states that we have calculated are listed in Table 3.1 assuming that the Fermi level is at VBM. According to Equation 3.1, at other Fermi levels one should simply add $q \times E_F$ to get the corresponding energy value. It should be noted that the formation energy of supercells with added electrons for Li, Na, B, Al, Ga, In and Tl are not presented since the calculated Bader charge of the cation in the supercell with added electron were more positive than neutral state (See Table 3.2). In other words, in this case, a supercell with added electron cannot be a representation of a negatively charged defect.
Table 3.1: Listed formation energy (in eV) of defects at different charge states. Fermi level is at VBM and the reported values are for Zn-rich condition. Formation energy of negative charge states of cation dopants Li, Na, B, Al, Ga, In and Tl has no meaning since the calculated Bader charge of the cation are more positive than neutral state (See Table 3.2) and therefore the supercell is not representative of a negatively charged defect.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Charge state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+1</td>
</tr>
<tr>
<td>$V_{Zn}$</td>
<td>-0.005</td>
</tr>
<tr>
<td>$V_{Sb}$</td>
<td>1.393</td>
</tr>
<tr>
<td>$Te_{Sb}$</td>
<td>0.444</td>
</tr>
<tr>
<td>$Li_{Zn}$</td>
<td>-1.431</td>
</tr>
<tr>
<td>$Na_{Zn}$</td>
<td>-0.132</td>
</tr>
<tr>
<td>$B_{Zn}$</td>
<td>1.890</td>
</tr>
<tr>
<td>$Al_{Zn}$</td>
<td>-0.000</td>
</tr>
<tr>
<td>$Ga_{Zn}$</td>
<td>0.122</td>
</tr>
<tr>
<td>$In_{Zn}$</td>
<td>0.161</td>
</tr>
<tr>
<td>$Tl_{Zn}$</td>
<td>0.563</td>
</tr>
</tbody>
</table>

Cation Dopants in Zn$_{39}$Sb$_{30}$

As shown in Figure 3.5, we also examined the neutral and donor charge states of several defects: Li, Na, B, Al, Ga, In, and Tl; only (LiZn$_{38}$Sb$_{30}$)$_{+1}$, LiZn$_{38}$Sb$_{30}$, and NaZn$_{38}$Sb$_{30}$ show lower formation energies than those for acceptor Zn vacancies, and only for certain ranges of the Fermi level under Zn-rich conditions. Therefore, we expect that none of the B, Al, Ga, In, and Tl dopants will introduce n-type conductivity in this material. Indeed, samples of Al-doped [117, 115], Ga-doped [114, 115] and In-doped [118, 115] Zn$_{39}$Sb$_{30}$ have been synthesized and characterized to be p-type, or, at most, exhibited only temporary n-type behavior (i.e., decrease in hole concentration) before reverting back to p-type behavior. We have shown that this unstable behavior is due to the fact that the formation energy of the donor states of Al, Ga, and In are higher than that of the acceptor zinc vacancies; this also explains the reports of very low solubility of these elements in zinc antimonide [115].
For the case of the alkali metals, especially Li, the formation energy is very low; this effect is even more pronounced close to the valence band. Both \((\text{LiZn}_{38}\text{Sb}_{30})^{+1}\) and neutral Li exhibit lower formation energies than the acceptor Zn vacancies – up to 0.447 eV above the valence band maximum (VBM), and even further up to 0.714 eV for the neutral Li dopant under Zn-rich conditions. While not explicitly detailed here, we also calculated the formation energy of Li in simple ZnSb, and found that it is indeed more favorable than acceptor Zn vacancies along the band gap. This raises the possibility of also having more stable but p-type \(\text{Li}_x\text{Zn}_{1-x}\text{Sb}\), in addition to \(\text{Li}_x\text{Zn}_{39-x}\text{Sb}_{30}\). It should be noted that the very low formation energy for lithium suggests that \(x\) should be very small, so this lightly doped compound is quite different from the wurtzite LiZnSb compound that has been predicted by Madsen [135] to be an excellent n-type thermoelectric, even though p-type samples were later prepared and reported by Toberer et al.[136] Thus, lithium appears to be soluble in the host material and is the most promising dopant defect to compete against zinc vacancy formation.

We performed Bader charge analyses on \(\text{LiZn}_{38}\text{Sb}_{30}\), \((\text{LiZn}_{38}\text{Sb}_{30})^{+1}\), and \((\text{LiZn}_{38}\text{Sb}_{30})^{-1}\); the \(+1/-1\) superscript denotes that we subtracted/added an electron from/to the unit cell of \(\text{LiZn}_{38}\text{Sb}_{30}\), and performed the geometry optimization and self consistent calculation on the charged system. The average Zn, Sb, and Li Bader charges are presented in Table 3.2. In all cases, Li donates more electrons than the average number of electrons donated by Zn atoms; thus, we can consider Li as a donor dopant. We also performed Bader charge analysis on \((\text{LiZn}_{38}\text{Sb}_{30})^{-1}\) to consider the possibility of acceptor Li dopants. The difference between the Bader charge of lithium in \((\text{LiZn}_{38}\text{Sb}_{30})^{-1}\) and \((\text{LiZn}_{38}\text{Sb}_{30})^{+1}\), compared to \(\text{LiZn}_{38}\text{Sb}_{30}\), is negligible (Table 3.2); therefore, both \((\text{LiZn}_{38}\text{Sb}_{30})^{-1}\) and \((\text{LiZn}_{38}\text{Sb}_{30})^{+1}\) unit cells cannot properly represent acceptor or donor lithium defects in the material, and no conclusions can be drawn based on their energies.
Table 3.2: Calculated average Bader charge of Zn, Sb and Li atoms in Zn$_{39}$Sb$_{30}$ and LiZn$_{38}$Sb$_{30}$ cells and cells with one electron removed from, (LiZn$_{38}$Sb$_{30}$)$^{+1}$, or added to, (LiZn$_{38}$Sb$_{30}$)$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>Zn$<em>{39}$Sb$</em>{30}$</th>
<th>LiZn$<em>{38}$Sb$</em>{30}$</th>
<th>(LiZn$<em>{38}$Sb$</em>{30}$)$^{+1}$</th>
<th>(LiZn$<em>{38}$Sb$</em>{30}$)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>+0.250</td>
<td>+0.244</td>
<td>+0.247</td>
<td>+0.239</td>
</tr>
<tr>
<td>Sb</td>
<td>-0.325</td>
<td>-0.337</td>
<td>-0.307</td>
<td>-0.363</td>
</tr>
<tr>
<td>Li</td>
<td>-</td>
<td>+0.833</td>
<td>+0.831</td>
<td>+0.837</td>
</tr>
</tbody>
</table>

Furthermore, the band structure and density of states of LiZn$_{38}$Sb$_{30}$ (Figure 3.8), compared to Zn$_{39}$Sb$_{30}$, shows a partially filled topmost valence band; this indicates acceptor-like behavior. Therefore, although lithium is the most thermodynamically favorable among the dopant and zinc vacancy defects considered in this study, it is only a shallow acceptor; thus, it will introduce holes in the material and induce p-type conductivity. A similar finding has been reported for substitutional lithium, Li$_{Zn}$, in ZnO [131]. The Fermi level in each case is set to zero and has been obtained by solving the charge balance of the charge defects, including zinc vacancies and electrons and holes. As shown in Figure 3.8, each lithium atom creates a hole; therefore, we can sum up the number of holes created by the lithium atom for a given concentration of Li in Li$_x$Zn$_{39-x}$Sb$_{30}$, and use this in Equation 3.9 to solve for the Fermi level. As previously discussed, a 2% dopant concentration of Li in Zn$_{39}$Sb$_{30}$ results in a 20% increase in the Seebeck coefficient. We stress, however, that even this small dopant concentration may change the band curvature, so that only changing the Fermi level due to doping may not fully capture the changes in electronic structure, although it does appear from Figure 3.8 that the band structures of Zn$_{39}$Sb$_{30}$ and LiZn$_{38}$Sb$_{30}$ appear to be very similar.

In order to understand the mechanism by which a Li atom lowers the energy of the unit cell and its effect on stability, we consider the nearest neighbors of the Zn atom that was
Figure 3.8: Band structure and density of states of undoped and Li-doped zinc antimonide. The Fermi level in undoped and 2% Li doped is set to zero and has been obtained by solving the charge balance of the charge defects including zinc vacancies and electrons and holes. The partially filled valence band (acceptor-like) has been shown with open circles.

It appears that alkali metal dopants, specifically Li, in β-Zn₄Sb₃, stabilize the host structure, counteract zinc vacancy formation, and induce even more favorable p-type conductivity than the undoped compounds. As a secondary option, Na also possesses a favorable energy of formation (up to 0.523 eV above the VBM) and high Bader charge of +0.759 compared to that of the average Zn atom in the undoped structure. While there remain some uncertainties...
Figure 3.9: Effect of Li-doping on the structure of Zn_{39}Sb_{30}. The Bader charge of each atom is printed under its name. The introduction of Li creates a more orderly and symmetric configuration, which stabilizes the structure.

...
coefficient calculation and the agreement with the best possible prediction in BTE-cRTA framework confirmed the calculated Fermi level and therefore calculated formation energy of the intrinsic defects. While improvements in the thermoelectric efficiency of Zn$_{39}$Sb$_{30}$ are very difficult to achieve, due to its high carrier concentration and presence of acceptor zinc vacancies, we propose that very low concentrations of Li dopants may stabilize the host material, lower the hole concentration, and increase the Seebeck coefficient.

### 3.2.2 Defect Calculation for Purifying SnS as Solar Cell Absorber

In a collaboration with Professor Tonio Buonassisi’s group at MIT, we aimed to assist, through defect formation calculations, their experimental efforts for purification of SnS via the control of the defects in this material. This would increase the recombination lifetime of excess minority carriers and make purified SnS more suitable as a potential absorber layer, with higher efficiency, in the solar cell. We have calculated, using the hybrid HSE functional, accurate formation energies of numerous defects in SnS. The results of these calculations can be seen in Figure 3.10. We have chosen a Hartree-Fock exchange mixing of 10% (AEXX = 0.1) to accurately calculate an indirect band gap of 1.1 eV, which is the same as experimental measurements [138].

Based on the results shown in Figure 3.10, and the minority carrier lifetime model developed by MIT, the most important point defects that can reduce the lifetime are reported as: O$_S$, V$_S$, Mo$_{Sn}$, Co$_{Sn}$ and Fe$_{Sn}$. More information regarding this model is available elsewhere[139].
3.2.3 Defects in ZnS and ZnO

Finally, we have calculated the defect formation energy of various n-type dopants in ZnS for both cubic and hexagonal supercells to find the most promising candidate for making the doped ZnS an excellent transparent conducting material in a solar cell. [17, 89].

First, to calculate the stability of alloying candidates, we calculated the enthalpy of formation of intrinsic defects, such as the zinc vacancy, $V_{Zn}$ and sulfur vacancy, $V_{S}$. Furthermore, extrinsic cation dopants B, Al, Ga, In and anion dopants F, Cl, Br, I all with possible charge states of $q \in \{-2, -1, 0, 1, 2\}$, were considered. At each Fermi level, the most favorable charge state for each defect is plotted in Figure 3.11 under Zn-rich and S-rich conditions for both cubic and hexagonal phases. According to these calculations, aluminum shows the most promising and stable formation at Fermi levels close to the CBM under Zn-rich conditions in
both phases. Close to the CBM, formation of all the candidates are less favorable than the formation of $V_{\text{Zn}}^{-2}$, which is the strong driver of p-type behavior due to Fermi level pinning; this makes it difficult to push the Fermi level closer to the CBM (i.e. n-type doping)[88, 119] similar to what we reported in Section 3.2.1 for zinc antimonide. There is an uncertainty associated with the levels at which $\text{Al}_{\text{Zn}}$ and $V_{\text{Zn}}$ cross as the calculated band gap with HSE functional is $3.24 \text{eV}$ compared to the experimental value of $3.54$ (3.91) for the cubic (hexagonal) phase. It is recommended to have the growth environment as rich as possible in Zn to reduce the possibility of the formation of zinc vacancies hence formation of $\text{Al}_{\text{Zn}}$ sites resulting in an n-type semiconductor with high carrier concentration and conductivity.

On the other hand, under S-rich conditions, $F_S$ forms more favorably compared to other anion dopants. However, it is only more favorable than the hole inducer, $V_{\text{Zn}}^{-2}$, deep inside the band gap, which results in low carrier concentrations. Therefore, considering only the stability analysis, Al is the most promising candidate. Our band gap and aMoBT calculations also show that Al is the best candidate. We will discuss this further in Section 4.2.3.

Our ab initio thermodynamic calculations for ZnS alloyed with Al and other dopants (not shown here) at different concentrations show that once alloyed, the hexagonal ZnS is more thermodynamically favorable than the cubic even at room temperature (See Figure 3.12)[17]. Hexagonal structure has been reported for Co-doped ZnS[140]. It is also expected that upon doping, a mixture of the two phases form and this may be the main reason for lower than expected conductivity measured in the polycrystalline samples in the literature [141, 142, 143, 144]. Also, there have been reports of polycrystalline doped ZnS samples with both phases present [145]. These can be explained with our calculations presented in Figure 3.12.
Figure 3.11: Formation energy of defects in cubic (top) and hexagonal (bottom) phases of ZnS. At each Fermi level, the most favorable charge state is plotted. The slope of the lines is equal to the charge of the defect (e.g., +1 for $\text{Al}^{+}_{\text{Zn}}$). The Fermi level ($x$-axis) ranges from 0 at the VBM, up to the calculated band gap (from HSE hybrid functional) of 3.24 eV for ZnS.
Figure 3.12: *ab initio* thermodynamic calculations for both cubic and hexagonal ZnS alloyed with Al with different concentrations. Hexagonal structure is more favorable than cubic for doped ZnS. The Gibbs energy (y-axis) includes the zero temperature contributions which is calculated via DFT and the vibrational entropy calculated via DFPT and phonopy code.

### 3.3 Summary and Conclusions

In this chapter, we have presented our methodology for *ab initio* calculation of the thermodynamic stability of various defects in semiconductors and how it can help us understand the behavior of real bulk semiconductors which are mainly governed by defects. It also helps us, more accurately, predict the behavior of doped and alloyed semiconductors before their synthesis. In a sense, these calculations are a bridge between the DFT calculations in defect-free idealized crystals and the real semiconductors with their impurities and defects.

We have presented our methodology and results for calculating the formation energy and phase stability in various compounds starting with the high performing thermoelectric material, zinc antimonide. We explained the unintended p-type behavior in this material and why it is difficult to dope it n-type. We also demonstrated that Li-doping can enhance the
ordering in the structure and reduce the carrier concentration hence higher stability and better performance due to a larger Seebeck coefficient.

We then presented our extensive \textit{ab initio} thermodynamic calculations for the solar cell material, SnS, which helps the experimental scientists to identify the most relevant defects so that they can improve the absorption and lifetime of the solar cell via the control of the concentration of these defects. These defects are $O_{S}$, $V_{S}$, $Mo_{Sn}$, $Co_{Sn}$ and $Fe_{Sn}$ which have a detrimental effect on the lifetime and hence efficiency of solar cells that may be synthesized with SnS as the p-type absorber. We also performed defect formation energy calculations for ZnS and ZnO; we showed that among the several candidates for n-type doping of ZnS, Al is the most thermodynamically favorable; we will discuss p-type and n-type transparent conducting ZnS doped with Cu and Al more in Chapter 4. Finally, we showed, via our finite-temperature \textit{ab initio} thermodynamic calculations, that doped/alloyed ZnS is more stable in the hexagonal structure than the cubic.

In conclusion, we demonstrated different methods of \textit{ab initio} thermodynamic calculation at 0 K and higher temperatures and how they can help us understand and control the electronic properties and stability of real semiconductors in presence of various defects.
Chapter 4

Combining aMoBT with \textit{ab initio} thermodynamics in search of new transparent conducting materials

\footnote{In this chapter, we combine our \textit{ab initio} electronic properties calculations (aMoBT, Chapter 2) and \textit{ab initio} thermodynamic calculations (Chapter 3) to theoretically evaluate a large number of candidate transparent conducting materials (TCM). TCMs have numerous applications and have attracted a lot of attention in recent years. They are an integral component of optoelectronic devices, including thin film solar cells, touch screens, and LCD displays. Increasing efforts have been devoted to identifying, synthesizing, and characterizing inexpensive, earth-abundant, and nontoxic materials for these purposes. We are particularly interested in searching for alternatives to the common TCMs, such as indium tin oxide (ITO), which can also provide variability in band alignment and energy level matching.}

\footnote{Parts of this chapter has been reprinted from the following reference submitted for publication.}

- Alireza Faghaninia, Kunal R. Bhatt, and Cynthia S. Lo. Alloying ZnS in the Wurtzite Phase to Create High-Performing Transparent Conducting Materials, Submitted, 2016 [17]
This can then be rewarded by improving transmission characteristics and enhancing the PV efficiency ([141]). The possibility of both n- and p-doping of the same material would confer a competitive advantage in device fabrication, much as it does for silicon.

We have studied Cu-doped ZnS as a p-type TCM and Al-doped ZnS an n-type counterpart for applications in solar cells and other devices, such as transparent p-n junctions and transistors. Furthermore, we have calculated the electron and hole mobility of Cu-doped ZnO as a TCM. Finally, we screened more than 75 binary and ternary oxides as candidates for transparent conducting oxides (TCOs) via our automation algorithm and methodology. We discuss the methods and results of these studies further in the rest of this chapter.

4.1 Methods

The methods for calculating the electronic properties (aMoBT) and defect formation energies is available in the previous chapters. Using these methods, we screened 75 compounds, downloaded though Pymatgen[146] and The Materials Project API, as transparent conducting oxide (TCO) candidates. We perform phonon calculations, as well as adaptive $k$-point-mesh non self-consistent calculations, to be used as inputs for aMoBT, with 391 $k$-points in the Brillouin zone, which is more dense around the CBM (VBM) than further $k$-points. In the case of an indirect gap semiconductor, the Python code, Dekode, automatically detects the CBM and VBM and makes two separate adaptive-mesh non self-consistent calculations. Large numbers of CPU hours are required in these types of calculations, particularly for phonon calculations. A schematic of the automated steps for screening of 75 compounds is demonstrated in Figure 4.1.
Figure 4.1: Schematic flowchart of the automated steps for screening of 75 compounds as candidate TCO materials. The abbreviations Geom., Self., Nself and Def. stands for geometry optimization, self-consistent, non self-consistent and Deformation potential calculations respectively. Starting from The Materials Project ID of the material, the Dekode code that we have developed will then perform geometry optimization, self consistent, non-self consistent and band structure calculation as well as phonon calculations to obtain the parameters that aMoBT needs. Later, the calculated properties (i.e. the band gap and conductivity values) will be collected. This procedure will be completed with defect calculations for better understanding of the selected compounds in reality. It is fully automated. It should be noted that the order of the calculated properties is more important in this high-throughput calculations than very accurate calculation of the properties of individual materials. However, one goal of this study is to investigate whether a simple effective mass calculation at the CBM or the VBM is good enough for sorting these candidates based on their conductivity.
We have selected the TCO candidate materials from 75 of the pre-selected n-type and p-type binary and ternary compounds that were introduced by Hautier et al. as a result of their high-throughput screening of more than 4,000 compounds [40, 41]. Therefore, we do not sort the materials based on their band gap, as they are already reported to have sufficiently large band gaps (hence, transparency). We do, however, calculate the conductivity of these materials via aMoBT, rather than just relying on the effective mass. We take into account various scattering mechanisms, as well as the full band(s) calculated \textit{ab initio}, as described in Chapter 2. Therefore, we expect aMoBT to rank the candidate materials more accurately than using a simple effective mass model, which is merely a calculation of the inverse of the second derivative of the band at its extremum (Equation 4.4); the latter not only lacks physical information but also relies heavily on only the extremum, while aMoBT takes into account the full band structure information (i.e., group velocity) at and around the extremum point as well as the electron-phonon interaction (see Chapter 2).

The screening algorithm outlined in Figure 4.1 is automated in a Python code named Dekode. This code reads the input file, MIKECAR\textsuperscript{10}, in which the user specifies the type of calculation(s) (i.e., Geom., Self., Def., etc.) to be performed along with a unique Materials Project identification number that is consistent with that used in the work of Hautier et al. [40, 41]. Furthermore, to be consistent and rule out any differences in the outcome due to the differences in the DFT setup, we downloaded and used the same input files (i.e., INCAR) as the studies of Hautier et al.

In the following, we explain how to calculate necessary aMoBT inputs \textit{ab initio}, so that we can predict the materials performance without using any experimental data. This is necessary

\textsuperscript{10}Dekode and MIKECAR are named after Michael T. Sullivan and Derreko I. Becker-Ricketts, the undergraduate researchers who contributed to this project by setting up parts of the Python codes and putting together a database of candidate materials.
Figure 4.2: Calculated phonon density of states of B$_6$O and positions of the transverse and optical phonon frequencies approximated automatically.

since most of the materials considered here are those with little to no available experimental data, but would be strong candidates for further efforts on synthesis and characterization. In other words, new materials discovery is meaningless when experimentally fitted parameters are used.

4.1.1 Calculation of Phonons

Polar optical phonon scattering originates from interactions between electrons and high-frequency optical phonons. It is the dominant inelastic electron scattering mechanism near (and above) the room temperature in compound semiconductors. This is attributed to the high energies of optical phonons being comparable to $k_B T$ at high temperatures. The scattering rates themselves are strongly dependent on the longitudinal polar optical phonon frequencies ($\omega_{LO}$ or $\omega_{po}$).
We have calculated and plotted the phonon density of states (DOS) of B$_6$O, as an example, in Figure 4.2. Dekode chooses the last optical peak in the phonon DOS as the longitudinal optical phonon frequency, $\omega_{po}$, as demonstrated in the Figure. Most of the phonon calculations are performed in $2 \times 2 \times 2$ supercells if the corresponding unit cell contains 16 or fewer atoms; this procedure yields better accuracy than just using the unit cell. We acknowledge that using even larger supercells may further improve the accuracy, but we settled on this procedure as the best balance of accuracy and computational cost for the first round of materials selection.

### 4.1.2 Calculation of Static and High Frequency Dielectric Constant

In order to calculate the static dielectric constant, we use density functional perturbation theory (DFPT), as implemented in VASP, to determine Born effective charges, dielectric and piezoelectric tensors, including local field effects in DFT, as well as the force-constant matrices and internal strain tensors[63, 64]. We do not use any experimentally measured dielectric constants. We employ the Lyddane–Sachs–Teller relation (Equation 4.1) to calculate the high frequency dielectric constant, $\epsilon_{\infty}$, after calculating the static dielectric constant and phonon DOS.

\[
\frac{\epsilon_{\infty}}{\epsilon_0} = \left(\frac{\omega_{TO}}{\omega_{LO}}\right)^2
\]

In Equation 4.1, $\omega_{TO}$ and $\omega_{LO}$ (same as $\omega_{po}$) are, respectively, the transverse and longitudinal optical phonon frequencies. In Section 4.1.1, we explained how the longitudinal optical
phonon frequency, $\omega_{LO}$, is calculated. Dekode then chooses the next largest peak at a frequency larger than half of the maximum calculated frequency, and assigns this as the transverse optical phonon peak frequency, $\omega_{TO}$. This is shown in an example DOS plot of B$_6$O in Figure 4.2. Again, this method is for fast estimation of the dielectric constants for high throughput screening and sorting of the studied materials based on their conductivities. Therefore, the relative ranking of the calculated properties is more important here than very accurate calculation of the properties themselves of individual materials. Due to the underestimation of the band gap, DFT tends to also systematically underestimate the static dielectric constant when DFPT is used for the phonon calculations.

4.1.3 Calculation of The Deformation Potential

To calculate the deformation potential, $E_D$, ab initio, we isotropically strain the material and calculate the energy of the conduction (valence) band of unit cells at different volumes. Then, we approximate the deformation potential using Equation 4.2:

$$E_D = -V \left( \frac{\partial E_{CBM}/VBM}{\partial V} \right)_{T \text{ at } V = V_0}$$

(4.2)

where $V$ is the volume, $E_{CBM}$ ($E_{VBM}$) is the energy of the CBM (VBM), and $V_0$ is the volume of the relaxed structure (i.e., zero pressure)$^{[65, 66]}$. It should be noted that since the absolute value of $E_{CBM}$ is a function of the volume itself, we use the difference between the energy of the first conduction band and the first valence (core) band. The deformation potential, $E_D$, which we calculate via Equation 4.2, is the volumetric average $E_D$. We have reported, in Table 2.2, $E_D$ values calculated for GaAs and InN in reasonable agreement with the reported data in the literature. However, as discussed previously, high accuracy
of specific properties of individual candidates is not the main goal of the high-throughput screening procedure implemented here.

4.2 Results and Discussions

4.2.1 Cu-doped ZnS as a P-type TCM

DFT Setup

To calculate the electronic structure of wurtzite (hexagonal, \(P6_{3}mc\)) and zinc-blende (cubic/sphalerite, \(F\bar{4}3m\)) \(\text{Cu}_x\text{Zn}_{1-x}\text{S}\), the unit cells were optimized using Kohn-Sham density functional theory (KS-DFT)[122, 35] as implemented in the Vienna ab initio Simulation Package (VASP)[56, 57, 58, 59]. We used the generalized gradient approximation of Perdew, Burke, and Ernzerhof[33] (GGA-PBE) to express the exchange-correlation potential and Projector Augmented Wave (PAW) potentials to represent the valence wavefunctions. Upon geometry optimization, the lattice constant for wurtzite (cubic) phase was increased by 0.6% (2.78%) compared to the experimental value[147, 148]. This is a common behavior when using a GGA-PBE functional. We then created, for the cubic phase, a \(2 \times 2 \times 2\) supercell, containing 32 zinc and 32 sulfur atoms, which we refer to as \(\text{Zn}_{32}\text{S}_{32}\). We simulated doping of copper by replacing Zn atoms with Cu in the supercell, or simply, \(\text{Cu}_n\text{Zn}_{32-n}\text{S}_{32}\) where \(n \in \{0, 1, 3, 7, 10, \text{ or } 12\}\) in this study (e.g., \(\text{Cu}_{10}\text{Zn}_{22}\text{S}_{32}\) is equivalent to \(x = 0.3125\) in \(\text{Cu}_x\text{Zn}_{1-x}\text{S}\)). For the wurtzite phase, we created a \(2 \times 2 \times 2\) supercell containing 32 atoms overall in \(\text{Cu}_n\text{Zn}_{16-n}\text{S}_{16}\), where \(n\) is chosen to be either 0 to 6 to simulate \(x = 0.0 - 0.375\). Also, we used the HSE06 hybrid functional to obtain accurate band gaps and density of
states (DOS), compared to PBE for semiconductors [149, 150, 151]. We used a $k$-point mesh of $4 \times 4 \times 4$ for DOS calculations, since the supercell was sufficiently large, and increasing the mesh to $6 \times 6 \times 6$ gives less than 0.01 eV difference in total energy. The energy cutoff for the plane wave basis set was set to 520 eV in all calculations.

**Density of State Calculations**

We examined the density of states (DOS) of wurtzite (hexagonal) $\alpha$-Cu$_x$Zn$_{1-x}$S and found that Cu substitution on the Zn site introduces 3$d$ related states, which are well hybridized with the valence band rather than generating electronic states within the band gap, as also reported previously[152]. We also found that, under S-rich synthesis conditions, the formation of compensating donors, such as S vacancies, could be suppressed. As reported by Woods-Robinson et al. [16], we expect there is at most 6-13% doping of Cu into the wurtzite ZnS lattice. The partial density of states of wurtzite Cu$_x$Zn$_{1-x}$S is presented in Figure 4.3.

The increase in the mobility of ZnS upon doping with Cu is attributed to the hybridization of Cu 3$d$ states with the S 2$p$ states at the VBM, as demonstrated in our DOS calculation in Figure 4.3.

**Geometry Optimization Calculations**

We have listed, in Table 4.1, the changes in lattice constant and the angles of the wurtzite and the cubic Cu$_x$Zn$_{1-x}$S supercells, with respect to undoped ZnS, upon the *ab initio* geometry optimization. At some concentrations of copper, the symmetry breaks. This is evident in the deviation of supercell angles from the original symmetry ($\alpha, \beta, \gamma = 90^\circ, 90^\circ, 90^\circ$ for the cubic and $90^\circ, 90^\circ, 120^\circ$ for the wurtzite); these are highlighted in the table. Table 4.1 shows
Figure 4.3: Partial density of states (PDOS) of (a) wurtzite Cu$_x$Zn$_{1-x}$S with $x = 0, 0.125$ and 0.3125 and (b) cubic Cu$_x$Zn$_{1-x}$S with $x = 0, 0.094$ and 0.3125. The primary contribution to the density of states from the Cu incorporation (red lines) is at the valence band edge. With increasing Cu concentration, the interaction of Cu 3$d$ states (red dashed lines) with S 2$p$ states (blue line) creates a hybridized valence band maximum. The optical gaps are reduced, but mid-gap states are not predicted. Dotted black lines denote the calculated VB and CB edges.
Table 4.1: The average change in the lattice constants and the mean squared deviation (MSD) of angles from undoped phase in the wurtzite and the cubic symmetries of Cu<sub>x</sub>Zn<sub>1-x</sub>S

<table>
<thead>
<tr>
<th>Hexagonal Cu:ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu concentration (%)</td>
</tr>
<tr>
<td>Change in lattice (%)</td>
</tr>
<tr>
<td>MSD in lattice angles (°)</td>
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</table>

<table>
<thead>
<tr>
<th>Cubic Cu:ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change in lattice (%)</td>
</tr>
<tr>
<td>MSD in lattice angles (°)</td>
</tr>
</tbody>
</table>

that at a concentration of Cu between 6.25% and 12.5% the symmetry is no longer wurtzite; this means that additional Cu does not incorporate in the crystal lattice. Similarly in cubic ZnS, this limit is under 6.25% copper. The lattice constant monotonically decreases with increase concentration of Cu. This is in agreement with the experimental observations [16].

In addition to the geometry optimization and DOS calculations, we performed phonon calculations, using density functional perturbation theory (DFPT) and the Phonopy code [2]. By including the vibrational entropy, enthalpy and the total energy calculated using DFT, we obtain the Gibbs free energy of both wurtzite and cubic Cu<sub>x</sub>Zn<sub>1-x</sub>S, as shown in Figure 4.4, based on the methodology described in Section 3.1.2. It can be seen that when undoped, the cubic phase is more stable than the wurtzite phase. However, at and above 6.25%-Cu, the order changes and the wurtzite Cu<sub>x</sub>Zn<sub>1-x</sub>S becomes more stable. This is consistent with observation of the (100), (101), (102) and (103) wurtzite (α) peaks in room temperature deposited Cu:ZnS samples [16].
Defect Formation Energy

We also used the HSE06 hybrid functional to accurately calculate the formation enthalpy of defects. The methods for calculating the formation energy of point defects were described in Section 3.1.1. For determining the chemical potentials, under Zn-rich, S-poor conditions, \( \Delta \mu_{Zn} = 0.0 \text{ eV} \) and \( \Delta \mu_S = \Delta \mu_{ZnS} = -3.01.0 \text{ eV} \), while under S-rich conditions, \( \Delta \mu_S = 0.0 \text{ eV} \) and \( \Delta \mu_{Zn} = \Delta \mu_{ZnS} = -3.01.0 \text{ eV} \). Also, we assume that Cu exists in the bulk phase, and is as rich as possible so that neither of secondary phases (i.e., CuS or Cu\(_2\)S) may form. Therefore, \( \Delta \mu_{Cu} < \min[\Delta H_f(CuS), \Delta H_f(Cu_2S)] = -0.4 \text{ eV} \). We also used the energy correction of Makov and Payne[96] to minimize the finite unit cell size electronic self-interaction error due to the periodic boundary condition. More details on our methodology for \textit{ab initio} defect formation energy calculation are available elsewhere[88].
Figure 4.5: Formation energy of zinc and sulfur vacancies and copper antisites in the hexagonal (cubic) ZnS under a. (c.) Zn-rich and b. (d.) S-rich conditions. At each Fermi level, only the most favorable charge state among -2, -1, 0, +1 and +2 is plotted. The slope of the lines represents the charge state of the defect. All energy values have been calculated using the hybrid functional HSE06. The highlighted regions denote Fermi levels outside of the calculated band gap.
Figure 4.5 shows, for both the hexagonal and the cubic phases, the formation energy of the sulfur vacancy, $V_S$, zinc vacancy, $V_{Zn}$, and copper antisite, $Cu_{Zn}$, while considering the possibility of the following charge states for each defect: -2, -1, 0, +1 and +2. At each Fermi level, only the most thermodynamically favorable charge state is plotted. Under Zn-rich conditions, the formation of donor $V_S^{+2}$ and $Zn_i^{+2}$ (interstitial zinc) are more favorable than $Cu_{Zn}$ close to the VBM. The electrons that are donated via these defects eliminate the holes, and therefore, they have a detrimental effect on hole conductivity that would be otherwise induced by doping of copper. However, under S-rich conditions, the acceptor $Cu_{Zn}$, is substantially more favorable than other defects, which indicates the possibility of doping ZnS with copper. Furthermore, the most favorable charge state of Cu is +1 for Fermi levels below the VBM.

**Electronic Properties Calculations**

For electronic properties calculations, we chose $k$-points close to the valence band maximum (VBM), which for these systems was always the $\Gamma$-point. An adaptive $k$-points mesh is used, which is denser close to the VBM. It should be noted that we only used the PBE (DFT) functional for electronic calculations, due to computational limitations. We use aMoBT code [23] for calculating the mobility and conductivity, which uses the *ab initio* band structures to solve the Boltzmann transport equation (BTE) by taking into account scattering mechanisms, such as ionized impurity and polar optical (PO) phonon scattering, as described in Chapter 2.

The mobility and conductivity are calculated under the assumptions that the systems are crystalline, and that all Cu atoms are ionized with either +1 or +2 charge states. It should be noted, however, that according to Figure 4.5, the Cu more likely ionizes with a +1
oxidation state. The fact that the mobility calculations with the +1 charge state assumption overestimate the experimental measurements is attributed to two reasons: 1) the samples are not fully crystalline and are mixed with amorphous phases, as reported [16]; hence, additional grain boundary scattering limits the mobility but is not considered here, and 2) some of the Cu atoms may be ionized with a +2 state, since the formation energy of these two states are similar (0.008 eV/atom difference), which results in a much stronger ionized impurity scattering — 4× that of Cu\(^{+1}\) — which results in mobility and conductivity values between the two limits calculated in Figure 4.6, assuming fully crystalline samples.

![Figure 4.6](image)

Figure 4.6: The calculated and experimental mobility (a) and conductivity (b) of crystalline Cu\(_x\)Zn\(_{1-x}\)S

Furthermore, according to Figure 4.6a, the mobility of Cu\(_x\)Zn\(_{1-x}\)S is expected to increase even at Cu-concentrations higher than 30%. However, the measured mobility decreases at higher copper concentrations[16]. This trend is also visible for conductivity in Figure 4.6b. This may be attributed to the fact that not all the copper is incorporated in the lattice in the experimental samples, and some copper is mixed in the amorphous phase [16].
4.2.2 Cu-doped ZnO as a TCM

Cu-doped ZnO at high dopant concentrations can be a suitable p-type TCM candidate. We calculated and plotted the mobility of both electron and holes at different concentrations of Cu and temperatures. We assume a fixed \( n = 1 \times 10^{18} \text{ cm}^{-3} \) so that we can study the effect of Cu on the band structure and its corresponding effect on the mobility, independent of carrier concentration. These results are presented in Figure 4.7. As shown in the Figure 4.7a, Cu-concentrations of 2.78% and 6.25% have similar improvements on the electron mobility. A reduction in the mobility over the temperature range is noticeable at 12.5%, but it drops back to the same order of magnitude as undoped ZnO at higher Cu-concentrations. On the other hand, according to Figure 4.7b, the hole mobility increases for increasing dopant concentration up to 12.5% Cu at low temperatures, and even higher for 25.0% Cu at higher temperatures, but it drops at higher Cu-concentration (e.g., 50%). Based on these calculations, \( \text{Zn}_{0.9375}\text{Cu}_{0.0625}\text{O} \) and \( \text{Zn}_{0.75}\text{Cu}_{0.25}\text{O} \) show the highest calculated electron and hole mobility respectively. Details regarding the methods of calculations and simulated crystal structures are available elsewhere [153].

4.2.3 Al-doped ZnS as an N-type TCM

As we have discussed throughout the chapter, transparent conducting materials (TCMs) are an integral component of optoelectronic devices, including thin film solar cells and LCD displays, and increasing efforts have been devoted to identifying, synthesizing, and characterizing inexpensive, earth-abundant, and nontoxic materials for these purposes. Currently, toxic cadmium-based compounds dominate the window layers in inorganic thin film photovoltaics, and the small band gap (e.g., 2.4 eV for CdS) limits the transparency of these
materials. Therefore, there is great interest in searching for alternatives that can also provide variability in band alignment and energy level matching, which can then be rewarded by improving transmission characteristics and enhancing the PV efficiency ([141]). For example, n-doped zinc oxide (ZnO), including Al-doped (AZO) [154, 155], F-doped [156], and Si-doped [157], has shown promise for widespread adoption, as the the highest reported conductivities of ZnO films are in the range of 5000 – 7000 S/cm and the highest reported Hall mobilities are about 60 cm$^2$/V·s [158]. Also the carrier concentrations of AZO samples have been reported to be $1.8 \times 10^{20} – 1.0 \times 10^{21}$ [159, 160]. However, defect-driven Fermi level pinning and unintentional n-type conductivity in ZnO makes p-type doping difficult [161]. Nevertheless, the possibility of both n- and p-doping of the same material would confer a competitive advantage in device fabrication, much as it does for silicon. Therefore, developing a comprehensive understanding of the defect physics of alternative wide-gap semiconductors is crucial for TCM design.

Figure 4.7: Calculated electron and hole mobility of Cu$_x$Zn$_{1-x}$O. Calculations are done using aMoBT at a fixed carrier concentration of $n = 1 \times 10^{18}$. 
Even though zinc sulfide (ZnS) has a similar electronic structure to, but with a higher band gap than, ZnO, it has only recently been identified as a potential host for dopant atoms to increase conductivity. The use of sulfur over oxygen reduces the problems associated with the localized character of the ZnO valence band, which is formed by O 2p orbitals [41]; instead, the incorporation of sulfur could delocalize the valence band minimum (VBM), lower the VBM effective mass, and potentially increase the hole mobility. Indeed, several such materials have recently been synthesized and characterized. Cu-doped ZnS has also shown promising characteristics, as it was recently shown to exhibit the best reported hole conductivity and optical transparency for a room temperature-deposited p-type TCM [152, 16]; pairing this with n-doped ZnS may result in many promising device applications for photovoltaics, optoelectronics and transparent devices [162]. Traverse et al. [163] enhanced the efficiency of thin film organic solar cells by introducing ZnS co-deposited with Al₂S₃; they reported that the wide band gap hexagonal zinc sulfide (ZnS) (\(E_g = 3.7\) eV) can be a good alternative to conventional materials as the anodic buffer layer in OPVs and IGS-based PVs, as it can be thermally deposited in a vacuum environment. Using chemical bath deposition (CBD), Long et al. [141], grew ZnS doped with 0-4% In. Jrad et al. [142], Liao et al. [143] and Nagamani et al. [144] have all grown 0-10% Al-doped ZnS (AZS). Relatively high values of electrical resistivity – on the orders of \(10^3\)−\(10^5\) Ω·cm – are reported in these studies for AZS. However, Pratgap et al. reported that polycrystalline AZS samples grown by a chemical precipitation method exhibited resistivities as low as 24 Ω·cm at the optimal 6% concentration of Al [164].

To better understand and control the properties of doped ZnS, we take a closer look at the structure and possible structural transformations upon doping. Previous studies [141, 142, 143, 164, 144] have focused on the cubic polymorph of ZnS, although there are differences in the XRD patterns of their samples. However, a few researchers have considered the
hexagonal polymorph as well. Hichou et al. [145] observed a polycrystalline mixture of both cubic ($\beta$) and hexagonal ($\alpha$) phases in their samples, as grown by spray pyrolysis techniques. Deepa et al. also reported hexagonal undoped ZnS and hexagonal Co-doped ZnS [140] prepared via chemical bath deposition, with varying crystallinity as a function of dopant concentration. We thus aim to explore the reasons for this phase complexity in ZnS, using \textit{ab initio} thermodynamics, and search for high-performing, yet less expensive, transparent conductors that may one day become the commercial standard.

In this section, we employ density functional theory (DFT) and aMoBT, an \textit{ab initio} transport model developed within the Boltzmann transport framework, to analyze the defect physics and screening of different cation and anion alloyed ZnS as candidates for n-type TCMs. Our hypothesis is that there exists an ideal composition of alloyed ZnS, which results in optimal transparent conducting behavior, as outlined above. We use DFT and phonon calculations to calculate the defect formation energy and the phase stability of ZnS alloyed with B, Al, Ga, In, F, Cl, Br and I, and propose Al as the most promising candidate. Also, using \textit{ab initio} thermodynamic calculations, we show that the hexagonal phase (wurtzite) of ZnS is more thermodynamically favorable, compared to the cubic (sphalerite) phase, upon doping over a wide temperature range. Finally, we calculate the theoretical limits for electrical conductivity of single crystalline AZS at different carrier concentrations and temperatures.

In order to calculate the electrical drift mobility, we use aMoBT [23], which explicitly solves the Boltzmann transport equation (BTE) using Rode’s iterative method [5]. The details of this model is available in Chapter 2.
For each composition of ZnS alloyed with B, Al, Ga, In, F, Cl, Br and I, the geometry of the unit cell is optimized, and the density of states, total energy and band structure are calculated. We use Kohn-Sham density functional theory (KS-DFT) [122, 35], as implemented in the Vienna \textit{ab initio} Simulation Package (VASP) [56, 57, 58, 59]. The generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) [33] is used to express the exchange-correlation potential, and Projector Augmented Wave (PAW) potentials [123, 124] are used to represent the valence wavefunctions. The initial structures are obtained from the ICSD and Materials Project [147, 148]. Upon geometry optimization, the lattice constant of the cubic phase increases by 0.6\%, and wurtzite phase increases by 2.4\%. We then create a $2 \times 2 \times 2$ supercell, containing 32 zinc and 32 sulfur atoms ($\text{Zn}_{32}\text{S}_{32}$ for the cubic phase and $\text{Zn}_{16}\text{S}_{16}$ for the hexagonal phase). We simulate alloying by replacing Zn atoms with M in the supercell, or simply, $M_n\text{Zn}_{32-n}\text{S}_{32}$ ($n \in \{0, 1, 2, 3, 4\}$) for the cubic phase and $M_n\text{Zn}_{16-n}\text{S}_{16}$ ($n \in \{0, 1, 2\}$) for the hexagonal phase; M can be B, Al, Ga, or In. Similarly for anion doping, S atoms are replaced with A, where A can be F, Cl, Br or I. Since Zn only has one occupation site in the cubic cell and two in the hexagonal cell, it does not matter which of the Zn atoms are replaced with the dopant atom. We confirmed this by examining all 32 Zn sites for the cubic supercell and all 16 Zn sites for the hexagonal supercell, when replaced by an Al site. The maximum difference in the energy of all the configurations was $4.8 \times 10^{-9}$ eV/atom and $2.2 \times 10^{-6}$ eV/atom, respectively, for cubic and hexagonal phases. Therefore, only the atom at the center resulting in the energy minimum is replaced by different dopant atoms to generate the defect formation energy plots. For higher concentrations of dopants, particularly for Al for which mobility calculations are also performed, we examined all 31 of the possible sites for the second Al dopant and performed geometry optimizations on these configurations. This is necessary because the symmetry is broken upon introduction of the first dopant. We then selected the system with the minimum energy representing 3.125\%
doping for the cubic cell and 6.25% doping for the hexagonal cell. The difference between
the maximum and minimum energy of these configurations is 0.003 eV/atom for the cubic
cell and 0.01 eV/atom for the hexagonal cell.

The energy cutoff for the plane wave basis set is set to 520 eV. We choose a $k$-point mesh of
$4 \times 4 \times 4$ for DOS calculations, since the supercell is sufficiently large that increasing the $k$-
point mesh to $6 \times 6 \times 6$ results in less than 0.01 eV difference in the total energy. The non-self
consistent energy calculations are performed in a special $k$-point mesh around the $\Gamma$ point, at
which the CBM occurs in the direct band gap ZnS and all the alloyed ZnS compounds. This
$k$-point mesh contains a total of 992 k-points (for unit cell GW calculations) and 391 points
(for supercell DFT calculations) in the Irreducible Brillouin Zone (IBZ), with adaptive mesh
spacing, to completely account for band anisotropy while remaining dense enough around
the $\Gamma$ point to obtain accurate group velocity and effective mass values.

In order to calculate the group velocities, $v(k)$, and the overall average effective mass, $m^*$,
we fit high-order polynomials to the calculated conduction band around the CBM, with
$R^2 > 0.99$. After polynomials are carefully fitted to the conduction band calculated $ab
initio$, $v(k)$ and $m^*$ are calculated using Equations 4.3 and 4.4, respectively:

$$
v(k) = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k} \quad \text{(4.3)}
$$

$$
m^* = \left( \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial k^2} \right)^{-1} \bigg|_{at \ k=0} \quad \text{(4.4)}
$$

It should be noted that we calculate $m^*$ only to determine its changes with composition
together with changes in overall electrical mobility. Therefore, careful and accurate calcula-
tion of the value of the effective mass itself is not the main goal of this study, as it does not
appear in the full band formulation of aMoBT. All phonon calculations are performed using
Table 4.2: Inputs to aMoBT, as calculated *ab initio* and/or measured experimentally. The bolded numbers are used in the present calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th><em>ab initio</em></th>
<th>Experimental[5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO phonon frequency, $\omega_{po}$ (THz)</td>
<td>9.5±0.2</td>
<td>10.6</td>
</tr>
<tr>
<td>Low-frequency dielectric constant, $\epsilon_0$</td>
<td>—</td>
<td>8.32</td>
</tr>
<tr>
<td>High-frequency dielectric constant, $\epsilon_{\infty}$</td>
<td>—</td>
<td>5.13</td>
</tr>
<tr>
<td>Deformation potential, $E_D$ (eV)</td>
<td>—</td>
<td>4.9</td>
</tr>
</tbody>
</table>

the Phonopy code [2]. The list of parameters that have been used in aMoBT for mobility calculations are provided in Table 4.2. We assume constant deformation potential, dielectric, elastic and piezoelectric constants for all systems, since mobility is less sensitive to these parameters than the band structure, density of states and optical phonon frequencies [23]. While we used the experimental values[5] for dielectric constants to avoid additional DFT error, they could, in principle, be calculated *ab initio* using DFPT. One value for PO-phonon frequency is reported in Table 4.2, along with the range in calculated values, as obtained using DFT for undoped ZnS. The larger dopant atoms reduce the frequency down to 9.3 THz (e.g., by I) while the smaller ones increase the frequency up to 9.7 THz (e.g., by B).

In order to calculate the formation energy of the defects, we use Equation 3.1 as described in Chapter 3:

$$
\Delta H_f(D, q) = E_{tot}(D, q) - E_{tot}(I, 0) - \sum_i \Delta n_i (E_i + \Delta \mu_i) + qE_F \tag{4.5}
$$

where $E_{tot}(D, q)$ and $E_{tot}(I, 0)$ are the total energies of the defective (e.g. Zn$_{31}$S$_{32}$ for simulating a zinc vacancy) and ideal supercell (i.e. Zn$_{32}$S$_{32}$), respectively, as calculated using the HSE hybrid functional. $E_i$ is the energy of bulk element $i$ and $\Delta n_i$ is the change in its numbers, $q$ is the charge state of the defect, $E_F$ is the value of the Fermi level (i.e., the sum of valence band maximum and relative Fermi level), and the chemical potential, $\Delta \mu_i$, is
determined by the growth conditions. Many possible intermediate phases can be formed by
the dopants together with either Zn or S atoms. We assume that the dopants are in their
elemental form. Therefore, as an example, under Zn-rich conditions, the chemical potential
of Zn is assumed to be 0, while that of S is \( \Delta \mu_S = \Delta H_{f,ZnS} = -1.63 \text{ eV} \); also, \( \Delta \mu_{Al} = 0 \).
However, under S-rich conditions, \( \Delta \mu_{Zn} = \Delta H_{f,ZnS} = -1.63 \text{ eV} \) and \( \Delta \mu_S = 0 \), but the chem-
ical potential of Al should be equal or lower than formation of the most stable intermediate
phase; therefore, \( \Delta \mu_{Al} = \frac{1}{2} \times \Delta H_{f,Al_{2}S_{3}} = -2.75 \text{ eV} \). Similarly, we have determined the
chemical potential of B, Ga, In, F, Cl, Br and I considering the following phases: \( \text{BS}_2, \text{B}_2\text{S}_3, \)
\( \text{B}_{12}\text{S}, \text{Al}_{2}\text{S}_3, \text{GaS}, \text{Ga}_2\text{S}_3, \text{InS}, \text{In}_2\text{S}_4, \text{In}_2\text{S}_3, \text{In}_3\text{S}_7, \text{In}_3\text{S}_4, \text{ZnF}_2, \text{ZnCl}_2, \text{ZnBr}_2 \) and \( \text{ZnI}_2 \). The
data for the energy of these phases have been extracted from Materials Project [147, 148]
via an in-house automated Python code which uses pymatgen [146]. The energy correction
of Makov and Payne [96] is also used to minimize the effect of charge self interaction un-
der periodic boundary conditions. More details on the methodology for defect formation
energy calculations are available elsewhere [88]. We use these calculations to quickly screen
many defects at different charge states to identify the competing and relevant defects and
dopants. Furthermore, we perform a more extensive \textit{ab initio} thermodynamic calculations in
the framework used by Jackson and Walsh [97]. We calculate the vibrational contribution to
the entropy (Gibbs free energy) of alloyed ZnS at relevant temperatures (i.e., room tempera-
ture and higher). The zero temperature contribution to the Gibbs energy is calculated using
DFT and the GGA-PBE functional, and the non-zero temperature contribution is calculated
via Phonopy [2]. These calculations are crucial for identifying the thermodynamically most
favorable phases of ZnS, before and after doping, at physically relevant temperatures. The
details of the calculations are also available elsewhere [153].
First, to calculate the stability of the dopant candidates, we calculated the enthalpy of formation of intrinsic defects, such as the zinc vacancy, $V_{Zn}$, and sulfur vacancy, $V_{S}$. Furthermore, the extrinsic cation dopants – B, Al, Ga, In – and anion dopants – F, Cl, Br, I – all with possible charge states of $q \in \{-2, -1, 0, 1, 2\}$, were considered. At each Fermi level, the most favorable charge state for each defect is plotted in Figure 4.8 under Zn-rich and S-rich conditions for both cubic and hexagonal phases. According to these calculations, the aluminum dopant is the only one that forms a stable compound at Fermi levels close to the CBM, under Zn-rich conditions, in both phases. Otherwise, for all other dopants, the compounds formed are less favorable than the formation of $V_{Zn}^{-2}$, which is the strong driver of p-type behavior due to Fermi level pinning; this makes it difficult to push the Fermi level closer to the CBM (i.e. n-type doping) [88, 119]. There is an uncertainty associated with the levels at which Al$_{Zn}$ and V$_{Zn}$ cross, as the calculated band gap with the HSE hybrid functional is 3.24 eV, compared to the experimental value of 3.54 eV for the cubic phase and 3.91 eV for the hexagonal phase. It is recommended to have the growth environment as rich as possible in Zn, to reduce the possibility of the formation of zinc vacancies. Then, the formation of Al$_{Zn}$ sites will result in an n-type semiconductor with high carrier concentration and electrical conductivity.

On the other hand, under S-rich conditions, $F_{S}$ forms more favorably compared to other anion dopants. However, it is only more favorable than the hole inducer, $V_{Zn}^{-2}$, deep inside the band gap, which results in low carrier concentrations. Therefore, considering only the stability analysis, Al is the most promising candidate.

Our *ab initio* thermodynamic calculations for ZnS alloyed with Al (shown in Figure 3.12) and other dopants at different concentrations show that once alloyed, the hexagonal phase is more thermodynamically favorable than the cubic phase, even at room temperature. The
Figure 4.8: Formation energy of defects in cubic (a and b) and hexagonal (c and d) phases of ZnS. At each Fermi level, the most favorable charge state is plotted. The slope of the lines is equal to the charge of the defect (e.g., +1 for $\text{Al}^{\frac{1}{2}}_{\text{Zn}}$). The Fermi level (abscissa) ranges from 0 at the VBM, up to the calculated band gap (from the HSE hybrid functional) of 3.24 eV for ZnS.
Table 4.3: Change in the lattice constant $|a|$ of cubic and hexagonal ZnS, upon alloying with Al at different dopant concentrations. Incorporation of Al increases the ZnS lattice constant at all dopant compositions.

<table>
<thead>
<tr>
<th>$x$ in $\text{Al}<em>x\text{Zn}</em>{1-x}\text{S}$ (%)</th>
<th>3.125</th>
<th>6.25</th>
<th>9.375</th>
<th>12.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic (%)</td>
<td>0.27</td>
<td>0.63</td>
<td>0.97</td>
<td>1.26</td>
</tr>
<tr>
<td>Hexagonal (%)</td>
<td>-</td>
<td>1.01</td>
<td>-</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Preference for the hexagonal phase has previously been reported for Co-doped ZnS [140]. It is also expected that, upon doping, a mixture of the two phases forms [145], which may be the main reason for the lower-than-expected conductivity measured for polycrystalline samples [141, 142, 143, 144]. This phenomenon can be explained with the calculations presented in Figure 3.12, which show the transition between cubic and hexagonal phases between 600-800 K. We also present in Figure 4.10 a comparison between Al:ZnS and Al:ZnO, where we show why Al is more easily integrated in the ZnO lattice compared to ZnS – the lack of two-phase complexity in ZnO and forming short/strong/ionic bonds between Al and O in AZO. Nevertheless, AZS is still a viable TCM, particularly if efforts are made to preferentially synthesize the hexagonal phase at lower temperatures.

Finally, the incorporation of Al in the ZnS lattice, whether cubic or hexagonal, results in an increases in the lattice constants. This is evident upon $ab\ initial$ geometry optimization of AZS at different dopant concentrations, as presented in Table 4.3. The hexagonal phase tends to expand more at lower concentrations of Al, but ultimately is limited to a net 1.25% increase in the lattice constant.

In the following, we compare Al:ZnS with a more commonly used Al:ZnO as a transparent conducting sulfide:
Comparing Al:ZnS with Al:ZnO

In addition to ZnS, we also calculated the formation energy of intrinsic defects and substitutional Al ($\text{Al}_{\text{Zn}}$) for ZnO in FIG. 4.9. It can be seen that incorporation of Al in ZnO lattice is much more energetically favorable than zinc vacancy formation, compared to ZnS. Another reason is the phase change (i.e., cubic to hexagonal) in ZnS upon doping, as discussed in the main text, while efforts in AZS synthesis have largely focused on producing the cubic phase[163, 141, 142, 143, 164, 144]. Note AZO does not have this complexity in its morphology. Therefore, Al is incorporated into ZnO with much shorter and stronger, ionic bonds, compared to ZnS. This has been illustrated in Figure 4.10.

Electronic Properties Calculations of Doped ZnS Compounds

Candidate TCMs must also possess good optical transparency and electrical conductivity. To qualitatively assess these properties, we first calculate the band gap and effective mass
of ZnS alloyed with various elements, and summarize the results in Table 4.4. As shown, most of the alloying elements, regardless of whether they are cations or anions, increase the electron effective mass of ZnS, particularly at high dopant concentrations. Of these, ZnS$_{1-x}$F$_x$ at 3.125%, and B$_x$Zn$_{1-x}$S, ZnS$_{1-x}$Cl$_x$, and ZnS$_{1-x}$Br$_x$ at 9.375% doping, show a significant increase in their effective masses, which is detrimental to the conductivity. The effect of dopants on effective mass can be attributed to the hybridization of the dopant s-orbital with the Zn-s and S-s orbitals at the CBM. This can also be seen in Figure 4.12.

On the other hand, Table 4.4 shows that alloying ZnS with Al gives the smallest reduction in the band gap with no mid-gap states present, even at high concentrations, which may preserve the optical transparency of the host material. Even at the high dopant concentration of 12.5%, the calculated band gap for AZS is 2.92 eV, which is only 0.32 eV lower than the calculated value for undoped ZnS. For comparison, Cl doping of 9.375% into the ZnS lattice
Table 4.4: Calculated band gap and effective mass of undoped ZnS and that alloyed with B, Al, Ga, In, F, Cl, Br and I. The effective mass of the alloyed systems has is calculated using the PBE functional only, while the band gap is calculated using the HSE hybrid functional and compared to the 3.24 eV value calculated for undoped ZnS.

<table>
<thead>
<tr>
<th></th>
<th>Effective mass</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS (exp.[165])</td>
<td>0.31</td>
<td>3.80</td>
</tr>
<tr>
<td>Cubic ZnS (GW)</td>
<td>0.25</td>
<td>3.69</td>
</tr>
<tr>
<td>Cubic ZnS (DFT)</td>
<td>0.171</td>
<td>2.02</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>0.173</td>
<td>2.07</td>
</tr>
<tr>
<td>M_xZn_{1-x}S</td>
<td>3.125 %</td>
<td>9.375 %</td>
</tr>
<tr>
<td>B</td>
<td>0.165</td>
<td>3.09</td>
</tr>
<tr>
<td>Al</td>
<td>0.171</td>
<td>3.11</td>
</tr>
<tr>
<td>Ga</td>
<td>0.173</td>
<td>2.91</td>
</tr>
<tr>
<td>In</td>
<td>0.171</td>
<td>2.85</td>
</tr>
<tr>
<td>ZnS_{1-x}A_x</td>
<td>3.125 %</td>
<td>9.375 %</td>
</tr>
<tr>
<td>F</td>
<td>0.184</td>
<td>2.75</td>
</tr>
<tr>
<td>Cl</td>
<td>0.167</td>
<td>3.07</td>
</tr>
<tr>
<td>Br</td>
<td>0.164</td>
<td>3.06</td>
</tr>
<tr>
<td>I</td>
<td>0.163</td>
<td>3.04</td>
</tr>
<tr>
<td>Al_xZn_{1-x}S</td>
<td>6.25 %</td>
<td>12.5 %</td>
</tr>
<tr>
<td>Cubic</td>
<td>0.167</td>
<td>3.04</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>0.176</td>
<td>3.09</td>
</tr>
</tbody>
</table>

results in a 1.16 eV reduction in the band gap. Thus, AZS is likely to remain transparent even as its conductivity improves over undoped ZnS.

As reported in Table 4.4, the band gap of ZnS slightly decreases upon introduction of dopants. However, the question is whether the increase in electron concentration overcomes both the increase in effective mass (and concomitant decrease in mobility) to yield a net increase in conductivity, and the reduction in band gap that decreases the optical transparency. aMoBT is thus used to calculate the electronic transport properties at relevant temperatures. Since the unit cell of ZnS is relatively small, we also perform GW band structure calculations to obtain the correct band shape; this results in a calculated effective
mass closer to experimental measurements (see Table 4.4). We perform aMoBT calculations for the hexagonal AZS. The calculated mobilities of ZnS at electron concentrations of 
\[ n \in \{10^{14}, 10^{18}, 10^{19}, 10^{20}, 10^{21}\} \text{ cm}^{-3} \], over the temperature range of 50-600 K, are shown in Figure 4.11a. These concentrations were chosen to best match the experimentally-available conductivity data at \[ n = 1.0 \times 10^{14} \text{ cm}^{-3} \] [166]. Furthermore, higher concentrations are also considered for higher dopant concentrations or higher ionization. Carrier concentrations of 
\[ 8.8 \times 10^{18} - 1.1 \times 10^{21} \text{ cm}^{-3} \] have been reported for doped ZnS[141], and AZS is even more likely to achieve \[ n = 10^{21} \] because Al is, as shown in Figure 4.8, marginally more energetically favorable than other doping candidates. As shown in Figure 4.11a, the decrease in the mobility due to the increase in carrier concentration (i.e., ionized impurity scattering) asymptotes as the electron concentration reaches \[ 1.0 \times 10^{20} \text{ cm}^{-3} \]. After that, ionized impurities are the main limiting scattering mechanism at all temperatures, and the mobility monotonically decreases with increasing concentrations. At \[ n = 1.0 \times 10^{21} \text{ cm}^{-3} \], the mobility is almost constant at all temperatures, with no scattering contribution from polar optical phonons. The effect of each scattering mechanism on the overall mobility can be seen in Figure 4.11b at \[ n = 1.0 \times 10^{18} \text{ cm}^{-3} \], where ionized impurities are the limiting scattering mechanism at low temperatures, and polar optical phonons are the limiting scattering mechanism at higher temperatures.

The calculated mobility by aMoBT is sensitive to the calculated band shape – particularly closer to the CBM, which dictates the effective mass. Therefore, we also report the calculated effective mass in Table 4.4. However, it should be noted aMoBT does not use the effective mass as a fitting parameter; rather, its results are merely sensitive to this value. As reported in Table 4.4, DFT underestimates the band gap and the effective mass. Since we need large supercells for simulating the process of alloying in ZnS, GW calculations are very computationally demanding for these large systems hence we used DFT for them.
Figure 4.11: Calculated mobility of 6.25% Al-doped ZnS from the band structure calculated \textit{ab initio} using DFT. a) The reduction in the mobility at higher electron concentrations, \( n \), as caused by ionized impurity scattering. b) Importance of different limiting scattering mechanisms at low temperatures.

The increase in effective mass as a result of alloying is inevitable, as shown in Table 4.4. However, aluminum does not significantly reduce the band gap, nor does it significantly increase the effective mass. Therefore, among the candidates studied here, aluminum makes an excellent dopant with high solubility, stability, and optical transparency (around 75\% [167]); in particular, the 6.25\% dopant concentration results in the highest conductivity and the lowest reduction in the band gap. Therefore, we propose 6.25\% as the optimal dopant concentration, which is consistent with the 6\% reported by Pratgap et al. [164], even though the cubic phase was studied there (see Table 4.4; 6.25\% Al is also optimal for the cubic phase). AZS thus exhibits relatively high electrical conductivity even though it is an inexpensive transparent conductor.

The effect of dopants on effective mass can be attributed to the hybridization of the dopant \( s \)-orbital with the Zn-\( s \) and S-\( s \) orbitals. This can be seen in Figure 4.12, where the partial...
Figure 4.12: Partial density of states (pDOS) of undoped and aluminum-doped ZnS. Note that the ordinate axis is logarithmic for clearer presentation of the pDOS of the orbitals on each atom.

density of states of undoped ZnS and Al$_x$Zn$_{1-x}$S are shown. The partial density of states, and, therefore, the effective mass, are affected in the conduction band edge via Al-s orbitals, which leads to an increase in the effective mass. Note that transition metal oxides, such as ZnO, have lower electron effective masses (around 0.2) compared to non-transition metal oxides, such as Al$_2$O$_3$, whose effective mass is around 0.4 [168]. Similar increases in the effective mass are observed for halogens substituting for sulfur in these materials.

Final Notes on Al-doped ZnS

The combined effect of the change in the band structure and carrier concentration is taken into account by calculating the electrical conductivity as $\sigma = nq\mu$, where $q$ is the charge of an electron and $\mu$ is the mobility. According to Figure 4.13, the conductivity can increase up to 6 orders of magnitude by doping ZnS with 6.25% Al. The increase in conductivity due to the combined effect of an increase in the carrier concentration that counteracts that
decrease in mobility due to doping. For example, in 6.25% Al, the 505,000-fold increase in the conductivity at \( n = 10^{21} \text{ cm}^{-3} \), compared to undoped ZnS at \( n = 10^{14} \text{ cm}^{-3} \), is the product of the 10,000,000-fold increase in carrier concentration and the 0.0505-fold decrease in mobility caused by alloying. Meanwhile, the calculated conductivity of 6.25% Al-doped ZnS at 300 K is 3830 S cm\(^{-1}\) at \( n = 1.0 \times 10^{21} \text{ cm}^{-3} \). This is comparable to the reported conductivity of 1000 – 5000 S cm\(^{-1}\) for AZO synthesized with \( n = 0.5 – 1.0 \times 10^{21} \text{ cm}^{-3} \) [169], but much higher than the corresponding values of 0.042 S cm\(^{-1}\)[164] and 10\(^{-3}\) S cm\(^{-1}\) reported for AZS films [167]. Again, we believe this discrepancy can be primarily attributed to the presence of the polycrystallinity and the mixed phases present in the experimentally synthesized samples discussed here, and secondarily due to the errors in the DFT calculations reflected in the underestimation of the effective mass and concomitant overestimation of the calculated conductivity at \( n = 10^{14} \text{ cm}^{-3} \) (Figure 4.13). A more accurate description of the band structure of alloyed ZnS would enable us to obtain the theoretical limits for conductivity in single-crystalline AZS. Nevertheless, the main findings outlined in this work confirm the viability of aluminum-doped ZnS, at dopant concentrations around 6%, as a high-performing transparent conducting material.

We used hybrid density functional calculations to obtain formation energies and band gaps of ZnS alloyed with B, Al, Ga, In, F, Cl, Br and I, and calculate the effective mass and electrical mobility and conductivity of these compounds at various dopant concentrations, temperatures, and carrier concentrations, to identify potential high-performing n-doped ZnS for transparent conducting applications. We found that aluminum is soluble in ZnS, and more significantly, leads to an increase in the electrical conductivity with minimal reduction in the band gap. Also, our calculations show that upon doping, the hexagonal phase of ZnS is more thermodynamically favorable to form than the cubic phase, which may be significant in guiding further experimental efforts in synthesis and characterization. We believe that AZS
Figure 4.13: Conductivity of undoped (black) and AZS (6.25% Al) at different carrier concentrations, as calculated using aMoBT. The overestimation of the conductivity by aMoBT is related to the underestimation of the effective mass (overestimation of group velocities) in DFT calculations.
is the best candidate for an n-type ZnS based transparent conductor, with 6.25% Al-doped ZnS exhibiting a calculated conductivity of $3830 \, \text{S} \cdot \text{cm}^{-1}$ at $n = 1.0 \times 10^{21} \, \text{cm}^{-3}$ at 300 K. The methodology outlined should also be broadly applicable to the design of compound semiconductors for optoelectronic applications.

### 4.2.4 High Throughput Automatic Screening of TCO Candidates

The overall central processing unit (CPU) time for all of the steps outlined in Figure 4.1 for each material varies greatly depending on how many electrons are in the unit cell. It takes 3 to 15 hours for all the calculation steps (except defect calculations) to be done on local 16-core nodes on our computer cluster, Partita, for each material to be finished and aMoBT calculations takes only small fraction of this time ($\approx 1–2$ minutes). The bottleneck of the calculations is the phonon DFPT calculations both because it is a time consuming calculation, due to the consideration of perturbations in all degrees of freedom, and it is done in a $2 \times 2 \times 2$ supercells for most of the materials screened here.

The binary and ternary oxides that we screened are pre-selected in the work of Hautier et al. [40, 41] for their high band gap and low effective mass; here, we do not rate them again based on the band gap. However, we do calculate the electrical mobility and conductivity of the materials. To investigate whether the effective mass is a good measure for predicting the conductivity of these materials, we considered all possible 2775 pairs of materials among these 75 that can be compared (i.e. $\binom{75}{2}$). In an example pair let $m_1^*$ and $m_2^*$ be the aMoBT calculated effective masses of the pairs and $\sigma_1$ and $\sigma_2$ their aMoBT calculated conductivities. If $m_1^* < m_2^*$ we expect that $\sigma_1 > \sigma_2$; hence, if the second statement is not true we count this as an error when sorting the materials based on their conductivity. Our calculations show
that using effective mass to approximate the order of conductivity in candidate materials is only good 71% of the time for n-type conductivity and 75% of the time for p-type. This 25% error in prediction has an impact when 4000+ compounds are screened as some of the most promising potential candidates may not be selected by the program.

We calculate the electron and hole conductivity at a hypothetical carrier concentration of \( n = 1.0 \times 10^{20} \text{ cm}^{-3} \). Since performing defect formation energy calculations are computationally expensive, we assume that the material is dopable to this concentration first and look at their defect energies only after a high value of conductivity is calculated for them. We list the top 10 electron and hole conductive materials among all candidates in Table 4.5. It is noteworthy that some of the best performing well-known TCOs such as In\(_2\)O\(_3\), ZnO and BaSnO\(_3\) are also selected in our screening process without the use of any experimental data which validates our methodology. According to Table 4.5, Na\(_2\)Sn\(_2\)O\(_3\), B\(_6\)O, HfPbO\(_3\) and Sb\(_4\)Cl\(_2\)O\(_5\) show both high electron and hole conductivity and can be investigated further for the possibility of both n-type and p-type dopability. Although Na\(_2\)Sn\(_2\)O\(_3\) has a very high p-type conductivity, we have calculated a DFT gap of 0.4 eV which is low even for DFT.
Table 4.5: The selected 10 most electron and hole conducting oxides among the 75 screened sorted based on their corresponding conductivities (in S/cm). Materials marked with * appear in both lists which shows their potential for both n-type and p-type TCO if they are also dopable.

<table>
<thead>
<tr>
<th>Top 10 electron conductors</th>
<th>formula</th>
<th>conductivity</th>
<th>space group</th>
<th>Top 10 hole conductors</th>
<th>formula</th>
<th>conductivity</th>
<th>space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_4$As$_2$O</td>
<td>3289.64</td>
<td>I4/mmm</td>
<td></td>
<td>Na$_2$Sn$_2$O$_3^*$</td>
<td>6058.93</td>
<td>I2$_1$3</td>
<td></td>
</tr>
<tr>
<td>B$_6$O</td>
<td>2983.53</td>
<td>R3m</td>
<td></td>
<td>K$_2$Sn$_2$O$_3$</td>
<td>2640.72</td>
<td>I2$_1$3</td>
<td></td>
</tr>
<tr>
<td>ZrPbO$_3$</td>
<td>2273.22</td>
<td>C2mm</td>
<td></td>
<td>Rb$_2$Sn$_2$O$_3$</td>
<td>2093.71</td>
<td>R3m</td>
<td></td>
</tr>
<tr>
<td>HfPbO$_3$</td>
<td>2177.17</td>
<td>Pmma</td>
<td></td>
<td>NaNbO$_2$</td>
<td>1586.96</td>
<td>P6$_3$/mmc</td>
<td></td>
</tr>
<tr>
<td>NaTiO$_2$</td>
<td>2146.30</td>
<td>R3m</td>
<td></td>
<td>K$_2$Pb$_2$O$_3$</td>
<td>1519.30</td>
<td>I2$_1$3</td>
<td></td>
</tr>
<tr>
<td>Na$_2$Sn$_2$O$_3$</td>
<td>1587.39</td>
<td>I2$_1$3</td>
<td></td>
<td>TiPbO$_3$</td>
<td>1314.80</td>
<td>P4mm</td>
<td></td>
</tr>
<tr>
<td>Cd$_2$SnO$_4$</td>
<td>1552.08</td>
<td>Pmcb</td>
<td></td>
<td>B$_6$O*</td>
<td>1264.71</td>
<td>R3m</td>
<td></td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>1533.24</td>
<td>R3c</td>
<td></td>
<td>HfPbO$_3^*$</td>
<td>1166.05</td>
<td>Pcmc</td>
<td></td>
</tr>
<tr>
<td>BaSnO$_3$</td>
<td>1690.60</td>
<td>Pm3m</td>
<td></td>
<td>Sb$_4$Cl$_2$O$_5$</td>
<td>1015.74</td>
<td>P2$_1$/c</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>1509.99</td>
<td>P6$_3$mc</td>
<td></td>
<td>Ti$_4$V$_2$O$_7$</td>
<td>928.02</td>
<td>P3m1</td>
<td></td>
</tr>
</tbody>
</table>

We have also performed defect formation energy calculations to evaluate the dopability (n-type or p-type) of these candidates. It should be noted that we use DFT in 2×2×2 supercells for these calculations. For more confidence, larger supercells, more defect types (i.e. interstitial, antisites and substitutional) and hybrid functional calculations are required. The results of these calculations are presented in Figure 4.14. We performed the defect calculations for K$_2$Sn$_2$O$_3$ and NaNbO$_2$ which have high p-type conductivities and relatively high DFT band gaps (underestimated) of 1.31 and 1.42 eV respectively. Furthermore, we have done the defect formation energy calculations for ZrPbO$_3$ with a large calculated DFT gap of 2.88 eV. Although this material is highly electron conductive, it also has a relatively high calculated hole conductivity of 469.33 S/cm. According to Figure 4.14 close to the VBM, the charge of the most energetically favorable vacancy (V$_{Sn}$ in K$_2$Sn$_2$O$_3$, V$_{Na}$ in NaNbO$_2$ and V$_{Pb}$ in ZrPbO$_3$) is negative which shows how these defects act as acceptors,
creating holes in the material. Therefore, based on the current calculations, it is more likely that \( \text{K}_2\text{Sn}_2\text{O}_3 \), \( \text{NaNbO}_2 \) and \( \text{ZrPbO}_3 \) are all p-type semiconductors.

\[ \text{4.3 Summary and Conclusions} \]

In this chapter, we combined our \textit{ab initio} electronic properties calculations via aMoBT and our \textit{ab initio} thermodynamic calculations to theoretically evaluate the candidates as transparent conducting materials (TCM). We started with p-type Cu-doped ZnS. Our calculations have shown the feasibility of making Cu:ZnS under S-rich synthesis conditions to avoid formation of sulfor vacancies. We demonstrated that Cu:ZnS most likely has a hexagonal (wurtzite) structure which is interesting since undoped ZnS is more stable in the cubic phase at room temperature. Furthermore, we showed that the increase in the mobility of Cu:ZnS compared to ZnS is due to the hybridization of Cu 3d with S 2p orbitals at the VBM. These calculations have been confirmed by room temperature deposited Cu:ZnS samples which have shown great promise as a wide band gap p-type TCM in the wurtzite phase\[16\].

Combining the promising p-type Cu:ZnS with an n-type doped ZnS provide great benefits in terms of compatibility of the crystal structure of both sides of the p-n junction so much as it has for Si. Therefore, we screened 8 cation and anion candidate dopants for n-type ZnS. We have performed \textit{ab initio} defect formation energy and high temperature \textit{ab initio} thermodynamic calculations to determine the stability of each of these candidates. We also performed electronic properties calculations via aMoBT to finally recommend Al-doped ZnS as the most promising candidate which shows higher stability and electrical conductivity as well as the least reduction in the band gap hence higher transparency. AZS too is more
thermodynamically favorable in the hexagonal (wurtzite) structure hence compatible with p-type Cu:ZnS.

Finally, we demonstrated the capability of our methodology by screening of 75 binary and ternary oxides as potential transparent conducting oxides (TCO). We developed codes to automate the DFT calculations of the inputs required by aMoBT such as: a dense k-point mesh of \textit{ab initio} band structure, density of states, phonon frequencies including longitudinal and transverse optical phonons, static and high frequency dielectric constants and finally the deformation potential for both the conduction and the valence bands. For each TCO candidate, starting from The Materials Project ID as the input, all of these properties are calculated and used to calculate the electrical conductivity of the material at different temperatures and carrier concentrations. The band gaps are also calculated. Although $K_2Sn_2O_3$ and $NaNbO_2$ have a relatively low DFT-calculated band gap ($\approx 1.5$ eV), it is well known that DFT underestimates the band gap. Furthermore, $ZrPbO_3$ shows both high band gap and conductivity as a p-type TCO. The fact that some of the best performing TCOs such as $In_2O_3$, $ZnO$, $BaSnO_3$, etc are also selected by this automatic screening process without the use of any experimental data validates our methodology. We showed that using a simple effective mass model for describing the electrical conductivity of semiconductors is not sufficiently accurate. Going a step further, we calculated the defect formation energy levels in some of the best performing TCO candidates to predict that they are more likely to be inherently p-type: $K_2Sn_2O_3$, $NaNbO_2$ and $ZrPbO_3$. However, accurate hybrid functional HSE calculations on larger supercells are required to confirm the calculated energy values.

In this chapter, we demonstrated the capability of the combination of our methods in predicting the semiconductors electronic properties in the screening of oxides and ZnS-based transparent conducting materials. We minimize our use of experimental data to obtain a
reliable and accurate, automatic and fast methodology for high throughput screening of new semiconductors based on their electronic properties. This avoid lengthy and costly experiments for synthesis and characterization in discovery of new and exciting materials for which no experimental data is available.
Chapter 5

Summary, Conclusions and Future Directions

In this work, we used density functional theory (DFT) calculations and the model we have developed, aMoBT, in the Boltzmann transport framework for understanding and designing semiconductors for photovoltaic and thermoelectric applications.

In Chapter 2, we explained in detail how we can calculate the electronic properties of semiconductors from first principles, with little to no reliance on experimental data. The \textit{ab initio} model for calculating the mobility and Seebeck coefficient in Boltzmann transport framework (aMoBT), which we developed, works in both single-band and coupled-band formulations for semiconductors with nondegenerate and degenerate bands, respectively. We use DFT to calculate the band structure, density of states, phonon dispersion and phonon density of states, longitudinal and optical phonon frequencies, dielectric constants, conduction and valence band deformation potential \textit{ab initio}. We then use this information to calculate the rate of some (or all) of the following scattering mechanisms: ionized impurity, acoustic phonon deformation potential, piezoelectric and dislocation scattering. We then solve the Boltzmann transport equation (BTE), using Rode’s iterative method that takes into account
the inelastic polar optical phonon scattering, to calculate the perturbation to the electron
distribution in the presence of a low electric (thermal) driving force to calculate the mobility
(Seebeck coefficient). aMoBT significantly outperforms similar available models for calcu-
lating the electronic properties of bulk semiconductors in terms of both accuracy and its
independence from experimental data.

We have validated aMoBT by comparing the calculated properties against experimentally-
measured data available in the literature. We did this for GaAs (n-type and p-type), n-type
InN and p-type Cu-doped ZnS, and in all cases the agreement with experimental data is
very good. We also performed sensitivity analysis by altering the crystal structure and the
values of the dielectric constants to show the importance of accurate DFT calculations for
obtaining accurate electronic transport properties. aMoBT is currently available to be used
by the public, and ushers the possibility of designing new and better semiconductors that
have not been synthesized previously, and to understand the limiting mechanisms in current
materials.

In Chapter 3, we presented our methodology for \textit{ab initio} calculation of the thermodynamic
stability of various defects in semiconductors, and how this can help us to understand the
behavior of real bulk semiconductors, which are mainly governed by defects. We have pre-
sented our methodology and results for calculating the formation energy and phase stability
in various compounds. We started with the high performing thermoelectric material, zinc
antimonide ($\beta - Zn_4Sb_3$). We explained the basis for the unintended p-type behavior in
this material, and why it is difficult to n-dope this material. We also demonstrated that
Li-doping can enhance the ordering in the structure and reduce the carrier concentration —
resulting in higher stability and better performance due to a larger Seebeck coefficient. We
then presented our extensive \textit{ab initio} thermodynamic calculations for the solar cell material,
SnS, which helps experimental scientists identify the most relevant defects, so that they can improve the absorption and lifetime of the solar cell via the control of the concentration of these defects. These defects are $O_{Sn}$, $V_{Sn}$, $Mo_{Sn}$, $Co_{Sn}$ and $Fe_{Sn}$, which have a detrimental effect on the lifetime, and hence, efficiency of solar cells that are synthesized with SnS as the p-type absorber. We also performed defect formation energy calculations for ZnS and ZnO. Furthermore, we showed that among the several candidates for n-type doping of ZnS, Al is the most thermodynamically favorable. The methods presented in Chapter 3 help us to understand and control the electronic properties and stability of real semiconductors in the presence of various defects.

In Chapter 4, we combined our \textit{ab initio} electronic properties calculations via aMoBT with our \textit{ab initio} thermodynamic analyses to theoretically evaluate a large number of candidate transparent conducting materials (TCMs). We started with p-type Cu-doped ZnS. Our calculations have shown the feasibility of making Cu:ZnS under S-rich synthesis conditions to avoid formation of sulfur vacancies. We demonstrated that Cu:ZnS most likely has a hexagonal (wurtzite) structure, which is interesting since undoped ZnS is more stable in the cubic phase at room temperature. Furthermore, we showed that the increase in the mobility of Cu:ZnS, compared to ZnS, is due to the hybridization of Cu 3$d$ with S 2$p$ orbitals at the VBM. These calculations have been confirmed by measurements on room temperature-deposited Cu:ZnS samples, which have shown great promise as a wide band gap p-type TCM in the wurtzite phase\cite{16}. Combining the promising p-type Cu:ZnS with n-type doped ZnS could provide great benefit in terms of compatibility of the crystal structure of both sides of the p-n junction, as it is for Si. Therefore, we screened 8 cation and anion candidate dopants for n-type ZnS. We performed \textit{ab initio} defect formation energy and high temperature \textit{ab initio} thermodynamic calculations to determine the stability of each of these candidates.
We also performed electronic properties calculations via aMoBT to finally recommend Al-doped ZnS as the most promising candidate, which shows higher stability and electrical conductivity, as well as the least reduction in the band gap (hence, higher transparency), compared to ZnS. AZS too is more thermodynamically favorable in the hexagonal (wurtzite) structure, which makes it physically compatible with p-type Cu:ZnS.

We demonstrated the predictive capability of our methodology by screening 75 binary and ternary compounds as transparent conducting oxide (TCO) materials. We developed codes to automate the DFT calculation of the inputs required by aMoBT, such as: 1) a dense k-point mesh of \textit{ab initio} band structure, 2) density of states, 3) phonon frequencies including longitudinal and transverse optical phonons, 4) static and high frequency dielectric constants, and finally, 5) the deformation potential for both the conduction and the valence bands. For each TCO candidate, starting from The Materials Project ID as the input, all of these properties are calculated and used to calculate the electrical conductivity of the material at different temperatures and conditions. The band gaps are also calculated. We thus introduce high performing TCO candidates, including K$_2$Sn$_2$O$_3$, NaNbO$_2$ and ZrPbO$_3$, as p-type transparent conductors with high conductivity, band gap and dopability. We showed that using a simple effective mass model for describing the electrical conductivity of semiconductors is not sufficiently accurate. Without needing to rely on experimental data, we obtain a reliable and accurate, automatic and fast methodology for high-throughput screening of new semiconductors based on their electronic properties. Our methodology is validated by confirming the viability of commonly used TCOs, such as doped indium oxide, zinc oxide and barium stannate, BaSnO$_3$. Computational tools enable us to avoid lengthy and costly experiments for synthesis and characterization, especially in the discovery of new and exciting materials for which no experimental data is available.
We acknowledge that predicting the properties of all types of materials with different compositions, defects and impurities and geometries is a very complex and challenging problem. We embarked on this quest in an attempt to improve the accuracy of the current models. There is certainly room for improvement. Future efforts can be focused on development of an aMoBT-2D model for new and exciting 2D materials. More scattering mechanisms interacting with the surface of these materials should be included, such as surface phonon scattering, deformation potential scattering, and electron-electron scattering. Furthermore, the current aMoBT assumes a low-field, and thus, a linear perturbation to the electron distribution (i.e., linear BTE). Reformulating aMoBT to incorporate higher order changes is also necessary, particularly in thin films with polar surfaces or monolayer 2D materials where electric field can be large. Furthermore, to improve the \textit{ab initio} thermodynamic model, one may include, in addition to the phonon modes, more phenomena such as spin excitation for ferromagnetic materials. This can be particularly rewarding in defect-driven magnetism in some materials. Finally, in terms of high-throughput automated calculations, after making a robust database that contains all the calculated property data, one could use machine learning techniques to find strong correlations between particular configuration(s) and excellent target properties, which then guide future experiments.
Chapter 6

References


Appendix A

Theory and Methods

A.1 Density Functional Theory

In this section we briefly review the derivation of Kohn-Sham equation which is the basis of the density functional theory (DFT). We use Vienna ab-initio simulation package (VASP) for our DFT calculations that uses Kohn-Sham equation to calculate the energies and band structure; therefore, it is important to be familiar with this theory and its advantages and disadvantages.

A.1.1 From Schrödinger equation to DFT

The most general form of the Schrödinger equation that describes a set of electrons and ions in time and space is shown in Equation A.1,

\[ i\hbar \frac{\partial \Phi(x, R, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Phi(x, R, t) + V \Phi(x, R, t) \]  

(A.1)
where \( x \) include full set of electronic positions and spin variables, \( \Phi(x, R) \) is the all-electron all-ion wave function, \( m \) is the electron mass, and \( V \) is the potential which we discuss later. Since the orbitals and energy states that are important for us in this work (i.e. the band structure) are stationary waves and independent of time, we introduce the time-independent Schrödinger equation. Using the separation of variables for Equation A.1, we can split the wave function into two parts which are function of space or time: \( \Phi(x, R, t) = \Phi(x, R)\varphi(t) \). This is a classic separation of variables; the left and right hand side of Equation A.1 will be independently functions of either time or space being equal to each other and therefore to a constant. This constant is the total energy \(^{11}\) It should be noted that the time dependent part is an exponential function of time where the expectation value of the wave function, which is a physical observable, is independent of time. Details of these derivations can be found in [170]. Therefore, we only need time-independent Schrödinger equation which is shown in Equation A.2,

\[
[T_N + T_e + V_{ee}(r) + V_{NN}(R) + V_{Ne}(r, R)]\Phi(x, R) = E\Phi(x, R)
\]  

(A.2)

where \( E \) is the energy, \( R \) is nuclei coordinates, \( r \) is electrons coordinates. It should be noted that the terms in the left hand side of Equation A.2 have unit of energy and can be lumped together as an energy operator, \( H \), called Hamiltonian operator as shown in Equation A.3. The Hamiltonian or energy operator contains the following terms: Kinetic energy of nuclei, \( T_N \), kinetic energy of electrons, \( T_e \), electron-electron potential, \( V_{ee}(r) \), nucleus-nucleus potential, \( V_{NN}(R) \), and nucleus-electron potential, \( V_{Ne}(r, R) \). These terms are respectively shown in Equation A.4 where \( p \) is the electron momentum operator shown in Equation A.5, \( M_I \) and \( m_i \) are the ion and the electron mass respectively, \( e \) is the electron charge equal to

\(^{11}\)Note that the unit of the energy constant is consistent with the potential and coefficient of the wave function on the left hand side.
1.60217657 × 10^{-19}C but 1 in atomic units, and \( Z \) is the charge of an ion in terms of electron charge.

\[
H\Phi(x, R) = E\Phi(x, R) \tag{A.3}
\]

\[
H = \sum_{i=1}^{N} \frac{p_{i}^2}{2M_i} + \sum_{i=1}^{N_e} \frac{p_{i}^2}{2m} + \sum_{i>j} \frac{e^2}{|r_i - r_j|} + \sum_{i>J} \frac{Z_i Z_J e^2}{|R_i - R_J|} - \sum_{i,I} \frac{Z_i e^2}{|R_i - r_I|} \tag{A.4}
\]

\[
p = -i\hbar \nabla \tag{A.5}
\]

To simplify Equation A.2, Born-Oppenheimer approximation is used which decouples the nuclear and the electronic motions due to their difference in time-scale. Therefore, the ions can be assumed to be fixed compared to the electrons. Therefore, Equation A.6 can be written:

\[
\Phi(x, R) = \Psi(x) \varphi(R) \tag{A.6}
\]

Recall that \( R \) in Equation A.6 is the position of the ions. Furthermore, \( \Psi(x) \) is the electronic wave function that can be written as \( \Psi(r) \) ignoring the spin index for simplicity. It can also be written as \( \Psi(r_1, r_2, ..., r_{N_e}) \), \( r_i \) being the position of electron number \( i \). \( \Psi(r) \) by itself cannot describe the electrons and it is not a physical observable. Instead \( \Psi^*(r) \times \Psi(r) \), where asterisk indicates a complex conjugate, is the probability that \( N_e \) electrons are at a particular set of coordinates, \( r_1, r_2, ..., r_{N_e} \). The time-independent Schrödinger equation therefore can be written for electrons as shown in Equation A.7. This equation can be again
written in Hamiltonian form: $H\Psi = E\Psi$. The general solution is a linear combination of infinite number of separable solutions. The equation can be further written for each of these wave functions with their corresponding constant which are the famous allowable quantized energy states. As can be seen, this is an eigenvalue problem with eigenvectors being the solutions, $\Psi_0$, $\Psi_1$, ... and eigenvalues being the energy states, $E_0$, $E_1$, ... also referred to as eigen-energies. These solutions are complete (i.e. any other function can be described as a linear combination of them) and they are orthogonal to each other[170]. The first solution is called the ground state which is the most important solution contributing the most to the final solution. Equation A.7 can be written only for the ground state as can be seen in Equation A.8.

\[
\left[ \frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i>j} \frac{e^2}{r_i - r_j} - \sum_{i,I} \frac{Z_I e^2}{R_I - r_i} \right] \Psi = E \Psi \tag{A.7}
\]

\[
\left[ \frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i>j} \frac{e^2}{r_i - r_j} - \sum_{i,I} \frac{Z_I e^2}{R_I - r_i} \right] \Psi_0 = E_0 \Psi_0 \tag{A.8}
\]

According to the Born-Oppenheimer approximation, ions move on the potential energy surface of this electronic ground state only. Therefore, by neglecting the quantum effects in ionic dynamics (Born-Oppenheimer), we can write classical Newtonian equation of motion with the first derivative of the ground state total energy with respect to ionic coordinates; this derivative is the force. The ground state total energy itself is a combination of the electronic ground state, the total energy ($\varepsilon_0(R)$) and ions energy, $V_{NN}(R)$ which was presented above and it is not difficult to calculate. This can be seen in Equation A.9.
\[ E_0(R) = \varepsilon_0(R) + V_{NN}(R) \]  

(A.9)

Forces acting on ions can be also calculated directly by solving Equation A.8 for the derivative of Hamiltonian with respect to the ionic coordinates which yields the same result. This is Hellmann-Feynman theorem and because of that the forces acting on ions on ground state are referred to as Hellmann-Feynman forces. Hence, with this combination of quantum and classical physics, we can optimize the structure with the minimum total ground state energy or the most stable ground state; after that, we can fix the ions to have a fixed background potential from ions. This procedure is technically called geometry optimization step.

With the help of Slater determinant, the all-electron wave function, \( \Psi(r) \), can be broken down into \( N_e \) number of one-electron wave functions called one-electron orbitals. This can be seen in Equation A.10 where \( r_i \) contains three coordinates of electron number \( i \). More details can be found in [171]. Equation A.8 can be written for each element of the matrix (i.e. orbitals).

\[
\Psi(r) = \frac{1}{\sqrt{N!}} \begin{vmatrix} 
\psi_1(r_1) & \psi_1(r_2) & \ldots & \psi_1(r_{Ne}) \\
\psi_2(r_1) & \psi_2(r_2) & \ldots & \psi_2(r_{Ne}) \\
& & \ldots & \\
\psi_{Ne}(r_1) & \psi_{Ne}(r_2) & \ldots & \psi_{Ne}(r_{Ne}) 
\end{vmatrix} \quad (A.10)
\]

Slater determinant breaks down a \( 3N_e \)-dimensional function into \( 3N_e \) three dimensional functions making the overall system much simpler to solve. Assuming that \( r \) is the position of the electron for which we write the equation, Hartree-Fock equation for one-electron
orbital, $\psi_i(\mathbf{r})$ can be written as in Equation A.11 in which the terms are kinetic, electron-ion, electron-electron, and exchange potentials respectively. Exchange potential is required in order for proper coupling of the equations for each independent electron.

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{|\mathbf{r}|} + e^2 \sum_{i \neq j} \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_i(\mathbf{r}) - e^2 \sum_{j, i \neq j} \int \frac{\psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \psi_j(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) 
\]

(A.11)

Hartree-Fock method is accurate but computationally very demanding. Just by looking at the Equation A.11, it can be seen how orbitals are coupled together through integral terms. To get around this difficulty, Hohenberg and Kohn proved that "The ground state energy from Schrödinger equation is a unique functional\(^{12}\) of the electron density" [171]. They also proved that there is a unique wave function for this ground state energy; in other words, a one-to-one mapping between the ground state wave function and the electron density exists. Therefore, Schrödinger equation can be written in terms of only one function, density, rather than each individual electron. This decouples the equations of orbitals and relate them only through the electron density, $n(\mathbf{r})$, and the effect of each electron on the density. Kohn and Sham formulated this theory as in Equation A.12 referred to as the Kohn-Sham equation.

The whole density functional theory (DFT) calculations are based on this equation.

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) 
\]

(A.12)

\(^{12}\)The word "functional" is used since density itself is a function and the ground state energy is the function of another function or simply a functional.
In Equation A.12, the terms are respectively kinetic energy, electron-ion(fixed) potential, Hartree potential, and exchange correlation potential. Hartree potential is basically electron-electron potential, $V_{ee}$, expressed in terms of electron density as shown in Equation A.13.

$$V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3r' \quad (A.13)$$

The first three terms are physical terms that we had seen before. However, the forth term is coming from the decoupling of the orbitals equation. Therefore, exchange-correlation potential is everything that we do not know about the potential in DFT. It is calculated from the first derivative of the exchange correlation energy, $E_{XC}$, (Equation A.14) with respect to density.

$$V_{XC}(r) = \frac{\delta E_{XC}(r)}{\delta n(r)} \quad (A.14)$$

There are different exchange correlation functional developed. The simplest is the local density approximation (LDA). It is called LDA since it uses exchange correlation potential of the uniform electron gas at the electron density observed at any given position hence "local". LDA gives a way to solve Kohn-Sham equation (Equation A.12) but it is only an approximation for the actual Schrödinger equation. A more advanced functional developed uses not only the local density but also the local gradient in the electron density which is why it is called the generalized gradient approximation (GGA)[34]. There are different ways through which information from the gradient of the electron density can be used. We use the one developed by Perdew-Burke-Ernzerhof (PBE) [33] which works fine for the solids. We refer to this functional as GGA-PBE. There are also hybrid functionals in which a
certain portion of Hartree-Fock exchange potential is added to DFT exchange correlation potential to improve the underestimation of the gap by DFT alone. Other drawbacks of DFT are described in section A.1.3. Hybrid functionals are more accurate; however, they are computationally demanding and can be very expensive for large systems.

A.1.2 self-consistent and non-self-consistent DFT calculation

Density of electrons is a function of orbitals as can be seen in Equation A.15. Therefore, in the Kohn-Sham equation (Equation A.12), the density is a function of the solution, orbitals, itself. As a result, this equation should be solved in an iterative way until the solution is self-consistent hence ”self-consistent DFT”. It means that starting from an electron density, Equation A.12 can be solved to obtain all orbitals and a new density can be calculated via Equation A.15 and the same procedure can be done for the new calculated density. This can be done until the electron density converges. The details on how to choose the initial density and also how to update the density in order for it to converge properly and rapidly are skipped here but can be found in the literature[35]. Once the density is calculated, the charge distribution and therefore all the terms in Equation A.12 are known; the density will be fixed and non-self-consistent calculation can be done in order to calculated orbitals and energies at any given k-point. Only at this step we can calculate the magnitude of energy states at each point in the unitcell and therefore the band structure.

\[ n_{KS}(r) = n(r) = 2 \sum_i \psi_i^*(r) \psi_i(r) \]  \hspace{1cm} (A.15)
In the periodic crystalline solids, by only calculating the energies at a unitcell and applying a periodic boundary condition, we can describe the solid in the bulk form. This unitcell or the Wigner-Seitz cell or the simulation box is the smallest periodic portion of the crystal lattice. Everything that has been described in this section, can be presented in the reciprocal space. The unitcell itself can be transformed into the Brillouin zone (BZ) which is the smallest periodic portion of the reciprocal lattice. The DFT calculations by VASP are actually done in reciprocal space. Since everything is done numerically, Equation A.12 is solved in VASP only on a grid across Briliouin zone called k-point mesh. Brillouin zone is the same concept as Wigner-Seitz cell which can be obtained from it with a transformation listed in Equation A.16 where \( \mathbf{a}_i \) are lattice vectors in the real space and \( \mathbf{b}_i \) are those transformed to the reciprocal space.

\[
\begin{align*}
\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \\
\mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot \mathbf{a}_3 \times \mathbf{a}_1}, \\
\mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot \mathbf{a}_1 \times \mathbf{a}_2}.
\end{align*}
\] (A.16)

The name k-point is coming from the fact that the position vector, \( \mathbf{r} \), has a counterpart in reciprocal lattice called wave vector, \( \mathbf{k} \), which is directly related to the electron momentum. By increasing the number of k-points, the calculation becomes more accurate but more computationally demanding. The number should be increased until the calculated property in which we are interested becomes insensitive to this number; throughout this study, we have looked at the total energy for convergence.
A.1.3 Drawbacks of DFT

When working with a model, it is important to be familiar with both advantages and disadvantages of it. The main disadvantages and errors in DFT calculations and particularly GGA-PBE functional are summarized below:

1. GGA-PBE Kohn-Sham equation is a good reformulation of the ground state of the Schrödinger equation which has been successful in materials modeling in Physics, Chemistry, Material Science, etc. However, it is still an approximation when exchange-correlation functionals such as GGA-PBE are used and it is not 100% accurate.

2. DFT is a ground state time-independent theory and it does not provide information for excited state or, in other words, higher state solutions to the Schrödinger equation. Different theories have been developed in order to model excited and ground state interaction such as the time dependent DFT (TD-DFT).

3. Self-interaction error: the electron for which the Kohn-Sham equation is solved is included in the overall electronic density. Therefore, electron is interacting with itself which is a non-realistic concept and error in calculations. This is magnified in systems with a few electrons. There are some self-interaction corrections available but since in solids the unitcell usually has many electrons, this error becomes negligible.

4. The famous band gap underestimation error: DFT has a reputation for underestimating the band gap of semiconductors and insulators very often. This is a known systematic DFT error due to discontinuity of exchange potential in Kohn-Sham DFT formulation[125, 172]. To overcome this, one may use more accurate hybrid functionals or GW method, which are computationally more expensive.
In this section, we briefly introduced DFT and how it is implemented in VASP. This is the first principle part of the model describing the electrons and ions with no specific labels. We can consider this part as a computer code which takes the structure of the unitcell and the number of k-points and other setup configuration and returns the energy states of the electrons at each k-point, $\varepsilon(k)$, which is the main input of the Boltzmann transport equation based on which we developed aMoBT.

### A.2 Boltzmann Transport Theory

Boltzmann transport theory is a microscopic model for macroscopic quantities such as mobility, diffusion coefficient, etc \[36\]. We have developed aMoBT for obtaining electronic properties of semiconductors using this theory. In this section, first the theory and the derivation of Boltzmann transport equation (BTE) will be reviewed; after the discussion on different elastic and inelastic electron scattering phenomena, we describe Rode’s\[5\] iteration method for solving BTE for calculating the perturbation to the carrier distribution.

#### A.2.1 Boltzmann Transport Equation

To describe the electron transport, we start from a simple model, the electron gas. In this model, the electron distribution is described by Fermi-Dirac (Equation A.17) distribution, $f_0$, which is for Fermions at equilibrium.

$$f_0(\varepsilon, T) = \frac{1}{1 + e^{(\varepsilon-\varepsilon_F)/k_BT}} \quad (A.17)$$
In absence of any external force at equilibrium, electrons distribution follows Fermi-Dirac form. However, the distribution can be changed via external forces such as an electric field or any temperature gradient. Furthermore, the distribution can be changed by inelastic scattering phenomena such as electron-optical phonon scattering which is described in section A.2.4. Boltzmann transport equation (BTE) has been developed to describe the distribution function in presence of external forces and inelastic scattering processes. The distribution is crucial for calculating macroscopic transport properties of materials.

The process of deriving BTE is to take into account the three main mechanisms through which the distribution may change:

- carriers’ diffusion
- external forces
- inelastic scattering phenomena

The distribution is not affected by elastic scattering process in which the energy of the pre-scattering state and the post-scattering state are equal. This has been shown by Rode [5]. The details and steps on how BTE is derived can be found in [36] resulting in the general form of BTE (Equation A.18) where \( f(k,T,t) \) is the distribution at \( k \), temperature \( T \), and time \( t \). \( \frac{\partial f(k,T)}{\partial t} \) is the temporal rate of change of \( f \) due to all scattering processes. \( \frac{dk}{dt} \cdot \nabla_k f(k,T,t) \) is due to external forces and \( v(k) \cdot \nabla_r f(k,T,t) \) is the diffusion term from carrier density gradient. \( v(k) \) is the group velocity of electrons and is calculated via Equation A.19.

\[
\frac{df(k,T,t)}{dt} = \left( \frac{\partial f(k,T,t)}{\partial t} \right)_s - \frac{dk}{dt} \cdot \nabla_k f(k,T,t) - v(k) \cdot \nabla_r f(k,T,t) \quad \text{(A.18)}
\]
\[ v(k) = \nabla_k \varepsilon(k) / \hbar \quad \text{(A.19)} \]

In steady state conditions, in presence of a low electric field, \( f(k, T, t) \) becomes \( f(k, T) \), \( \frac{df(k, T, t)}{dt} \) goes to zero, and \( \frac{dk}{dt} \) can be replaced by \( \frac{eE}{\hbar} \). Therefore, Equation A.18 can be reduced to Equation A.20 where \( s(k', k) \) is the differential scattering rate from the state \( k' \) to the state characterized by \( k \). The equations for the rate of different scattering mechanisms have been calculated and is available in literature [37, 5]; they will be discussed in the following sections.

\[ v(k).\nabla_r f(k, T) + \frac{eE}{\hbar}.\nabla_k f(k, T) = \int \left[ s(k', k)f(k', T)(1 - f(k, T)) \right. \\
- \left. s(k, k')f(k, T)(1 - f(k', T)) \right] dk' \quad \text{(A.20)} \]

### A.2.2 Relaxation Time Approximation

Equation (A.20) can be further simplified to Equation A.25 using Equations A.21, A.23, and A.24.

\[ f(k, T) = f_0(k, T) + xg(k, T) \quad \text{(A.21)} \]

\[ xg(k, T) = g'(k, T) \quad \text{(A.22)} \]
\[ \nabla_r f_0(\varepsilon, T) = \frac{\partial f_0(\varepsilon(k))}{\partial \varepsilon(k)} \left[ \nabla_r \varepsilon_F - \frac{\varepsilon(k) - \varepsilon_F}{T} \nabla_r T \right] \] (A.23)

\[ \nabla_k f_0 = \frac{\partial f_0(\varepsilon(k))}{\partial \varepsilon(k)} \nabla_k \varepsilon(k) = \hbar v(k) \frac{\partial f_0(\varepsilon(k))}{\partial \varepsilon(k)} \] (A.24)

\[ \frac{\partial f_0(\varepsilon(k))}{\partial \varepsilon(k)} v(k) \left[ -\frac{\varepsilon(k) - \varepsilon_F}{T} \nabla_r T + eE - \nabla_r \varepsilon_F \right] = -\left( \frac{\partial f(k)}{\partial t} \right)_s + v(k) \nabla_r g'(k, T) \] (A.25)

In case we have a uniform electric field, \( E \), in an infinite system maintained at a uniform temperature, Equation A.25 reduces to Equation A.26.

\[ -eE \frac{\partial f_0(\varepsilon(k))}{\partial \varepsilon(k)} v(k) = -\left( \frac{\partial f(k)}{\partial t} \right)_s \] (A.26)

While Equation A.26 might look simple, it is very complicated to solve; therefore, the relaxation time approximation (RTA) has been introduced and used in many studies which is presented in Equation A.27 where \( \tau \) is the relaxation time, the time it takes electrons to form equilibrium distribution after external force is removed.

\[ -\left( \frac{\partial f(k)}{\partial t} \right)_s = \frac{g'(k)}{\tau} \] (A.27)

At temperature \( T \), the distribution, \( f(k, T) \) can be described by Equations A.28-A.30 within RTA:

\[ f(k, T) = f_0(\varepsilon, T) - \nabla_k f_0(\varepsilon, T).\delta k \] (A.28)
\[ \delta k = \frac{-eE\tau(\varepsilon, T)x}{\hbar} \]  

(A.29)

\[ f(k, T) = f_0(\varepsilon, T) + e\tau(\varepsilon, T)\frac{df_0(\varepsilon, T)}{d\varepsilon}v(k)E \]

(A.30)

The constant relaxation time approximation (cRTA) is the basis of BoltzTraP [38] code that has been used in part of this research in order to calculate electronic properties of zinc antimonide, GaAs, etc to compare with the results of aMoBT. Equations A.33-A.37 are extracted from Madsen’s[38] paper and are used in BoltzTraP code. The derivation procedure with cRTA assumption is available[173] and is not presented in detail here.

From \( \tau(\varepsilon, T) \) and having the \( \varepsilon(k) \), the band structure, we can define \( \tau(k) \). Furthermore, the band number, \( i \), can be introduced which specifies energy state or in other words, the band index at each \( k \)-point. In this way, \( \varepsilon(k, T) \) changes to \( \varepsilon(i, k) \) considering zero temperature. Additionally, wave vector, \( k \), can have the subscripts \( \alpha, \beta, \) and \( \gamma \) each of which can represent the \( x, y, \) or \( z \) directions. This transition of notation and subscripts is due to the fact that equations discussed so far are in closed form while in the rest of this section equations for numerical calculations are presented. Equation A.19 can be rewritten in the new notation (Equation A.31). Furthermore, the elements of the effective mass tensor (Equation A.32) and conductivity tensor (Equation A.34) can be calculated:

\[ v_\alpha(i, k) = \frac{1}{\hbar} \frac{\partial \varepsilon(i, k)}{\partial k_\alpha} \]

(A.31)

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where $N$ is the total number of k-points sampled and $\delta(\varepsilon - \varepsilon(i, k))$ is Kronecker delta which is equal to 0 when $\varepsilon \neq \varepsilon(i, k)$ and is equal to 1 when $\varepsilon = \varepsilon(i, k)$, with a tolerance of $d\varepsilon$; the reason for the tolerance is that the energy values have been obtained numerically and might not be exactly equal to each other. Now, the conductivity tensor elements, $\sigma_{\alpha\beta}$ (Equation A.35), and the electronic contribution to the thermal conductivity tensor elements, $k^e_{\alpha\beta}$ (equation A.36), and the Seebeck coefficient tensor elements, $S_{ab}$ (Equation A.37), at the temperature $T$ and Fermi energy $\varepsilon_F$ can be calculated. The fact that energy states have been calculated in zero temperature, makes chemical potential and Fermi energy equal; therefore, instead of the chemical potential, $\mu$, the Fermi energy, $\varepsilon_F$, has been used. The dependence of the conductivity tensor on the temperature is captured only via the dependence of Fermi-Dirac (equation A.17) distribution on the temperature and no other phenomena such as electron-phonon interaction is taken into account. This is an important limitation of this theory and one reason for the development of aMoBT.

$$\sigma_{\alpha\beta}(T, \varepsilon_F) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[ -\frac{\partial f(T, \varepsilon_F, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon$$ (A.35)
\[ k_{\alpha\beta}^e(T,\varepsilon_F) = \frac{1}{e^2 T \Omega} \int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon - \varepsilon_F)^2 \left[ -\frac{\partial f(T,\varepsilon_F,\varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (A.36) \]

\[ S_{ab} = (\sigma^{-1})_{aa} v_{ab} \quad (A.37) \]

\[ v_{\alpha\beta}(T,\varepsilon_F) = \frac{1}{e T \Omega} \int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon - \varepsilon_F) \left[ -\frac{\partial f(T,\varepsilon_F,\varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (A.38) \]

Under the assumption that the relaxation time, \( \tau \), is constant and independent of energy or momentum, all of elastic scattering mechanisms are lumped into one single constant and inelastic scattering mechanisms are neglected which is an oversimplification. Due to this simplification, a lot of details on electron transport is lost which result in inaccurate prediction of electronic properties over a temperature range. With this assumption, Equation A.35, as an example, will be reduced to Equation A.39.

\[ \sigma_{\alpha\beta}(T,\varepsilon_F) = \frac{e^2 \tau}{N \Omega} \int \left[ \sum_{i,k} \sigma_{\alpha\beta}(i,k) \delta(\varepsilon - \varepsilon(i,k)) \right] d\varepsilon \quad (A.39) \]

Constant relaxation time approximation drawbacks have been discussed in chapter 2.

### A.2.3 Elastic scattering processes

In section A.2.2, we simplified Equation A.20 ignoring the details of the term originating from electrons scattering and the details of \( s(k',k) \) and \( s(k,k') \): differential scattering rates
to and from state $k$ respectively. The scattering mechanisms can be elastic or inelastic. In elastic scattering mechanism, the energy of the pre-scattering state is equal to that of the post-scattering state; therefore, the equilibrium electrons distribution (Equation A.17) remains unchanged. In this case, effort is made to find the scattering rate inverse of which is the relaxation time for specific scattering mechanisms such as neutral, ionized impurity, piezoelectric, and deformation potential acoustic mode scattering mechanisms each of which will be discussed in the following sections. However, in an inelastic scattering event, the distribution changes and effort is made to estimate the change in the distribution enabling calculation of macroscopic electronic properties. The connection between these two major types of scattering is through overall differential scattering rate in Equation A.20 which comprises inelastic, $s_{\text{inel}}(k, k')$, and elastic scattering rate, $s_{\text{el}}(k, k')$, as shown in Equation A.40.

$$s(k, k') = s_{\text{inel}}(k, k') + s_{\text{el}}(k, k') \quad (A.40)$$

**Ionized Impurity Scattering**

When a charged center exists inside the bulk material, as a result of coulombic interactions between the electron and ions, electrons scatter to different states or in other words, they get distracted by the electric field surrounding the ionixed impurities which results in the reduction of the mobility.

Poisson’s equation is solved for the screened potential, $\phi$ surrounding the impurity which is given by Equations A.41-A.43 where $q$ is the charge of the impurity, $\epsilon_0$ is the static dielectric permittivity, $D_s$ is the density of states (DOS) of electrons, $n$ is the carrier concentration, and $\beta$ is the inverse screening length.
\[ \phi = \frac{q}{4\pi\varepsilon_0 r} e^{-\beta r} \]  
(A.41)

\[ \beta^2 = \frac{e^2}{\varepsilon_0 kT} \int D_s f(1 - f) dk \]  
(A.42)

\[ D_s = \left( \frac{k}{\pi} \right)^2 \]  
(A.43)

It should be noted that \( D_s \) presented in Equation A.43 is the density of state with the free electron assumption. Numerically calculated and more accurate DOS for any system can be used in Equation A.42. The differential scattering rate for the ionized impurity scattering is given\[5\] by Equation A.44,

\[ s_{ii}(k', k) = \frac{e^4 N}{4\pi^2 \varepsilon_0^2 \hbar} \frac{G(k', k)}{(|k' - k|^2 + \beta^2)^2} \delta(\varepsilon - \varepsilon') \]  
(A.44)

where \( G(k, k') \) is the overlap integral (Equation A.45) which is equal to unity for a parabolic band and less than unity for Kane’s\[5\] band. \( \xi \) is the spin index denoting spin orientation, \( \downarrow \) or \( \uparrow \), and the asterisk denotes the complex conjugation.

\[ G(k, k') = \frac{1}{2} \sum_{\xi, \xi'} \left| \int \psi_{k' \xi}^*(r) \psi_{k \xi}(r) dr \right|^2 \]  
(A.45)

Following Kane’s band theory details of which are presented in \[5\], \( G(k, k') \) can be rewritten in a simpler way such as in Equation A.46 for which the a and c are given in Equations A.47
and A.48 in terms of $k$ and effective mass.

$$G(k', k) = [a(k)a(k') + c(k)c(k')x]^2$$ \hspace{1cm} (A.46)

$$a^2(k) = \frac{1 + \alpha}{2\alpha}$$ \hspace{1cm} (A.47)

$$a^2(k) + c^2(k) = 1$$ \hspace{1cm} (A.48)

$$\alpha^2(k) = 1 + \frac{2\hbar^2k^2}{m\varepsilon_g} \left( \frac{m}{m^*} - 1 \right)$$ \hspace{1cm} (A.49)

It should be noted that Equation A.49 is derived from the band theory and is for a constant empirical effective mass. This part can be further improved by using the group velocity as a function of momentum which is calculated directly from the \textit{ab initio} band structure via Equation A.19.

From Equations A.44-A.49, straightforward equations for ionized impurity scattering rate can be derived as shown in Equation A.50. Note that $\hbar k/\text{md}$ can always be replaced by \textit{ab initio} group velocity, $v(k)$.

$$\nu_{ii} = \frac{e^4N\text{md}}{8\pi\varepsilon_0^2\hbar^4k^3} \left[ Dln \left( 1 + \frac{4k^2}{3} \right) - B \right]$$ \hspace{1cm} (A.50)
In this equation, $\nu_{ii}$ is the scattering rate caused by ionized impurities with a total concentration of $N$,

$$N = N^+ + N^- + p$$  (A.51)

where $N^+$, $N^-$, and $p$ are the respective concentrations of ionized donors, acceptors, and holes. Since the differential scattering rate for ionized impurity is independent of the sign of their charge[5], $q$, we can add all of them into the single concentration of $N$. However, it should be noted that if the donors or acceptors have a charge state, $Z$, more than +1 or -1, the concentration of ions themselves should be multiplied by $Z^2$ to obtain $N^+$ or $N^-$, since the screening effect grows with the second power of the charge state of the ionized impurities. The rest of the parameters of Equation A.50 can be calculated as functions of the wave vector, the effective mass, and the inverse screening length:

$$\frac{1}{d} = \frac{m \partial \varepsilon}{\hbar^2 k \partial k} = 1 + \frac{m/m^* - 1}{\alpha}$$  (A.52)

$$D = 1 + \frac{2 \beta^2 c^2}{k^2} + \frac{3 \beta^4 c^4}{4 k^4}$$  (A.53)

$$B = \frac{4 k^2}{1 + 4 k^2 \beta^2} + \frac{8 \beta^2 + 2 k^2 c^2}{\beta^2 + 4 k^2 c^2} + \frac{3 \beta^4 + 6 \beta^2 k^2 - 8 k^4}{(\beta^2 + 4 k^2) k^2 c^4}$$  (A.54)

parameters $a$, $c$, and $\alpha$ are calculated by Equations A.47, A.48, and A.49. At last, we should note, that as discussed in Chapter 2 we calculate these parameters directly from the wavefunction of the CBM or the VBM. Furthermore, we do not need to calculate or use any empirical parameters such as $m$ or $d$.  

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Piezoelectric Acoustic Modes

In general, in some cubic crystal structures at low temperatures (<50-60K), the piezoelectric tensor is non-vanishing originating from ionic polarization, strain-dependent polarization, and electronic polarization[5]. This scattering mechanism takes place by electron interactions with long wavelength longitudinal and transverse phonons. Since these phonons have a very low energy, piezoelectric acoustic scattering mechanism is elastic. In a similar way as described in Section A.2.3, Equation A.55 can be derived for the piezoelectric scattering rate:

\[ \nu_{pe} = \frac{e^2 k_B T P^2 m d}{6\pi \hbar^3 \varepsilon_0 k} (3 - 6c^2 + 4c^4) \]  

(A.55)

where P is the dimensionless piezoelectric coefficient which depends on the crystal structure, and experimentally measured spherically averaged elastic constants for longitudinal, \( c_l \), and transverse, \( c_t \), modes. Details and equations for P, \( c_l \), and \( c_t \) are available in Appendix C or Ref. [5], pages 35-36.

Deformation Potential

This type of scattering becomes important only for temperatures above a few degrees Kelvin and is originated from the deformation-potential interaction with long-wavelength acoustic vibrations (phonons)[5]. The scattering rate can be calculated,

\[ \nu_{ac} = \frac{e^2 k_B T E_l^2 m d k}{3\pi \hbar^3 c_l} (3 - 8c^2 + 6c^4) \]  

(A.56)
where $E_1$ is the deformation potential with units of eV per strain or simply the unit of energy; it is the magnitude of the conduction (valence) band edge shift (in eV) per unit strain due to the acoustic vibration. Also, $c_l$ is the spherically averaged elastic constant for longitudinal modes described in more detail in Appendix C and Ref. [5].

### A.2.4 Inelastic scattering processes

Unlike elastic scattering event during which energy of an electron remains constant, after an inelastic scattering process the kinetic energy of the electron changes; therefore, when electron scatters from the momentum state $k$ to $k'$, we have $\varepsilon \neq \varepsilon'$ and also $k \neq k'$. Thus, electron distribution is no longer the equilibrium Fermi-Dirac distribution which was shown in Equation A.17. Under the low-field assumption described earlier, the small deviation from the equilibrium distribution can be written in terms of a linear perturbation term, $g$, shown in Equation A.21 where $x$ is the cosine of the angle between the vanishing small force which in this case is a small electric field, $E$, and wave vector, $k$. In order to obtain the term $g$, we need to solve the BTE (Equation A.20) for which we can use Rode’s iteration method [5, 174].

**Rode’s iteration method**

It can be seen that Equation A.20 can be solved iteratively starting from the first guess for distribution given by Equation A.17. $f(k, T)$ and $f(\varepsilon, T)$ can be converted to each other when Kohn-Sham equation is solved for $\varepsilon(k)$ with a fixed potential or non-self consistent calculation as described in Section A.1.2. Alternatively, in Rode’s formulation [5], this is given by isotropic band relation shown in Equation A.57. In Equations A.57-A.58, the
conduction band and the group velocity are written analytically in terms of \( k \), electron mass, \( m \), and also the experimental effective mass, \( m^* \).

\[
\varepsilon(k) = \frac{\hbar^2 k^2}{2m} + \frac{\varepsilon_g(\alpha - 1)}{2} \tag{A.57}
\]

\[
v(k) = \frac{\hbar k}{m} \left( 1 + \frac{m/m^* - 1}{\alpha} \right) \tag{A.58}
\]

These equations need the experimental parameter inputs and have the implicit isotropic band assumption. This assumption is implied by using the scalar \( k \) instead of \( \mathbf{k} \) since energy in all directions are the same function of \( k \); so, \(|k|\) or simply \( k \) can be used.

For simplification, we can plug in Equation A.21 to Equation A.20 and assuming that \( \mathbf{E} \) lies along the \( z \) axis, Equation A.59 can be obtained in which \( x' \) is the cosine of the angle between \( \mathbf{k}' \) and \( \mathbf{E} \).

\[
v \frac{\partial f(r)}{\partial z} + \frac{e\mathbf{E}}{\hbar} \frac{\partial f(k)}{\partial k} = -g \int [s(k,k')(1 - f(k')) + s(k',k)f(k')]dk' \tag{A.59}
\]

\[
+ \frac{3}{2} \int_{-1}^{1} x \int x'g(k')[s(k',k)[1 - f(k)] + s(k,k')f(k)]dk'dx
\]

Using the assumption that conduction band is isotropic, Equation A.59 can be reduced to Equation A.60,
\[
v \frac{\partial f(r)}{\partial z} + \frac{eE}{\hbar} \frac{\partial f(k)}{\partial k} = \int X g(k') [s(k', k)[1 - f(k)] + s(k, k') f(k)] dk' \quad (A.60)
\]

\[- g \int [s(k, k')][1 - f(k')] + s(k', k) f(k')] dk' \]

where \( X \) is the cosine of the angle between \( k \) and \( k' \). It should be noted that for general anisotropic band structure, the original Equation A.59 should be used. After decoupling differential scattering rate function, \( s \), into the elastic and inelastic parts as done in Equation A.40, Equation A.60 can be reduced to Equation A.61 since \( s_{el}(k, k') = s_{el}(k', k) \).

\[
g \left\{ \int [s_{inel}(k, k')[1 - f(k')] + s_{inel}(k', k) f(k')] dk' + \int (1 - X) s_{el}(k, k') dk' \right\} \quad (A.61)
\]

\[= \int X g(k') [s_{inel}(k', k)[1 - f(k)] + s_{inel}(k, k') f(k)] dk' - v \frac{\partial f(r)}{\partial z} - \frac{eE}{\hbar} \frac{\partial f(k)}{\partial k} \]

To simplify Equation A.61, we define \( \nu_{el} \) in Equation A.62 which comes from the relaxation time approximation equation when no inelastic scattering exist. Furthermore, scattering out rate, \( S_o \), is defined in Equation A.63 and scattering in, \( S_i \), rate is defined in Equation A.64.

\[\nu_{el} = \int (1 - X) s_{el}(k, k') dk' \quad (A.62)\]

\[S_o = \int [s_{inel}(k, k')[1 - f(k')] + s_{inel}(k', k) f(k')] dk' \quad (A.63)\]

\[S_i(g') = \int X g(k') [s_{inel}(k', k)[1 - f(k)] + s_{inel}(k, k') f(k)] dk' \quad (A.64)\]
Now we can write the perturbation, $g$, as in Equation A.65 as a function of the integrals and parameters described. The iteration procedure can be done via this equation: starting from Fermi-Dirac distribution which gives the first guess, $g_1 (g_0 = 0)$ and continuing calculation of $g_{i+1}$ until it converges to a unique value. The proof that this $g$ is unique can be found in detail in section 5 of chapter one of the book[5].

$$g = \frac{S_i (g') - \nu (\frac{\partial f}{\partial z}) - \frac{eF}{\hbar} \frac{\partial f}{\partial k}}{S_0 + \nu_{el}}$$  \hspace{1cm} (A.65)$$

In case we want to calculate the drift mobility, $\mu$, which is defined as the average drift velocity per unit electric field in the limit of zero electric field[5], no additional forces such as the temperature gradient are considered and the crystal is assumed to be uniform and isotropic. This results in the second term in Equation A.65 to be zero and therefore $g$ can be iteratively calculated via Equation A.66; when calculated, we obtain the mobility via Equation A.67. Hence, the main step is to calculate the perturbation, $g$.

$$g = \frac{S_i (g') - \frac{eF}{\hbar} \frac{\partial f}{\partial k}}{S_0 + \nu_{el}}$$  \hspace{1cm} (A.66)$$

$$\mu = \frac{\hbar}{3m} \frac{\int k^3 (g/Edk)}{\int k^2 fdk}$$  \hspace{1cm} (A.67)$$

Now that the electron distribution and consequently mobility are known, the Seebeck coefficient can be calculated via Equations A.68-A.71 where $S$ is the Seebeck coefficient, $J$ is the current density, and $\sigma = ne\mu$ is the electrical conductivity $n$ being the density of carriers.
\[ J = \sigma [E - (\nabla \varepsilon_F / e) - S \nabla T] \quad (A.68) \]

When \( J = 0 \), as in the open circuit measurement of \( S \):

\[ S = \frac{F}{\frac{\partial T}{\partial z}} \quad (A.69) \]

\[ S = - \frac{\partial \varepsilon_F}{\partial z} / e + \frac{J}{\sigma} \frac{\partial T}{\partial z} \quad (A.70) \]

\[ S = k_e \left[ \int k^2 f(1 - f) \frac{\varepsilon_k}{kT} dk \right] - \frac{\varepsilon_F}{kT} - \frac{J}{\sigma} \frac{\partial T}{\partial z} \quad (A.71) \]

Details of these derivations can be found in Ref. [5]. It should be noted that Equation A.71 was derived for free electrons density of state. Numerical, \textit{ab initio}, density of state can be used for better accuracy as discussed in Chapter 2.

**Polar Optical phonon scattering**

Optical phonon scattering is originated from the interaction of electrons with high-frequency optical phonons. The longitudinal optical modes have an associated electric polarization wave in heteropolar II-VI and III-V compounds which provides the dominant inelastic electron scattering mechanism near room temperature in direct semiconductors. The high energy of optical phonons is comparable to \( k_BT \) at room temperature which is why this type of scattering is limiting the mobility at high temperatures[5].
In section A.2.4, we learned that given the scattering out, \( S_o \), and the scattering in, \( S_i \), rates for a particular scattering mechanism, the electronic distribution and therefore the drift mobility and Seebeck coefficient can be calculated. \( S_o \) and \( S_i \) are calculated via Equations A.72 and A.73.

\[
S_o = (N_{po} + 1 - f^-)\lambda^-_o + (N_{po} + f^+)\lambda^+_o
\]  
\[(A.72)\]

\[
S_i(g(k')) = (N_{po} + f(k))\lambda^-_i g^-(k) + (N_{po} + 1 - f(k))\lambda^+_i g^+(k)
\]  
\[(A.73)\]

\[
N_{po} = \frac{1}{\exp(h\omega_{po}/k_BT) - 1}
\]  
\[(A.74)\]

\[
\lambda^+_o(k) = \beta^+ \left[ (A^+)^2 ln \left| \frac{k^+ + k}{k^- - k} \right| - A^+ cc^- - aa^+ cc^+ \right]
\]  
\[(A.75)\]

\[
\lambda^+_i(k) = \beta^+ \left[ \frac{(k^+)^2 + k^2}{2k^+k} (A^+)^2 ln \left| \frac{k^+ + k}{k^- - k} \right| - (A^+)^2 - \frac{c^2(c^+)^2}{3} \right]
\]  
\[(A.76)\]

\[
\beta^+ = \frac{e^2\omega_{po}md^+}{4\pi\hbar^2k} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right)
\]  
\[(A.77)\]

\[
A^+ = aa^+ + \frac{(k^+)^2 + k^2}{2k^+k} cc^+
\]  
\[(A.78)\]
Similarly, $\lambda_o^-$ can be calculated. $\lambda_o^+$ and $\lambda_o^-$ are energy-dependent scattering rates. $\lambda_o^+$ is the rate of scattering out with phonon absorption (+ sign) and $\lambda_o^-$ is the rate of scattering out by phonon emission. On the other hand, + and − superscripts have different meanings for scattering in rates. $\lambda_i^+$ is rate of scattering in with phonon emission while $\lambda_i^−$ is rate of scattering in with phonon absorption.
Appendix B

Literature Review for Thermoelectric Materials

In this section, we go through different thermoelectric (TE) materials, their figure of merit, and the advantages and disadvantages as a possible candidate for medium temperature range (450-850K [26]) power generation applications. It should be noted that this literature review was done in the year 2011. Rowe [20] has summarized different TE materials at different temperature ranges in one graph which can be seen in Figure B.3. Figure B.1 as well as Figure B.2 show some thermoelectric materials and the temperature ranges at which they have the best performance.

MgSn has a low ZT but it is cheap[20]. YbAl$_3$ is n-type and according to [20] has a high power factor which makes it good for waste heat recovery. Also, Ca$_3$AlSb$_3$ is a good candidate for waste heat recovery at high temperature range with ZT=0.8 at 1000K [175]. It is also reported that [176] Ca$_{5}$Al$_{2}$Sb$_{6}$, a relatively inexpensive Zintl compound, when doped with 25% Na (x=0.25 in Ca$_{5-x}$Na$_x$Al$_2$Sb$_6$) has a ZT value of 0.6 at 900K.
Bi$_2$Te$_3$ (Bismuth Telloride) is a very popular thermoelectric material. Its alloys have figure of merit of around 1. This material can be alloyed and doped both n- and p-type. The p-type Bi$_2$Te$_3$ is an alloyed combination of 75% Sb$_2$Te$_3$ and 25% Bi$_2$Te$_3$ [177] and the n-type material is much less alloyed Bi$_2$Te$_3$. The optimum compositions for Bismuth Telloride thermoelectric cooling alloys are reported to be Bi$_2$Te$_2.7$Se$_0.3$ for the n-type and Bi$_{0.5}$Sb$_{1.5}$Te$_3$ for the p-type semiconductor with ZT~1 near the room temperature [1].

According to Wang et al. [177], one of the reasons the potential of this material became evident since 1950s and 1960s is that it can become both n-type and p-type with proper doping. This material can be doped with Sb. Even Te can be replaced with Se and become Bi$_2$Se$_3$. Bi$_2$Se$_3$ is similar to Bi$_2$Te$_3$; however, it has interesting characteristics which have been
Figure B.2: Comparison between some thermoelectric materials and their temperature ranges[19]

reviewed by Wang et al.[177]. A p-type ZT more than 1 (∼1.5) is calculated in this paper after hole-doping (since this material is naturally n-type). Lattice thermal conductivity of the bulk Bi₂Se₃ is 2 W/mK[177].

PbTe especially Ti doped PbTe is known as a high performance TE material[177]; however, it is toxic. PbSe is a good high-temperature TE material[177]. Experimentally measured bad gap is approximately 0.3-0.35 eV.

**B.1 Oxide Thermoelectric Materials**

Ohtaki has published a good review article on oxide TE materials, their history and the progress which has been made in this field [21]. As it can be seen in Figure B.4, different oxides have covered significant portion of waste heat temperature ranges.
Figure B.3: Different thermoelectric materials in different temperature ranges[20]

The reasons these materials have been disregarded until the early 1990s are as followed[21]:

1. in metal-oxygen bonds, conducting electrons have been localized near positively charged metals. These localized electrons are called small polarons. As a result of forming these polarons, the bond is less covalent and the number of electrons between atoms and overlapping of the orbitals between atoms are less than covalent which results in 2-3 orders lower mobility than that in the covalent bond.[21]

2. Large bonding energies of ionic bonds and the small atomic mass of oxygen result in high speed elastic wave propagation yielding high lattice thermal conductivity, $k_{ph}$. [21]

On the other hand, oxide thermoelectric materials are 1) highly durable at high temperatures in the air, 2) non-toxic, 3) inexpensive, 4) having minimal in environmental impact.
In$_2$O$_3$.SnO$_2$ is a In$_2$O$_3$-based complex oxide which was one of the first oxides investigated with the highest ZT value of 0.06. By electron doping via Ge$^{4+}$ instead of In$^{3+}$, ZT=0.45 at 1273K has been reported for In$_{1.8}$Ge$_{0.2}$O$_3$ [21]. Also, La$_{1-x}$Sr$_x$CrO$_3$ is a perovskite-type oxide with high electrical conduction and thermal durability. A figure of merit, ZT=0.14 has been reported at 1600K for La0.85Sr0.15CrO$_3$

CaMnO$_3$ is another perovskite-type oxide with a conduction mechanism similar to La$_1-x$Sr$_x$CrO$_3$

$^{13}$ ZT=0.16 was obtained at 900°C for (Ca$_{0.9}$Bi$_{0.1}$)MnO$_3$.

$^{13}$small polarons hopping with thermally activated carrier mobility
Ca$_3$Co$_4$O$_9$ (Co-349) with other layered materials such as Ca$_2$Co$_2$O$_5$(Co-225) had a ZT=1.2-2.7 at 873K[178] or $\text{ZT} \geq 1.1$ for $[\text{Bi}_{0.87}\text{SrO}_2]_2[\text{CoO}_2]_{1.82}$ or $[\text{Bi}_2\text{Sr}_2\text{O}_4]_y\text{CoO}_2$ or BC-222. Polycrystalline Co-349 is much more strongly anisotropic and because of that ZT value remain as low as 0.3 for this material. All of these have been measured on whiskers$^{15}$ of 50-200mm along the in-plane direction.[179] Figure of merit of these types of materials can be seen in Figure B.5. More information on Co-349 and Mn-113 can be found in [19].

NaCo$_2$O$_4$ is one of the first layered cobalt oxides. Polycrystalline NaCoO$_2$ has a ZT=0.7-0.8 after improvements[178].

SrTiO$_3$ (Strontium titanate) is not a very good thermoelectric material and needs doping. Nb-doped Strontium Titanate (such as SrTi$_{0.8}$Nb$_{0.2}$O$_3$) seems to be promising; however, even these doped materials have the best ZT of 0.37 at 1000K according to [180]. Reasons for ZT improvement after Nb doping have been described in [21].

Inside zinc oxide, ZnO, the bonds are more covalent because of relatively higher electronegativity of Zn compare to other metals decreasing the localization effect. undoped ZnO is a naturally n-type semiconductor showing increasing $\sigma$ with increasing temperature[21] and has better thermoelectric behavior at high temperatures. Maximum ZT of its components, 0.30 at 1273K, is for $x=0.02$ in Zn$_{1-x}$Al$_x$O[21]. This value is still one of the largest among n-type oxides[21]. The drawback of this material is high thermal conductivity and therefore low efficiency. In [21] they managed to improve ZT to ZT=0.65 at 1273K for Zn$_{0.96}$Al$_{0.02}$Ga$_{0.02}$O by co-doping of Ga and Al into ZnO and decreasing lattice thermal conductivity without decreasing so much from the conductivity, $\sigma$.

$^{14}[\text{Ca}_2\text{Co}_3\text{O}_5]_y\text{CoO}_2 \ (y \sim 0.62)$

$^{15}$ribbon-like single crystals
In Figure B.6 the development of oxide thermoelectrics in addition to some new materials are not demonstrated. They are described in the following.

**B.2 Polymers**

Most of the polymers are poor thermal conductors which makes them interesting candidates for TE applications. One of the major problems is their electrical conductivity. Attempts have been made in order to increase electrical conductivity and Seebeck coefficient of these materials without too much affecting thermal conductivity. There are problems regarding these materials which have been briefly reviewed in [181]. According to [182] the two major
problems of this kind of materials are the aging and instability even in an inert environment. However, the power factor keeps increasing with increasing $\sigma$ which is a result of doping and it does not have a maximum. This phenomenon can be a result of one dimensional electron transport in chains of polymers[182].

**B.3 Silicides**

The most popular materials of this type are Si-Ge alloys which are very good at high temperatures and have applications in spacecrafts. $ZT_{max}=1$ is reported for n-type SiGe and
$ZT_{\text{max}} = 0.7$ for p-type SiGe [22]. Figure B.7 shows different silicides and their important thermoelectric characteristics [22]. $A'$ is a qualitative measure of thermoelectric efficiency. Usually when this parameter is high, $ZT$ is high too; however, that is not always true. $A'$ is defined according to [22]:

$$A' = \frac{T}{300} \left( \frac{m^*}{m_e} \frac{T}{k_l} \right)^{3/2}$$

(B.1)

Where $m^*$ is the carrier effective mass, $\mu$ is the mobility in $\text{cm}^2/\text{V-s}$, and $k_l$ is the lattice thermal conductivity in $\text{mW/cm-K}$. The relationship between $A'$ and $ZT$ does not always hold.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Point, K</th>
<th>Type</th>
<th>$m^*/m_e$</th>
<th>$\mu$ (cm²/V·sec)</th>
<th>$\lambda_{\text{ph}}$ (mW/cm·K)</th>
<th>$A'$</th>
<th>$ZT_{\text{max}}$</th>
<th>$E_g$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Si,Ge)</td>
<td>1550</td>
<td>n</td>
<td>1.4</td>
<td>68</td>
<td>44</td>
<td>2.6</td>
<td>1.0</td>
<td>0.7</td>
<td>2, 3</td>
</tr>
<tr>
<td>(Si,Ge)</td>
<td>1550</td>
<td>p</td>
<td>1.2</td>
<td>40</td>
<td>44</td>
<td>1.2</td>
<td>0.7</td>
<td>0.7</td>
<td>2, 4</td>
</tr>
<tr>
<td>Mg₂(Si,Sn)</td>
<td>1300</td>
<td>n</td>
<td>(1)</td>
<td></td>
<td></td>
<td>14</td>
<td>0.8</td>
<td>0.7</td>
<td>12, 13</td>
</tr>
<tr>
<td>Mg₂(Si,Ge)</td>
<td>1360</td>
<td>n</td>
<td>1.2</td>
<td>108</td>
<td>21</td>
<td>6.8</td>
<td>1.07</td>
<td>0.74</td>
<td>14, 15</td>
</tr>
<tr>
<td>Mg₂(Si,Ge)</td>
<td>1360</td>
<td>p</td>
<td>2.3</td>
<td>22</td>
<td>21</td>
<td>3.7</td>
<td>1.68</td>
<td>0.74</td>
<td>14, 15</td>
</tr>
<tr>
<td>CrSi₂</td>
<td>1763</td>
<td>p</td>
<td>5</td>
<td>15</td>
<td>68</td>
<td>2.5</td>
<td>0.35</td>
<td></td>
<td>23-26</td>
</tr>
<tr>
<td>CrSi₂</td>
<td>1763</td>
<td>n</td>
<td>20.2</td>
<td>0.15</td>
<td>68</td>
<td>0.2</td>
<td>0.35</td>
<td></td>
<td>23-22</td>
</tr>
<tr>
<td>MnSi₁.₇₅</td>
<td>1550</td>
<td>p</td>
<td>(1)</td>
<td>40</td>
<td>29</td>
<td>1.4</td>
<td>0.7</td>
<td>0.67</td>
<td>32,33,36,37</td>
</tr>
<tr>
<td>ReSi₂</td>
<td>2250</td>
<td>p</td>
<td>(1)</td>
<td>105</td>
<td>55</td>
<td>1.9</td>
<td>0.12</td>
<td></td>
<td>24, 27</td>
</tr>
<tr>
<td>FeSi₂</td>
<td>1255</td>
<td>p</td>
<td>4</td>
<td>4</td>
<td>40</td>
<td>0.8</td>
<td>0.2</td>
<td>0.9</td>
<td>43</td>
</tr>
<tr>
<td>FeSi₂</td>
<td>1255</td>
<td>n</td>
<td>(1)</td>
<td>2</td>
<td>40</td>
<td>0.05</td>
<td>0.4</td>
<td>0.9</td>
<td>44</td>
</tr>
<tr>
<td>Ru₂Si₃</td>
<td>1970</td>
<td>n</td>
<td>2.9</td>
<td>10</td>
<td>40</td>
<td>1.2</td>
<td>1.08</td>
<td></td>
<td>49, 52</td>
</tr>
<tr>
<td>Ru₂Si₃</td>
<td>1970</td>
<td>p</td>
<td>2.9</td>
<td>29</td>
<td>40</td>
<td>3.6</td>
<td>1.08</td>
<td></td>
<td>49, 52</td>
</tr>
</tbody>
</table>

Figure B.7: Characteristics of some silicides [22]
B.3.1 Alkali and Alkaline earth silicide

Mg$_2$(Si,Sn) solid solutions with ZT value of 0.8 have been reported[22]. Mg$_2$Si$_{0.6}$Ge$_{0.4}$ has ZT=1.68 [22]. This high value of figure of merit is suspicious since ZT=0.2 is reported in [183] where this alloy has been prepared by BMA$^{16}$ method. In addition, the p-type Ga doped Mg$_2$Si$_{0.6}$Ge$_{0.4}$ has been reported to have a maximum ZT of 0.36 at 625K [184]. BaSi$_2$ has high Seebeck coefficient but high thermal conductivity; as a result, ZT=0.2 at 300K. Doping and alloying might help yet chemical reactivity and low melting point may be a problem.[22]

B.3.2 Rare earth silicide

These silicides (Sc, Y, La-Lu) are metallic silicides which are not thermoelectric anymore except for $\alpha$-LaSi$_2$ which is counted as low band gap n-type semiconductor.

B.3.3 Goup 4B and 5B silicides

All silicides from group IVB (Ti, Zr, Hf) and VB (V, Nb, Ta) are metallic. Alloys of Nb$_x$Ta$_{1-x}$Si$_y$Ge$_{2-y}$ have been investigated and a sample of NbSiGe had ZT=0.5[22].

$^{16}$Bulk Mechanical Alloying
B.3.4 Cr, Mo, W silicides

CrSi$_2$ is a semiconductor with a large effective mass, consistent with magic number of VEC$^{17}$=14". Performance can be further improved by alloying and decreasing thermal conductivity. It has a very small band gap at high temperature and therefore not useful for high-temperature waste heat recovery applications. α-MoSi$_2$ and WSi$_2$ with larger band gap can be made useful for TE applications.

B.3.5 Mn and Re silicides

MnSi$_x$ such as Mn$_{11}$Si$_{19}$, Mn$_{15}$Si$_{26}$ and Mn$_2$Si$_{47}$ are promising. Performance and references in which these types of materials are discussed are described in Figure B.7.

B.3.6 Fe, Ru, and Os silicides

β-FeSi$_2$ is called iron disilicide. It is cheap and relatively easy to prepare but inefficient. According to [20], it can be used in cars. ZT=0.4 has been reported[22] for n-type iron disilicide. Ru$_2$Si$_3$, Os$_2$Si$_3$ and Os$_2$Ge$_3$ are similar to Ru$_2$Ge$_3$ and Ru$_2$Sn$_3$ in structure. To date, large ZT values have not been realized for these materials due to doping difficulties[22]. OsSi$_2$ has the same structure as β-FeSi$_2$. However, since Os is heavier than Fe, OsSi$_2$ would have a lower thermal conductivity. Further investigations are required to make any conclusions.

$^{17}$Valence Electron Count

196
**B.3.7 Co, Rh and Ir silicides**

CoSi and CoSi'2 are inexpensive but have high carrier concentration and therefore are not good thermoelectrics. Ir$_3$Si$_4$ and Ir$_4$Si$_5$ are both metallic. Ir$_3$Si$_5$ and IrSi$_3$ need further investigations.

**B.3.8 Ni, Pd and Pt silicides**

All Ni group silicides are metallic. However, Ni and Pt alloys seem interesting. Germanides can also be interesting to study. They may have lower thermal conductivity and larger mobility but at the same time lower melting point and smaller band gap which is not good[22].

**B.4 Zinc Antimonides**

After careful consideration of all of these candidates, we chose zinc antimonides for this work (Chapter 3) for the reasons mentioned below:

1. Zinc is earth abundant and inexpensive. Therefore a thermoelectric material can be cheaper if it contains Zn rather than rare and expensive elements. Antimony, Sb, is not as abundant as Zn though the combination of both of them make zinc antimonides more abundant than other promising thermoelectrics such as Bi$_2$Te$_3$.

2. β-Zn$_4$Sb$_3$ has a very low $k$ and $ZT = 1.3$ has been reached at 670k [31]. This figure of merit is very promising. Also, the complex structure of this material makes it very interesting to study for further improvements in thermoelectric efficiency.
3 Because of its large figure of merit in medium temperature range, $\beta$-Zn$_4$Sb$_3$ can be a good replacement for the toxic PbTe thermoelectrics in the same temperature range.

4 $\beta$-Zn$_4$Sb$_3$ has a record for high figure of merit in medium temperature range in which we are interested. The maximum ZT occurs at 670K [31]. Most of the industrial waste heat sources and concentrated solar thermal systems are in this temperature range.

The summary of thermoelectric materials search has been reported in Table B.1. In this table, low temperature range is defined as temperatures up to 450K, medium from 450 to around 850K, and high refers to 850 up to 1300K according to [26]. Also, Figure B.8 demonstrates the maximum ZT of different types of thermoelectric materials that have been reported in the literature up to the year 2011 where this literature review was done.
<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. range</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>$ZT_{max}$ at $T=\pm$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Te$_3$ alloys</td>
<td>low</td>
<td>High ZT</td>
<td>not stable at high temperatures, mildly toxic</td>
<td>$\pm$1 at 400K</td>
<td>[1], [177]</td>
</tr>
<tr>
<td>SiGe alloys</td>
<td>high</td>
<td>stable at high temperatures</td>
<td>inefficient at intermediate temp.range</td>
<td>0.7-1 at 1000K</td>
<td>[22], [26]</td>
</tr>
<tr>
<td>PbTe/CdTe</td>
<td>medium</td>
<td>high ZT</td>
<td>toxic</td>
<td>1.2 at 723K</td>
<td>[185], [177]</td>
</tr>
<tr>
<td>SrTi$<em>{0.8}$Nb$</em>{0.2}$O$_3$</td>
<td>high</td>
<td>inexpensive</td>
<td>low ZT</td>
<td>0.37</td>
<td>[180], [21]</td>
</tr>
<tr>
<td>NaCo$_2$O$_4$</td>
<td>high</td>
<td>-</td>
<td>-</td>
<td>0.7-0.8 at 1000K</td>
<td>[1]</td>
</tr>
<tr>
<td>Al$<em>{0.02}$Zn$</em>{0.98}$O</td>
<td>high</td>
<td>-</td>
<td>-</td>
<td>0.3 at 1000K</td>
<td>[1]</td>
</tr>
<tr>
<td>In$<em>{1.8}$Ge$</em>{0.2}$O$_3$</td>
<td>high</td>
<td>stable</td>
<td>low efficiency</td>
<td>0.45 at 1273K</td>
<td>[21]</td>
</tr>
<tr>
<td>La$<em>{0.85}$Sr$</em>{0.15}$CrO$_3$</td>
<td>high</td>
<td>stable</td>
<td>low ZT</td>
<td>0.14 at 1600K</td>
<td>[21]</td>
</tr>
<tr>
<td>(Ca$<em>{0.9}$Bi$</em>{0.1}$)MnO$_3$</td>
<td>high</td>
<td>stable</td>
<td>low ZT</td>
<td>0.16 at 1173K</td>
<td>[21]</td>
</tr>
<tr>
<td>Ca$_2$Co$_2$O$_5$</td>
<td>high</td>
<td>high ZT</td>
<td>difficult preparation procedure</td>
<td>1.2-2.7 at 873K</td>
<td>[178]</td>
</tr>
<tr>
<td>Zn$<em>{0.96}$Al$</em>{0.02}$Ga$_{0.02}$O</td>
<td>high</td>
<td>stable at high temperatures</td>
<td>low ZT</td>
<td>0.65 at 1273K</td>
<td>[21]</td>
</tr>
<tr>
<td>p-type skutterudites</td>
<td>high</td>
<td>high ZT</td>
<td>rare or toxic elements</td>
<td>+1.1 at 950K</td>
<td>[19]</td>
</tr>
<tr>
<td>n-type skutterudites</td>
<td>high</td>
<td>high ZT</td>
<td>rare or toxic elements</td>
<td>-0.8 at 900K</td>
<td>[19]</td>
</tr>
<tr>
<td>La$_{0.9}$Fe$<em>3$CoSb$</em>{1.2}$</td>
<td>medium</td>
<td>high ZT</td>
<td>rare or toxic elements</td>
<td>1.1 at 750K</td>
<td>[186]</td>
</tr>
<tr>
<td>Material</td>
<td>Temp. range</td>
<td>Advantages</td>
<td>Disadvantages</td>
<td>$ZT_{max}$ at $T =$</td>
<td>Ref.</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-------------</td>
<td>-----------------------------------</td>
<td>----------------------------------------------------</td>
<td>---------------------</td>
<td>-------</td>
</tr>
<tr>
<td>BaSi$_2$</td>
<td>low</td>
<td>high thermopower</td>
<td>chemical reactivity, high thermal conductivity</td>
<td>0.2 at 300K</td>
<td>[22]</td>
</tr>
<tr>
<td>Mg$<em>2$Si$</em>{0.6}$Ge$_{0.4}$</td>
<td>medium</td>
<td>non-toxic</td>
<td>inefficient</td>
<td>0.36 at 625K</td>
<td>[184]</td>
</tr>
<tr>
<td>$\beta$-FeSi$_2$</td>
<td>-</td>
<td>inexpensive, easy to prepare</td>
<td>inefficient</td>
<td>-0.4</td>
<td>[22]</td>
</tr>
<tr>
<td>SiGe</td>
<td>high</td>
<td>stable at high temperatures</td>
<td>inefficient</td>
<td>+0.7, -1 at 1000K</td>
<td></td>
</tr>
<tr>
<td>Polyaniline</td>
<td>-</td>
<td>ease of processing</td>
<td>aging and instability</td>
<td>-</td>
<td>[181], [182]</td>
</tr>
<tr>
<td>Polyacetylene</td>
<td>-</td>
<td>ease of processing</td>
<td>aging and instability</td>
<td>1.3 at 670K</td>
<td>[181], [182]</td>
</tr>
<tr>
<td>AgSbTe$_2$</td>
<td>medium</td>
<td>-</td>
<td>-</td>
<td>1.53 at 500K</td>
<td>[185]</td>
</tr>
<tr>
<td>YbAl$_3$</td>
<td>-</td>
<td>high power factor</td>
<td>low efficiency</td>
<td>(-)</td>
<td>[20]</td>
</tr>
<tr>
<td>Ca$_3$AlSb$_3$</td>
<td>high</td>
<td>inexpensive</td>
<td>-</td>
<td>0.8 at 1000K</td>
<td>[175]</td>
</tr>
<tr>
<td>Ca$_{5-x}$Na$_x$Al$_2$Sb$_6$</td>
<td>high</td>
<td>relatively cheap</td>
<td>-</td>
<td>0.6 at 900K</td>
<td>[176]</td>
</tr>
<tr>
<td>Bi$_2$Se$_3$</td>
<td>low</td>
<td>high ZT</td>
<td>toxic, not studied completely</td>
<td>±1.5</td>
<td>[177]</td>
</tr>
<tr>
<td>Zn$_4$Sb$_3$</td>
<td>medium</td>
<td>non-toxic, relatively cheap</td>
<td>metastable, only p-type</td>
<td>1.3 at 670K</td>
<td>[1], [31], [91]</td>
</tr>
</tbody>
</table>
Figure B.8: Maximum ZT and the corresponding temperature for different thermoelectric materials. The unknown type is a material for which the author was unable to find their type from the literature. The references from which these values have been extracted can be found in the text.
Appendix C

User manual for aMoBT on nanoHUB.org

Disclaimer: This document is meant to be a guide for the users of aMoBT on nanoHUB.org to facilitate a complete employment of the available features. The content is NOT guaranteed to be scientifically accurate and certified/peer-reviewed and the researchers should use the suggestions at their own responsibility.

C.1 Introduction

*ab initio* Model for Mobility calculation using Boltzmann Transport equation (aMoBT) is a model that uses the *ab initio* band structure (preferably using GW) and explicitly solves BTE to obtain the small perturbation to the electron distribution assuming low-field transport.

Currently ionized impurity scattering as well as charged dislocation and piezoelectric and deformation potential scatterings are taken into account as elastic scattering mechanisms and polar optical phonon as an inelastic scattering mechanism. You can go through the
Figure C.1: Flowchart of aMoBT, from *ab initio* calculations to the calculated mobility and Seebeck coefficient. For more detailed information regarding aMoBT, see [23].

examples and change parameters to see the effect on transport properties or you can upload your own band structure and density of states files generated with VASP (Vienna ab initio Simulation Package) for transport calculations. Figure C.1 provides an overview of aMoBT from *ab initio* calculations to the calculated mobility and Seebeck coefficient. For more detailed information, see [23].

If you want to upload your VASP files for your system, you need to choose the "New" option from the top left drop-down menu in aMoBT and then upload the EIGENVAL file from a non-self consistent calculations in a dense k-point mesh around your CBM/VBM (for an n-type/p-type semiconductor) as well as PROCAR (generated with LORBIT = 11 flag in INCAR). Also, you need to upload DOSCAR and OUTCAR from the self-consistent calculations. It is preferable that the DOSCAR is generated with NEDOS more than 3000 and less than 10,000 (if it is 10000 or more, this number is not readable from DOSCAR). If you had any questions, feel free to send an email to alireza.fagahninia@gmail.com
C.2 Logistics

The graphical user interface (GUI) for aMoBT has been prepared using Rappture which is available on nanoHub.org. We present, in the following, some features of this GUI from which 3 and 4 are only relevant to some users.

1. You can run several simulations with different values for temperature, dielectric constants, etc. You can access those simulation through the blue bar on the lower right side of the window. To save the output of different simulations, you can access and download the Output for each simulation.

2. To calculate mobility at different temperatures, rather than running separate simulations at those temperatures, you can run one simulation at different temperatures which is much faster since band structure fitting is done only once. To do that, you can simply enter your data points in Experimental data for mobility field like the following example and then switch Compare to experiment? to "yes". In the following, the first column is temperature and the second is the mobility. The column for mobility should not be left empty. If you have experimental data at those temperatures, of course they can be entered instead of repeated "1000":

```
50 1000;
100 1000;
200 1000;
300 1000;
400 1000;
500 1000;
```
3. If you are running aMoBT on Internet Explorer, the screen might go dark. Refresh will fix it. For more information, please contact nanoHub.org.

4. If you are running aMoBT on windows 8 touch screen laptop, if you use Google Chrome, you might not be able to use the mouse. If only the touch screen is working, an alternative solution is to use a different browser. Generally, the users might have some difficulty using the tool with Google Chrome. For more information, please contact nanoHub.org

In the following all the inputs and outputs of aMoBT are briefly described:

C.3 Inputs

C.3.1 Material

Material: Here you can choose your material of interest, currently there are 3 examples available together with corresponding mobility and Seebeck coefficient experimental data. The followings are the options for this input:

Option 1. n-GaAs example (default): this example is for a pure GaAs sample with a very low electron concentration of $n = 3.0 \times 10^{13}$. Other parameters are obtained $ab initio$[23]. In order to make this example faster to run, the band structure and the density of states are already carefully fitted to polynomials in a dense mesh containing 8531 k-points.
Option 2. n-InN example: the purpose of this example is to illustrate the effect of charge dislocation scattering on limiting the mobility of InN. Here again, all the default parameters are obtained ab initio. Furthermore, to make this example faster to run, the band structure and the density of states are already carefully fitted to polynomials in a dense mesh containing 8531 k-points.

Option 3. n-ZnS example: this is an example of uploaded data with all four files, EIGEN-VAL, PROCAR, OUTCAR and DOSCAR (output files of VASP[56, 57, 58, 59]) already uploaded. The main purpose of this example is for user to see how the next option, ”New”, should look like.

Option 4. New: this option can be used for uploading the files for a new system. Note that choosing this option will generate new set of default values for parameters that are not for any specific material. The user is responsible for choosing the appropriate values for each parameter. However, the deformation potential, $E_d$, and piezoelectric constant, $P$, might not be important particularly at higher temperatures (>200K). It is a good idea to run the simulation with correct polar optical frequency and dielectric constants, etc. and change $E_d$ and $P$ only if they are limiting the mobility at the selected temperature(s).

Option 5. Upload: this option is used to upload all necessary VASP files together. You can select this after choosing ”New” to upload all the files. Otherwise, by right clicking on the white field in front of each file, and choosing ”Upload...”, that specific file can be uploaded.

Option 6. Download: you can use this option to download the files for ZnS example as sample files for a working example.
C.3.2  *ab initio* band structure and density of states

This field is just an indicator for the program to use either the pre-fitted band structures for faster calculations in the examples, or to use the uploaded band structure (If Material is set to ”New”). After the user chooses any option for Material, this field will automatically set to the proper option and it should not be changed after that.

C.3.3  Type of the conductivity

This field decides whether electron (n-type) or hole (p-type) mobility is calculated. If ”n-type” is chosen, aMoBT will calculate the transport properties based on the conduction band edge, at and around the ”reference k-point”. If ”p-type” is chose, aMoBT will calculate the transport properties based on the valence band edge, at and around the k-point determined as the reference k-point . It should be noted that changing the type does not affect the results of the two examples: ”n-GaAs” and ”n-InN” as their conduction bands are pre-set to fitted polynomials to provide a faster demonstration.

C.3.4  Type of formulation

This field determines whether aMoBT uses single-band model or coupled band. Coupled band model is relevant in degenerate CBM or VBM where interband scattering exist. For more information on this formulation see [49] This option should be left to the default: ”automatic” in which case appropriate formulation will be used depending on the type of the input band structure: coupled-band formulation will be used only if degenerate band exists which is the case for most p-type semiconductors; otherwise, a single band formulation will
be used. One may manually choose "single band" or "coupled band" options to compare the
two formulation but of course only one of them is relevant and correct for each input. It is
recommended to leave this field unchanged from "automatic".

C.3.5 "Tempearture, T(K)" and "Compare to experiment?"

This is the temperature at which the properties are calculated if the field "Compare to
experiment?" is set to "no". Otherwise, if the data is compared to experiment, the mobility
and Seebeck coefficient are evaluated at the experimental data entry points that are specified
in Experimental data for mobility. It should be noted that the Seebeck coefficient in this
case is only at the specified Carrier concentration. Unfortunately, currently, if the user wants
to calculate the Seebeck coefficient at different T’s and n’s, they have to switch "Compare
to experiment?" to "no" and then calculate each point separately as opposed to a single
simulation run.

C.3.6 Maximum number of iterations to obtain g

This is the maximum number of iterations set when solving the Boltzmann transport equa-
tion using Rode’s[5] iteration method to obtain the perturbation to the electron distribution,
g. Usually the average difference in two consecutive g’s (Printed in Output) drop by one
or two orders of magnitude within 5 iterations.
C.3.7 Free electron DOS?

If this is set to "no" then the uploaded \textit{ab initio} density of states (DOS) will be used in transport calculations and everything will be integrated in energy space. Otherwise, if "yes", the free-electron DOS will be used which works better at high carrier concentrations and high temperatures. Everything will be integrated in k-space in this case. See [23] for more details.

C.3.8 k-point of CBM/VBM for n-/p-type conductivity

Here you can set the fractional coordinate of the k-point at which the conduction band minimum (CBM) or the valence band maximum (VBM) is located in either the n- or p-type semiconductor. Here we call this the "reference k-point". It should be noted that for accurate calculation of the transport properties, one should use the k-point mesh that is suggested (or a denser one) in "Supporting Docs". However, if the CBM/VBM does not occur at the Γ-point with the coordinate "0.0 0.0 0.0", one should generate a new k-point mesh using the KPOINTS\_generator\_for\_aMoBT.m available under the tab "Supporting Docs" using the new reference k-point and calculate the EIGENVAL based on that.

C.3.9 Polar optical phonon frequency, $\omega_{po}$ (THz)

To calculate this parameter \textit{ab initio}, one needs to calculate the phonon band structure and density of states. One method is to use Phonopy [2] code, after the force constants are obtained using DFPT, to get these frequencies in THz. For the available examples of aMoBT calculations: GaAs, InN and ZnS, the optical phonon frequency at Γ point, $\omega_{po}$,
that we are looking for, is in very good agreement with experimental measurements. There is an approximation in choosing the optical phonon frequency from the last phonon DOS peak. Users are responsible for the accuracy of the values they set for all input parameters of aMoBT particularly $\omega_{po}$, $\epsilon_0$ and $\epsilon_{\infty}$ (see the next section) on which the results are sensitive.

### C.3.10 Dielectric constants: $\epsilon_0$ and $\epsilon_{\infty}$

Dielectric constants can be calculated *ab initio*. You can refer to VASP manual. However, the calculated values are not always accurate. The calculated properties are sensitive to the values of dielectric constants [23]. It is relatively simple to calculate the high frequency dielectric constant, $\epsilon_{\infty}$, based on the calculated static dielectric constant, $\epsilon_0$, from DFPT which is generally reliable. Once the phonon density of states (DOS) is calculated which is required for $\omega_{po}$ anyway, $\epsilon_{\infty}$ can be calculated via Lyddane-Sachs-Teller relation (equation C.1):

$$
\epsilon_{\infty} = \epsilon_0 \times \left( \frac{\omega_{TO}}{\omega_{LO}} \right)^2
$$

(C.1)

where $\omega_{TO}$ and $\omega_{LO}$ are transverse and longitudinal optical phonon frequencies respectively.

### C.3.11 Deformation Potential

Deformation potential is ”how much the energy level of CBM/VBM changes per unit change in the volume” times ”the equilibrium volume”. In order to obtain this value *ab initio* please see [23]. Also, experimental values for deformation potential for some III-V semiconductors are available in [5].
C.3.12 Piezoelectric coefficient, $P$

The piezoelectric coefficient is a unitless parameter which is a function of piezoelectric and elastic constants of the material all of which can be calculated \textit{ab initio}. The user can run the simulation with default values first to check if the mobility is limited by piezoelectric scattering at the corresponding temperature(s). The experimental values for this input parameter for some III-V semiconductors can be found in the literature [5]. Piezoelectric coefficient, $P$, can be calculated using equation C.2 for sphalerite crystal structure:

\[
P^2 = h_{14}^2 \epsilon_0 \left[ (12/c_l) + (16/c_t) \right] / 35 \quad \text{(C.2)}
\]

\[
c_l = (3c_{11} + 2c_{12} + 4c_{44}) / 5 \quad \text{(C.3)}
\]

\[
c_t = (c_{11} - c_{12} + 3c_{44}) / 5 \quad \text{(C.4)}
\]

Also, for wurtzite crystal structure, $P$ can be calculated using equation C.5[5]:

\[
P^2 \perp = 4\epsilon_0 \left( 21h_{15}^2 + 6h_{15}h_x + h_x^2 \right) / 105c_l + \epsilon_0 \left( 21h_{33}^2 - 24h_{33}h_x + 8h_x^2 \right) / 105c_l \quad \text{(C.5)}
\]

\[
P \parallel = 2\epsilon_0 \left( 21h_{15}^2 + 18h_{15}h_x + 5h_x^2 \right) / 105c_l + \epsilon_0 \left( 63h_{33}^2 - 36h_{33}h_x + 8h_x^2 \right) / 105c_l \quad \text{(C.6)}
\]

\[
h_x = h_{33} - h_{31} - 2h_{15} \quad \text{(C.7)}
\]

\[
c_l = (8c_{11} + 4c_{13} + 3c_{33} + 8c_{44}) / 15 \quad \text{(C.8)}
\]

\[
c_t = (2c_{11} - 4c_{13} + 2c_{33} + 7c_{44}) / 15 \quad \text{(C.9)}
\]
where $h_{ij}$ and $c_{ij}$ are independent elements of piezoelectric and elastic tensors respectively. Also, $c_l$ and $c_t$ are longitudinal and transverse spherically averaged elastic constants. For more information, see [5].

C.3.13 **Dislocation density, $N_{\text{dis}}$ (1/cm²)**

In some materials, such as InN, charged linear dislocations cause electron scattering and limit the electron mobility. See [8] for more information. The density of these linear dislocations are measured and reported in 1/cm²; however, for electron scattering the overall density is required. We assume that these dislocations are homogeneously distributed along the $c$-axis. Therefore, the value entered for ”Dislocation density, $N_{\text{dis}}$ (1/cm²)” will be divided by 0.565 nm which is the equilibrium lattice constant of InN. The user must recalibrate ”Dislocation density, $N_{\text{dis}}$ (1/cm²)” based on this number and the actual lattice constant of their material.

C.3.14 **Carrier concentration, $n$ (1/cm³)**

The carrier concentration can be explicitly entered here. It should be noted that this carrier concentration is assumed to be constant at all temperatures (>20K). The Fermi level is calculated based on this value. See [23] for more information.

The experimental values for input parameters described in sections C.3.9-C.3.14 for some III-V semiconductors can be found in the literature [5].
**C.3.15 Experimental data for mobility**

This field is for the mobility vs. temperature data to compare with the calculated mobility. Once "Compare to experiment?" is set to "yes", the transport properties will be calculated at each temperature that is specified in this field. For example, if the input is the following (note the correct format):

```
300 1000;
400 500
```

then the transport properties will be calculated at 300K and 400K to be compared with 1000 \( cm^2/V \cdot s \) and 500 \( cm^2/V \cdot s \) respectively.

**C.3.16 Exp. data for Seebeck coeff.**

This field has to be filled out similar to Experimental data for mobility but for Seebeck coefficient, \( S \), vs. carrier concentration, \( n \), data. Unfortunately, \( S \) vs. \( T \) plot is not currently available. The users can run single-point calculations at different temperatures for \( S \) vs. \( T \) comparisons.

**C.3.17 Input files: EIGENVAL, PROCAR, OUTCAR, DOSCAR**

If "New" is selected for Material, then, 4 input files can be uploaded two of which are required: EIGENVAL and OUTCAR. As described in Introduction, the EIGENVAL file should be
from a non-self consistent calculations in a dense k-point mesh around your CBM/VBM (for an n-type/p-type semiconductor) as well as PROCAR (generated with LORBIT = 11 flag in INCAR). The number of k-points must be less than 10,000 points. Also, you need to upload DOSCAR and OUTCAR from the self-consistent calculations. It is preferable that the DOSCAR is generated with NEDOS more than 3000 and less than 10,000 (if it is 10000 or more, this number is not readable from DOSCAR). EIGENVAL is required for the band structure and group velocity calculations. OUTCAR is required for extracting lattice matrix and volume. PROCAR is optional for more accuracy in calculation of s-p hybridization in the conduction band; if PROCAR is not available the conduction(valence) band wave function is assumed to be completely s-like(p-like). DOSCAR is optional for extracting the total density of states to be used when Free electron DOS? is set to ”no”; if DOSCAR is not available, the free electron DOS is used.

C.4 Outputs

C.4.1 Mobility (cm$^2$/V·s)

This simply plots the calculated mobility at the specified temperature. In case that ”Compare to experiment?” is set to ”yes”, this will be the calculated mobility at the last temperature point that is specified in Experimental data for mobility as input.
C.4.2 Seebeck coefficient (µV/K)

This simply plots the calculated Seebeck coefficient at specified carrier concentration. Unlike the previous plot, even if "Compare to experiment?" is set to "yes", this will be the calculated Seebeck coefficient at the specified carrier concentration that is specified in Carrier concentration, n (1/cm³) as input.

C.4.3 Effective mass (average)

The calculated average effective mass based on the uploaded band structure. For more details on how the effective mass is calculated, see [23].

C.4.4 Group velocity of electrons

The plot of the calculated electron group velocity vs. k, based on the uploaded band structure. For more details on how the group velocity is calculated from the polynomials that are fitted to the conduction band, see [23].

C.4.5 Mobility vs. T

The calculated and experimental mobility vs. temperature all in one plot. If Compare to experiment? is set to "yes" the calculated mobilities will be plotted at all the temperatures that were specified by the user at Experimental data for mobility as input. Each line represent the mobility if it was only limited by a specific scattering mechanism. Furthermore, the overall mobility is also plotted to be compared to the experimental values entered before. It
should be noted that if Compare to experiment? is set to "no" only the experimental data (if any) will be plotted.

C.4.6 Seebeck coefficient vs. n

The calculated and experimental Seebeck coefficient vs. carrier concentration. Unlike the previous plot, even if Compare to experiment? is set to "yes" the calculated Seebeck coefficients will be plotted at only the specified Carrier concentration, n (1/cm$^3$). It should be noted that if Compare to experiment? is set to "no" only the experimental data (if any) will be plotted.

C.4.7 Output

This is the printed output with some useful information such as the accuracy of the fit to the band structure, DOS, etc. as well as the calculated effective mass, mobilities, Seebeck coefficient. This file also contain some warnings in case, for example, more data points are required for fitting polynomials, etc.
C.5  Version notes

C.5.1  Version 2.1.1

The PROCAR and DOSCAR files are no longer required. Only EIGENVAL file and OUTCAR file are required. If DOSCAR is not uploaded a free electron density of state is assumed and if PROCAR is not uploaded the conduction(valence) band is assumed to be fully s-like(p-like).

For Quantum ESPRESSO (QE) users: the Python code named ”QE-to-VASP.py” is now available under the supporting documents. This code generates the EIGENVAL and OUTCAR files from a QE self consistent or non-self consistent calculation (line-mode band structure is not supported). Usage: python QE-to-VASP.py -f YOUR-QE-OUTPUT-FILE

C.5.2  Version 2.0.1

Substantial changes were made compared to the previous versions. A coupled band formulation is added to the program to take into account the inter-band scattering in semiconductors with degenerate bands. aMoBT now automatically decides which formulation to be used based on the uploaded EIGENVAL file. This version has been tested with p-type GaAs with a degenerate valence band. DFT band structure with spin orbit coupling taken into account was used as the input band structure. Very good agreement with experimental data was obtained.
C.5.3 Version 1.1.1

Based on the uploaded OUTCAR, aMoBT now automatically calculates the predicted density of the material. Furthermore, based on the value of LSORBIT printed in the OUTCAR file that is uploaded by the user, aMoBT determines whether the \textit{ab initio} calculations have been done with spin-orbit coupling. Subsequent treatment of EIGENVAL and PROCAR will be determined based on this. This is particularly important in semiconductors with a degenerate band.

C.5.4 Version 1.1.0

The k-point at which the conduction band minimum (CBM) or the valence band maximum (VBM) is located in the semiconductor can now be entered as an input. See reference k-point for more information.

The type of the semiconductor (n-type/p-type) can be determined for calculating the electron/hole mobility, conductivity, etc.

C.5.5 Version 1.0.2

The low-field mobility and Seebeck coefficient can be calculated in a semiconductor with a single conduction band governing the transport properties with the CBM at Γ-point. If the conduction band has a single dominant band (an example is shown in the snapshots of aMoBT) but not at Γ point, the transport properties can still be easily calculated but not with this version on nanoHub.
Please contact alireza.faghaninia@gmail.com if you had any question. Comments and feedbacks are most certainly always welcome.